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Syntheses of organic compounds in the presence of the fused iron catalyst and their mechanisms and kinetics

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ABSTRACT. New synthetic possibilities of the reduced promoted fused iron catalyst in intermolecular and intramolecular amination, cyanation, hydrogenation-dehydrogenation, and hydrodeoxygenation reactions and intermolecular and intramolecular dehydration, polymerisation, and isotope exchange are examined. The mechanisms and kinetics of the reactions leading to the synthesis of amines, alcohols, hydrocarbons, and other organic compunds are discussed. A laser Raman spectroscopic method is described for the investigation of heterogeneous organic catalysis *in situ*.

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I. Introduction

The problem of the development of new effective methods of synthesis of organic compounds remains, as before, of current interest in the field of organic synthesis and petrochemistry. The experimental data accumulated hitherto make it possible to differentiate the principal approaches which are most often used in the development of catalytic syntheses. By arranging the approaches in the order based on the decrease in the relative novelty of the reactions and catalysts, we obtain the following list:

(1) New reactions + new catalysts;
(2) Known reactions + new catalysts;
(3) New reactions + known catalysts;
(4) Known reactions + known catalysts.

The first approach is heuristic and the fourth involves the optimisation of known syntheses. In the present review, attention is concentrated on the second and third approaches, namely on the preparation of organic compounds of different classes using the reduced promoted fused iron catalyst (RPFIC), which is known primarily as the catalyst of the synthesis of ammonia from hydrogen and nitrogen and of organic compounds from CO and H_2. Since a large number of monographs and reviews (see, for example, Refs. 1–4) have been devoted to these two processes, they are not considered in this review.

Fused iron catalysts have a number of significant advantages, among which one should include in the first place the simplicity and ecological purity (lack of waste) in their preparation, low cost, high thermal stability permitting the use of catalysts of this type in highly exothermic processes (hydrogenation, hydrogenolysis, etc.), stability and mechanical strength which permit their use in reactors with a fluidised catalyst bed (fluid process), as well as the ease of varying their chemical composition (by employing as promoting agents various oxides or their mixtures), on which depend the activity and selectivity of the catalytic action. All the foregoing factors create, in our views, the necessary groundwork for a more comprehensive investigation of the RPFIC in order to synthesise organic compounds of different classes.

II. Fused iron catalysts: preparation, activation, and investigation

Several methods are used to prepare RPFIC. The following is most widely used under laboratory conditions. The initial mixture is made up from dry powders (60–120 mesh) comprising Fe_3O_4, whose fraction in the mixture is 90–95 wt. %, and promoting additives, which are usually Al_2O_3, SiO_2, K_2O, CaO, MgO, V_2O_5, BaO, Cr_2O_3, and MnO_2. By varying the composition of the initial mixture, it is possible to obtain catalysts with different activities, selectivities, and stabilities. The mixture of oxides is fused in a water-cooled steel crucible lined with asbestos and kaolin, fusing being effected with the aid of an electric arc generated by steel or copper electrodes, which are also water-cooled. The melting point of the mixture of oxides is 1500–1600 °C and the fusion time is 60–120 s. The ingots formed are comminuted and screened into fractions, from which the fraction with a grain size of approximately 1–3 mm is usually taken for preparative purposes in organic synthesis.

The catalyst is activated (reduced) at 400–480 °C and a hydrogen pressure of 1–50 atm, the reduction time being 4–50 h. Completion of the reduction of the catalyst is checked from the amount of water evolved, which is usually close to the stoichiometric amount. The catalyst activated in this way is pyrophoric and it is therefore stored and inserted into and removed from the reactor in a protecting gas atmosphere (CO_2, Ar, N_2). Depending on the composition and the preparation conditions, the reduced catalyst has a specific surface of 10 ± 5 m^2 g^{-1} (BET method, N_2).

The phase and elemental compositions of the RPFIC, both before and after reduction with hydrogen, have been the object of continuous study.[1,3,5–13] In the melting stage with promoting agents,

partial interaction of the components is already observed, leading to the formation of a multiphase multicomponent alloy.[5,12] When the latter is reduced with hydrogen, the iron oxides with different stoichiometries are almost quantitatively converted into α-Fe^0. At the same time, the displacement of the promoting agent and their compounds from the bulk of the catalyst onto the surface is observed. Certain other processes also occur, as a result of which the bulk phase and the surface of the RPFIC acquire different compositions.[1,5,6,13]

Thus the surface of the promoted fused iron catalyst for the synthesis of ammonia, containing (calculated relative to the non-reduced specimen) 2% Al_2O_3(Al/Fe = 0.16), 1% K_2O(K/Fe = 0.012), and 1.5% CaO(Ca/Fe = 0.015), the remainder being Fe_3O_4,† acquired, as shown by X-ray photoelectron spectroscopy, a composition‡ corresponding to the component ratios Al/Fe = 2.0, K/Fe = 0.78, and Ca/Fe = 1.2 after reduction with hydrogen.[13] Thus the fraction of Fe^0 on the surface of the given RPFIC was less than 50%.

Measurements of the fraction of Fe^0 on the surface of the RPFIC by the selective adsorption method agree with the results obtained by the X-ray photoelectron spectroscopic method.[1,5,14]

Information about the structure and properties of surface compounds directly in the course of the activation of heterogeneous catalysts and catalysis in their presence can be provided in principle by IR spectroscopy. Considerable advances have been achieved recently in the measurement of the IR spectra of adsorbed molecules.[15] However, the application of this method under real activation and catalytic conditions involves considerable experimental difficulties which become impossible to overcome for RPFIC owing to the strong absorption of IR radiation by the latter.

In this connection, the data on the activation of the RPFIC obtained by laser Raman spectroscopy *in situ* are of special interest. Despite the advantages of Raman spectroscopy over IR spectroscopy in the study of this catalyst (they have been described in detail[16]), there have so far been only two studies in which the method was applied to the RPFIC. In these studies, the interactions of H_2 and D_2 with the surfaces of RPFIC having the composition $5V_2O_5$ [17] and $3Al_2O_3 + 1K_2O$ [18] were investigated. Treatment of the RPFIC with H_2 is accompanied by the appearance of absorption bands in the region of $\sim$980 cm^{-1} [17] (Fig. 1) and $\sim$1950 cm^{-1},[18] which may indicate the presence on the surface of hydride-like forms of hydrogen having the structure

$$\overset{H^{\delta-}}{\underset{Fe^{(\delta+)}}{\diagup\diagdown}}Fe \quad \text{and} \quad \overset{H^{\delta-}}{|}\,Fe^{\delta+}\,.$$

The surface of the RPFIC before the start of the catalytic reaction on the latter can be represented as shown[19] in Fig. 2. This scheme reproduces two significant features in the structure of the RPFIC surface. The first is associated with the presence of Fe^0 and hydride hydrogen on the surface. The second is due to the high concentration of oxide promoting agents on the surface, which suggests, in its turn, the existence on it of Brønsted and Lewis acid–base centres (pairs). Thus RPFIC can be classified as bifunctional heterogeneous catalysts which are capable of manifesting simultaneously both oxidation-reduction (hydrogenation-dehydrogenation) and acid–base properties.

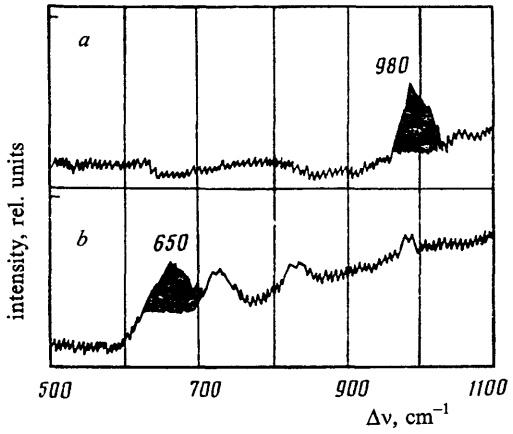


Figure 1. The Raman spectra *in situ* of the surface of an iron melted catalyst promoted with 5% V_2O_5 in the course of activation with protium or deuterium [187 °C, $p_{H_2(D_2)}$ = 0.2 MPa]:[17] *a*, H_2, $\nu_H \simeq 980$ cm^{-1}; *b*, D_2, $\nu_D \simeq 650$ cm^{-1}.

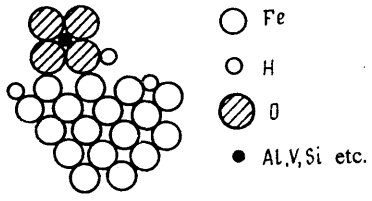


Figure 2. Schematic representation of the surface of a reduced promoted fused iron catalyst.[19]

Naturally, under the conditions of catalysis where there is direct interaction of the RPFIC with the reactants, the composition of the multiphase and multicomponent catalysts can undergo appreciable additional changes.[3,7,8,11,20–23] The effects of the reaction medium on the RPFIC have been studied in greatest detail in relation to syntheses from CO and H_2.[3,7,8,20,21,23] It has been established that, as a result of such interaction, the catalyst is enriched in iron carbides (ε-carbide, χ-carbide, etc.) and iron oxides of different composition ($Fe_{1-x}O$) both in the bulk phase and on the surface.

III. Modified Fischer–Tropsch syntheses

These include syntheses from CO and H_2 with the addition of a third component in which organic compounds belonging to different homologous series are formed. The use of a third component leads on the one hand, to new synthetic possibilities of the Fischer–

† An abbreviated formulation of the composition of the RPFIC will be used henceforth in the text, for example, $2Al_2O_3 + 1K_2O + 1.5CaO$.

‡ The composition of the RPFIC surface is understood as the composition of the surface layer 10–30 Å thick.

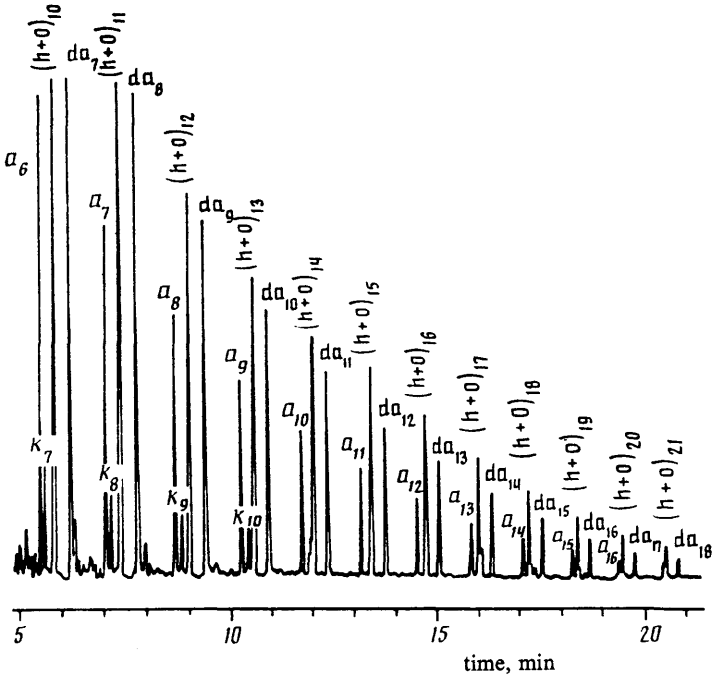


Figure 3. A fragment of the chromatogram of the products of synthesis from CO, H_2, and $(CH_3)_2NH$: h—alkanes; o—alkenes; a—alkanols; k—alkyl methyl ketones; da—dimethylalkylamines.

Tropsch reaction (FT-synthesis), associated primarily with the introduction of functional groups into individual components of the FT-product§ and, on the other hand, it makes it possible to discover and refine the mechanism of the interaction of CO and H_2. The third component, added directly to the synthesis gas, frequently plays simultaneously several functions, among which one should include, apart from those mentioned above, the functions of a chemical label, chemical trapping agent, synthesis initiating reagent, etc. As a rule, this component undergoes a wide variety of intrinsic reactions both with and without the participation of the components of the synthesis gas. Ammonia, primary and secondary amines, acetylenes and some of its derivatives, etc., are used as modifying substrates in FT-syntheses.

1. The Fischer–Tropsch synthesis modified by ammonia or alkylamines

The first example of such FT-synthesis is the preparation of alkylamines from CO, H_2, and ammonia.[24,25] In the presence of the RPFIC $5Al_2O_3 + 7BaO$ at 175–205 °C, a synthesis gas ($H_2:CO = 2$) pressure of 20 MPa, and an ammonia concentration of 8 vol. %, a product containing up to 30% of alkylamines was obtained. The alkylamines consisted of 88.5% of primary amines, 8.5% of secondary amines, and 3% of tertiary alkylamines.[26]

§ Here and henceforth the components of the FT-product are understood to be organic compounds of one class (hydrocarbons, alcohols, etc.).

In order to increase the yield of alkylamines in the FT-synthesis with participation of ammonia, catalysts of different composition have been used.[27–29] The best result (selectivity with respect to alkylamines of 50%) was achieved in the presence of a RPFIC prepared on the basis of natural magnetite.[29]

Methods have been developed for the synthesis of secondary alkylamines from CO, H_2 and n-butylamine [30] or methylamine,[31] and also for the synthesis of tertiary alkylamines from CO, H_2, and dimethylamine.[32] At 168–175 °C, a synthesis gas pressure of 10–14 MPa, and for $H_2:CO:$methylamine = 1:1:1.25 ratios, the yield of alkylamines reached 35–35 g m^{-3} in terms of the converted synthesis gas with a selectivity with respect to n-alkylmethylamines of 78%.[31]

It is noteworthy that, together with alkylamines, other components of the FT-products, especially alkanols, are formed in all cases when ammonia or alkylamines are used as modifying additives.[23–32]

Using high performance gas–liquid chromatography on quartz capillary columns and chromatograph-linked mass spectrometry, a detailed study has been made of the composition of the products of synthesis from CO, H_2, and ammonia[33] and dimethylamines[32,34,35] (Fig. 3 of Table 1).

The mechanisms of the formation of alkylamines in modified FT-syntheses have been examined[28,32–35] and it has been shown[32–35] that the mechanism proposed by Henrici-Olive,[28] which presupposes competition between CO and NH_2 for insertion in the metal–alkyl bond, does not operate when the reaction is carried out in the presence of the RPFIC. The probable pathways leading to the

formation of alkylamines in the presence of RPFIC can be represented schematically as follows:[32-35]

$$n\,CO + (2n+1)\,H_2 \xrightarrow[-(n-1)H_2O]{} [OI]_n \xrightarrow{+H_2} C_nH_{2n}O$$

$$[OI]_n \xrightarrow[-H_2O]{+HNR^1R^2,\ H_2} C_nH_{2n+1}NR^1R^2,$$

where $[OI]_n$ is an oxygen-containing intermediate in which the number of carbon atoms is n and R^1, R^2 = H or Me.

One of the pathways in this scheme leads to the formation of amines as a result of the direct hydroamination of the surface oxygen-containing intermediate $[OI]_n$—the precursor of an aldehyde, ketone, or alcohol, while the other pathway leads to the hydroamination of the alkanals and alkyl methyl ketones $C_nH_{2n}O$—the primary components of FT-products. The scheme proposed above agrees with the data in Table 1 and with the fact that the alkanols formed under the conditions of the FT-synthesis with the addition of a third component are not aminated.[34,35]

Table 1. Composition of Fischer–Tropsch synthesis products (wt. %) with participation of ammonia and dimethylamine (RPFIC $1Al_2O_3 + 1.5BaO + 0.4SiO_2$, 176 °C, 12 MPa, $H_2 : CO = 4$).

Reaction	Alkanes	Alkenes	Alkanols	Alkyl-methyl ketones	Alkyl-amines	Unidentified components	Refs.
$CO + H_2$	26.5	9	50	3.5	—	11	[33]
$CO + H_2 + (CH_3)_2NH$ (5%)	29	8.5	18	3.5	26*	15	[32]
$CO + H_2 + NH_3$ (12%)	32	11.5	6.5	2	37**	11	[33]

* Alkylamines $C_nH_{2n+1}N(CH_3)_2$, where $1 \leqslant n \leqslant 17$.

** Alkylamines $C_nH_{2n+1}NH_3$ including 3.5% of di-n-alkylamines.

2. The Fischer–Tropsch synthesis modified by acetylene and its derivatives

The addition of acetylene or its derivatives makes it possible in the first place to increase the productivity of the FT-synthesis.

The productivity of the gas-phase synthesis from CO and H_2 with the addition of 1.5% of C_2H_2 at 170–190 °C, p_{CO} = 11 MPa, and p_{H_2} = 3.5 MPa in the presence of the RPFIC $2Al_2O_3 + 0.5V_2O_5 + (0.5-1)K_2O$, calculated relative to the product which is a liquid at 20 °C, amounted to 60–65 g h^{-1} (litre cat.)$^{-1}$ [36,37] against 40–45 g h^{-1} (litre cat.)$^{-1}$ in the usual FT-synthesis. The achievement of the acetylene-modified FT-synthesis in the liquid phase makes it possible to increase the productivity to 450 g h^{-1} (litre cat.)$^{-1}$.[38]

The study of the products of the FT-synthesis from CO, H_2, and $HC{\equiv}{}^{14}CH$ showed that the molar radioactivity of all the alkanols, starting with 1-propanol, is constant and close to the molar radioactivity of the added acetylene,[39] i. e. acetylene (or its radioactive fragment) is incorporated singly in the growing hydrocarbon chain. This fact suggests that the observed increase in productivity is caused by the initiating role of acetylene, which gives rise to a primary C_3 complex on interaction with the synthesis gas.[40,41]

The FT-syntheses modified by compounds having the general formula $R-C{\equiv}CH$, where R = Ph, CH_2OH, CH_2OCH_3, or $CH_2O(CH_3)_3$, have been investigated.[42-47] In the presence of the RPFIC $(3-4)(SiO_2 + Al_2O_3 + V_2O_5) + (0.5-1)K_2O$, the interaction of the synthesis gas with phenylacetylene yields mainly aromatic alkyl-substituted alcohols and hydrocarbons having the composition $Ph(CH_2)_nX$, where n = 3–8 and X = OH or H. Most of the added phenylacetylene is then hydrogenated to styrene and ethylbenzene and gives rise to oligomers. Apart from the components containing an aromatic ring, the product contains up to 25% of n-alkanes, alkanols, and alkanals. Certain characteristics of the phenylacetylene-modified FT-synthesis are presented in Table 2.

Table 2. Characteristics of the gas-phase and liquid-phase syntheses of aromatic alkyl-substituted alcohols from CO, H_2, and $PhC{\equiv}CH$ (150 °C, 10 MPa, $CO : H_2 = 1$, $v = 10^3$ h^{-1}).[44]

Process	Productivity, g h^{-1} (litre cat)$^{-1}$			Selectivity, %			Losses, %	Conversion, %
	$\Sigma Ac_{ph} + Ad_{ph}$	H_{ph}	ΣAc, Ad, H	$\Sigma Ac_{ph} + Ad_{ph} + H_{ph}$	EB + ST	oligomers		
Liquid-phase (C_6H_6 soln)	48	21	1—1.5	21	43	1	6	29
Gas-phase	15	5	6—8	7	15	70	3	5

Notation. v is the space velocity of the synthesis gas, $\Sigma Ac_{ph} + Ad_{ph}$ the overall content of alcohols and aldehydes incorporating the $Ph(CH_2)_2$ fragment, H_{ph} hydrocarbons containing the $Ph(CH_2)_2$ fragment, ΣAc, Ad, H the overall content of alkanols, alkanals, and alkanes, EB + ST the overall content of ethylbenzene and styrene.

The synthesis of bifunctional compounds—αω-diols and alkoxyalcohols—from CO, H_2, and substituted acetylenes have also been achieved in the presence of RPFIC:[45-47]

$$CO + H_2 + HC{\equiv}CCH_2OH \rightarrow HO(CH_2)_nOH + H_2O,$$

$$CO + H_2 + HC{\equiv}CCH_2OR \rightarrow HO(CH_2)_nOR + H_2O,$$

where R = CH_3 or $C(CH_3)_3$ and n = 4–7.

In terms of their reactivity in the synthesis, the initiating reagents can be arranged in the sequence $HC{\equiv}CH > PhC{\equiv}CH > (CH_3)_3COCH_2C{\equiv}CH \simeq CH_3OCH_2C{\equiv}CH > HOCH_2{\equiv}CH$.

It has been shown[48] that oct-1-yne, hex-1-yne, and hex-3-yne participate, like acetylene, in the propagation of the hydrocarbon chain in their interaction with the synthesis gas. On the other hand, acetonitrile, butyne-1,4-diol, and the halogenoalkynes $HC{\equiv}CCH_2X$, where X = Cl or Br, do not possess the properties of initiating reagents in the FT-synthesis.

IV. Reactions of alcohols, aldehydes, and olefins under the conditions of the Fischer–Tropsch synthesis

In order to elucidate the possible involvement of oxygen-containing compounds in FT-synthesis in the presence of RPFIC of different composition, the reactions of the methanol $^{14}CH_3OH$,[49-51] the ethanols $CH_3{}^{14}CH_2OH$, $^{14}CH_3CH_2OH$, $CH_3{}^{14}CD_2OH$, and $CD_3{}^{14}CH_2OH$,[52-54] the propanols $CH_3CH_2CH_2OH$, CH_3CH_2.

.$^{14}CH_2OH$, $CH_3{}^{14}CH_2CH_2OH$, $^{14}CH_3CH(OH)CH_3$,[49,55,56] the butanols n-C_4H_9OH, $^{14}CH_3CH(CH_3)CH_2OH$, and $C_3H_7{}^{14}CH_2OH$,[49,51,55] benzyl alcohol,[57] the formaldehyde $H^{14}CHO$,[50] the ethanals $CD_3{}^{14}CHO$ [58] and $CD_2D^{14}CHO$,[59] and propanol[55,56] were investigated. It was established that the principal reactions of alkanals under the conditions of the FT-synthesis are their hydrogenation to the corresponding alcohol, decarbonylation to alkanes containing 1 carbon atom less, and oxidation to the corresponding acid.[55,58,59] On the other hand, acetaldehyde added to the synthesis gas is partly decomposed via the reaction[59]

$$2CH_3CHO+2H_2=C_4H_9OH+H_2O.$$

Under the conditions of FT-synthesis, alcohols undergo ester condensation:[55,59]

$$2C_4H_9OH=C_3H_7COOC_4H_9+2H_2$$

and enter into a homologisation reaction:[51]

$$C_4H_9OH+CO+2H_2=C_5H_{11}OH+H_2O.$$

Aromatic alkyl-substituted alcohols and hydrocarbons $Ph(CH_2)_nX$, where X = OH or H and n = 2–4, were first obtained in FT-synthesis with added benzyl alcohol. The conversion of $PhCH_2OH$ reaches 90% in the presence of the RPFIC $2Al_2O_3$ + $0.8V_2O_5$ + $0.5K_2O$. The main alcohol reaction product is then toluene, benzene and bibenzyl being formed in small amounts.[57]

Studies on syntheses from CO and H_2 with added alkenes CH_3CH_2CH = $^{14}CH_2$,[60] CH_2 = $^{14}CH_2$,[56,61,62] CH_2 = CH_2,[63] and CH_2 = $C(CH_3)CH$ = CH_2 [64] are important for the understanding of the mechanism of the FT-synthesis and ways of intensifying it. The principal reaction of olefins is their hydrogenation (to the extent of 80–90%) to the corresponding alkanes. On the other hand, but-1-ene is partly converted into n-pentane and pent-1-ene in the presence of RPFIC $2Al_2O_3$.[60]

However, under the conditions of FT-synthesis in the presence of RPFIC alkenes are capable of entering to a definite extent also into the oxo synthesis reaction,[60,62] the yield of alcohols increasing with increase in their concentration (Table 3).

Table 3. The influence of ethylene on the yield of alcohols in synthesis from CO and H_2 in the presence of the RPFIC $2Al_2O_3$ + $0.5V_2O_5$ + $0.5K_2O$ [62] (2–2.5 MPa, H_2 : CO = 3.8).

T, °C	C_2H_4 concentration, %	Relative yield of $C_nH_{2n+1}OH$ with different n				
		1	2	3	4	5
204	7	0.4	1.0	1.0	0.3	0.2
204	15	0.3	1.0	1.3	0.4	0.3
230	50	0.3	1.0	13.0	0.6	0.5
230	0	0.3	1.0	0.4	0.2	0.1

Studies on the reactions of aldehydes, alcohols, and olefins under the conditions of FT-synthesis[49–65] have shown that in the presence of the RPFIC the contribution of reactions with participation of these compounds with formation of the FT-product is as a rule low and amounts to only several per cent.

Apart from the synthesis from CO and H_2, the synthesis from CO and H_2O (the Kölbel–Engelhardt synthesis), which results in the formation of products close in composition to the FT-product, has also been achieved.[66]

The synthesis from CO and H_2O in the presence of RPFIC was first achieved in the presence of the catalyst for ammonia synthesis at a temperature of 300 °C, a pressure of 4 MPa, and for the ratio CO : H_2O = 2–2.5. Under these conditions, the conversion of CO reaches 84% and the main products are alkanes and alkenes.[67] The formation of alkanes in the Kölbel–Engelhardt synthesis (KE-synthesis) is formally regarded as a result of the combination of the water gas reaction[4] and the FT-synthesis:

$$(2n+1)\,CO+(2n+1)\,H_2O=(2n+1)\,CO_2+(2n+1)\,H_2 \quad \text{(water gas reaction)},$$
$$n\,CO+(2n+1)\,H_2=C_nH_{2n+2}+n\,H_2O \quad \text{(FT-synthesis)}$$
$$(3n+1)\,CO+(n+1)\,H_2O=C_nH_{2n+2}+(2n+1)\,CO_2 \quad \text{(KE-synthesis)}$$

Similar combinations of stoichiometric equations can be formulated also for the formation of other components of the KE-products—alkenes, alkanols, alkanals, etc.

The results obtained in the synthesis from CO_2 and H_2 in the presence of RPFIC, whose main product is ethanol, have been published.[68] At 335–370 °C and 20–40 MPa and for H_2 : CO_2 = 3 and a space velocity of the synthesis gas of $10^4(2-3)$ h^{-1}, the productivity of the process with respect to ethanol is 30–45 g h^{-1} (litre cat.)$^{-1}$. Together with ethanol, appreciable amounts of methanol, 1-propanol, and acetic acid are formed.

The products of the Fischer–Tropsch synthesis with participation of a third component, the Kölbel–Engelhardt synthesis, and the synthesis from CO_2 and H_2 are complex mixtures of organic products with a broad range of compositions in terms of different fractions. Alcohols and amines can be isolated from the products by familiar chemical methods (in the form of borates or hydrochlorides respectively). After their separation by fractionation into comparatively narrow fractions, they can find applications as raw materials for the preparation of plasticisers, surfactants, etc. The remainder of the products can be used as additives to hydrocarbon fuels or as a hydrocarbon raw materials suitable for further processing by traditional methods.

The processes examined are not at present competitive in relation to the familiar methods of synthesis of functional derivatives of hydrocarbons (alcohols, amines). However, in view of the possibility of their being carried out on the basis of virtually any hydrocarbon raw material, including a renewable raw material, the above synthesis will become increasingly more promising for practical use as the petroleum resources are exhausted.

This is why the interest in the study of syntheses from carbon oxides and hydrogen is at present growing continuously.

V. Syntheses of nitrogen-containing compounds

1. Hydroamination of oxygen-containing compounds

(a) Hydroxy-compounds. The deliberate search for effective catalysts of the reaction involving the amination of alcohols, which is prosecuted also at the present time, led at the beginning of the 1960's to development of an effective RPFIC for the synthesis of alkylamines from alkanols and ammonia in the presence of hydrogen.[69] The best yield of amines, stable in time, are attained in the presence of the RPFIC having the composition $5V_2O_5$.[70]

In the interaction of the RPFIC with a mixture of an alcohol, ammonia, and hydrogen, there is a possibility of the formation, during the amination reaction on the surface and in the bulk of the catalyst, of iron nitrides, carbonitrides, and oxides, which can influence the activity and selectivity of the catalyst. This problem has been partly considered in relation to the gas-phase reaction of 1-butanol with an ammonia–hydrogen mixture ($C_4H_9OH : NH_3 : H_2 = 1 : 8 : 24$) at 120–170 °C in the presence of three modified specimens of the RPFIC $5V_2O_5$.[22] The first specimen was enriched in iron ε-nitride, the second in iron carbonitride, and the first in iron oxides. In the presence of all three specimens, the yield of butylamines was significantly lower than in the presence of the initial RPFIC after prolonged use. This shows that, on contact between the RPFIC and the reaction mixture containing more than 70% of H_2, iron nitrides, carbonitrides, and oxides accumulate in the catalyst at least in amounts which can be detected from the change in the yield of amines.

A consequence important for the preparative gas-phase synthesis of amines, consisting in the fact that the stable activity and selectivity of the RPFIC can be maintained by retaining a high H_2 concentration in the initial gas mixture, follows from the data of the above study.[22]

In terms of their ability to enter into the amination reaction in the presence of the RPFIC $5V_2O_5$, alkanols can be arranged in the sequence[70,71] 1-octanol ≃ 2-octanol > 3-octanol > 4-octanol ≃ 2-methyl-4-heptanol ≃ 2-ethyl-1-hexanol.

On the other hand, in the amination of $C_nH_{2n+1}OH$, where $n = 5-10$, the conversion and overall selectivity with respect to alkylamines are independent of n, although the selectivity with respect to secondary alkylamines increases somewhat with increase in n.[72]

Table 4. Amination of 1-octanol in the presence of a RPFIC (210 °C, 5 MPa, space velocity of n-$C_8H_{17}OH$ 1.2 h^{-1}).[73]

State of aggregation of alcohol	$H_2:NH_3:ROH$	Conversion of ROH, %	Composition of amines, %		
			$C_8H_{17}NH_2$	$(C_8H_{17})_2NH$	$(C_8H_{17})_3N$
Gas*	15:12:1	88	75	21	4
Gas	34:3:1	45	38	50	12
Liquid	4:3:1	46	20	72	8

* 230 °C, space velocity of the alcohol 0.35 h^{-1}.

The amination of primary alcohols in the presence of RPFIC is a consecutive reaction leading to the formation of primary, secondary, and tertiary amines. In this reaction, it is always difficult to attain a high selectivity with respect to each amine separately. In order to increase the yield of secondary amines from alkanols and ammonia, a novel procedure has been proposed, consisting in carrying out the reaction in a film of the liquid alcohol.[73] In the amination of 1-octanol, this procedure makes it possible to increase the selectivity with respect to secondary amines from 21 to 72% (Table 4).

Optimum conditions have been found for the preferential synthesis of primary, secondary, or tertiary alkylamines from primary alcohol and ammonia under hydrogen pressure.[74–77] In the amination of 1-alkanols $C_{n+1}OH$, where $n = 6-12$, in the presence of the RPFIC $5V_2O_5$ at 260–295 °C, mixtures of alkylamines containing up to 96% of $C_nH_{2n+1}NH_2$, or up to 60% of $(C_nH_{2n+1})_2$, or up to 70% of $(C_nH_{2n+1})_3N$ were obtained. In all cases, amines containing the alkyl fragment of the initial alcohol are formed.[78]

Alkanols with a branched carbon skeleton (2-ethyl-1-hexanol and 2,2-dimethyl-1-propanol) are also aminated in the presence of RPFIC with high yields of the corresponding primary amines.[79,80]

Important results concerning the kinetics and mechanism of the amination of alkanols by ammonia in the presence of RPFIC have been obtained.[81–87] It has been established that the dependence of the rate of amination of the alcohol on its partial pressure at a constant rate of supply is characterised by a maximum in the region of $p_{ROH} = 0.02-0.03$ MPa.[83,85] This suggested that the kinetic equation for the reaction has a rational-fractional form, the power exponent of p_{ROH} in the denominator of the equation being greater than in the numerator.[83–85] The occurrence of the kinetic isotope effect in the amination of $CH_3(CH_2)_6CD_2OH$ and CH_3CD_2OH [82,84,85] permitted an inference about the character of the rate-limiting stage of the process. Within the framework of the Langmuir–Hinshelwood–Hogan–Watson kinetic model, a multistage amination mechanism has been proposed in which the rate-limiting stage is the dehydrogenation of the initial alcohol to the aldehyde.[84,85] The rate of amination of primary alkanols at moderate[84] and atmospheric[85] pressures is described by the equation

$$W = \frac{k \cdot b_{ROH} \cdot p_{ROH}}{(1 + b_{ROH} \cdot p_{ROH} + b_{H_2O} \cdot p_{H_2O})^2},$$

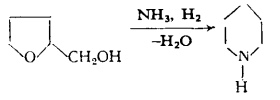
where k is the amination reaction rate constant, p_{ROH} and b_{ROH} are respectively the partial pressure and adsorption coefficient of the alcohol, and p_{H_2O} and b_{H_2O} are respectively the partial pressure and absorption coefficient of H_2O. The equation describes satisfactorily all the experimental data in the temperature range 180–270 °C and in the range of alcohol conversions 11–96%.

Fused iron catalysts exhibit an activity also in the *N*-alkylation of dimethyl- and methyl-amines.[86–88] Thus, in the reaction of 1-octanol with CH_3NH_2 in the presence of the RPFIC $1V_2O_5$ + 0.85BaO at temperatures in the range 230–240 °C, at a pressure of 2 MPa, for the ratios $H_2 : CH_3NH_2 : C_8H_{17}OH = 16 : 4 : 1$, and for a rate of supply of the alcohol at 350–400 g h^{-1} (litre cat.)$^{-1}$, the conversion of the alcohol reaches 93% and the overall selectivity with respect to amines is 93%, of which 70% corresponds to methyl-n-octylamine.[88] The kinetic equation proposed for the description of the interaction of alcohols with ammonia is also applicable to the reactions of alkanols with $(CH_3)_2NH$.[86,89]

Effective methods have been developed for the preparation of amines from alicyclic[90–92] and aromatic alkyl-substituted[93] alcohols and ammonia in the presence of RPFIC. Under conditions optimal for the synthesis of primary amines [315 °C, $p_{NH_3} = 3.2$ MPa, $p_{H_2} = 1.8$ MPa, rate of supply of cyclohexanol 36 mol h^{-1} (litre cat.)$^{-1}$] the conversion of the alcohol into amines is 88.5% for a selectivity with respect to cyclohexylamine of 95%.

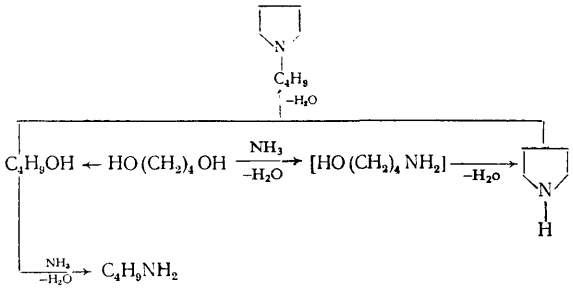
It was shown above that reactions involving the amination of alcohols with different structures take place selectively in the presence of RPFIC with formation mainly of the corresponding primary amines. In contrast to this, in the hydroamination of

tetrahydrofurfuryl alcohol (THFA) the main reaction product is not tetrahydrofurfurylamine but piperidine, whose yield is 51%:[94-96]



By virtue of the availability of the THFA, which is obtained from a renewable natural raw material, this synthesis of piperidine can be of interest for practical use.

Fused iron catalysts are used not only for intermolecular amination but also for intramolecular amination. Thus the interaction of butane-1,4-diol (BD) with an ammonia–hydrogen mixture in the presence of RPFIC results in the formation of pyrrolidine and its derivatives.[97] Under optimum conditions [260 °C, p_{NH_3} = 2, p_{H_2} = 2.8, and p_{BD} = 0.14 MPa; rate of supply of BD 560 g h^{-1} (litre cat.)$^{-1}$], the conversion of BD is 99% for a selectivity with respect to pyrrolidine above 70%.[97] The principal reactions of BD in the presence of RPFIC are illustrated schematically below:



The syntheses of piperazine from diethanolamine, of 1-alkyl- and 1,4-dialkyl-piperazines from *N*-alkyldiethanolamines, as well as morpholine from diethylene glycol have also been achieved.[97-99]

Table 5. Hydroamination of aldehydes and ketones [230 °C, p_{H_2} = 2.5 MPa, p_{NH_3} = 1.3 MPa, $p_{R^1COR^2}$ = 0.05 MPa,[102] $V_{R^1COR^2}$ = 20 mol h^{-1} (kg cat.)$^{-1}$]

Initial carbonyl compound	Amine formed	Conversion, %	Selectivity w.r.t. amine, %
2-Heptanone	2-Aminoheptane	93	95
4-Heptanone	4-Aminoheptane	92	92
2-Octanone	2-Amino-octane	92	95
2-Nonanone	2-Aminononane	90	96
Octanol	1-Amino-octane	87	90
Cyclohexanone	Cyclohexylamine	98	98
1-Phenyl-2-propanone	2-Amino-1-phenylpropane	85	93
Acetophenone*	1-Amino-1-phenyl ethane	96	70

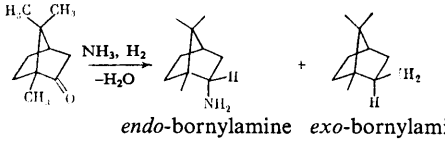
* Temperature 210 °C, rate of supply of acetophenone 9 mol h^{-1} (kg cat.)$^{-1}$.

(b) Carbonyl compounds. Aliphatic aldehydes can be hydroaminated to amines in the presence of RPFIC.[69] The kinetics of the hydroamination of carbonyl compounds have been investigated in relation to 2-octanone.[100,101] The kinetic isotope effect has been noted in the hydroamination of butanone when H_2 in the initial reaction mixture was replaced by D_2 and a multistage process mechanism, corresponding to this observation, was proposed, in which the addition of hydrogen to the ketimine is regarded as the rate-limiting stage. The kinetic equation assumes the form

$$W = \frac{k\, p_{H_2}^{0.5}}{1 + b_{H_2O} p_{H_2O}},$$

where k is the apparent hydroamination rate constant, p_{H_2} and p_{H_2O} are the partial pressures of H_2 and H_2O respectively, and b_{H_2O} is the adsorption coefficient of H_2O. The optimum conditions for the synthesis of primary amines from certain aldehydes and ketones of different structure in the presence of RPFIC $5V_2O_5$ have been determined using this equation[102] (Table 5).

In certain cases, the RPFIC exhibits a stereoselectivity unusual for metallic heterogeneous catalysts. Thus in the hydroamination of *d,l*-camphor,[103-105] its overall conversion into *endo*- and *exo*-bornylamines reaches 92% for the *endo* : *exo* = (1.4–1.8) : 1 ratio.



endo-bornylamine *exo*-bornylamine

Such stereoselectivity has been examined in a study[105] where it was shown that its most probable cause is the "imine–enamine" tautomerism on the acid–base centres of the RPFIC. However, one cannot rule out also a relation between the unusual stereoselectivity and the characteristic features of the coordination of the sterically hindered camphor molecule on the active centres of the RPFIC.

(c) Esters and ethers. In the hydroamination of aliphatic symmetrical and asymmetric esters in the presence of the RPFIC $5V_2O_5$, both the alcoholic and acid components of the ester molecule participate in the replacement of the ester group by the amino-group:[106-108]

$$R^1CH_2OOCR^2 \xrightarrow[-H_2O]{NH_3} R^1CH_2NH_2 + R^2CH_2NH_2.$$

At 280–300 °C, p_{NH_3} = 1.5–2.3, p_{H_2} = 2.6–3.5, and $p_{R^1CH_2OOCR^2}$ = 0.06–0.01 MPa and for a specific rate of supply of the ester of 200–500 g h^{-1} (litre cat.)$^{-1}$, the conversion of the latter reaches 86% for a selectivity of 70–88% with respect to primary alkylamines and 12–30% with respect to secondary alkylamines. On the other hand, ethers (diethyl ether, t-butyl methyl ether, tetrahydrofuran, and 1,4-dioxane) are not aminated in the presence of RPFIC.[108]

2. The interaction of oxygen-containing compounds with ammonia

It was shown above that alkylamines are formed from a vapour–gas mixture of an alcohol, aldehyde, ketone or ester, ammonia, and hydrogen on contact with RPFIC. The interaction of alcohol with ammonia in the absence of hydrogen in the presence of RPFIC of different composition ($2Al_2O_3 + 5Cr_2O_3$; $2Al_2O_3 + 2.5MnO_2$; $2Al_2O_3 + 0.5V_2O_5$; $5Al_2O_3 + 2.5K_2O$) has been investigated.[109,111] At 300–320 °C and for an alkanol : ammonia = 1 : 1–3 ratio and a rate of supply of the alcohol of 4–4.5 mol h^{-1} (litre cat.)$^{-1}$, $C_3H_7C{\equiv}N$, $C_5H_{11}C{\equiv}N$, and $C_8H_{17}C{\equiv}N$ are formed from 1-butanol, 1-hexanol, and 1-nonanol respectively in 80–85% yields. The rate of cyanation of alkanols to nitriles is independent of the length of the carbon chain.[109,110] Data concerning the influence of the structure of the oxygen-containing

group on its conversion into nitriles are presented in Table 6.[111]
A general mechanism of the conversion of alcohols into amines and nitriles is presented below.

Scheme 1

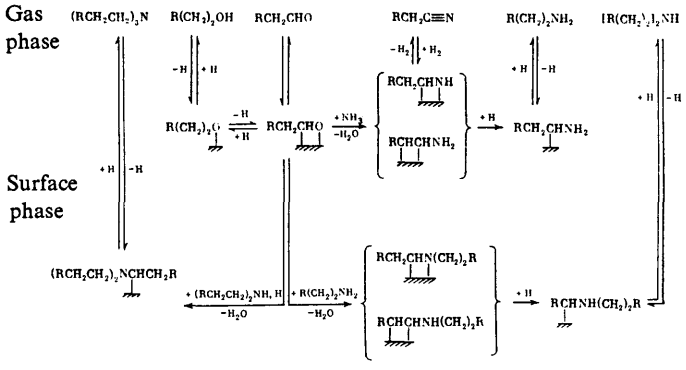


Table 6. Interaction of oxygen-containing compounds with NH_3 in the presence of the RPFIC $2Al_2O_3$ at 320 °C.[111]

Initial compound	Content of nitriles in reaction mixture, %			Content of amines, %
	$C_3H_7C{\equiv}N$	$C_2H_4C{\equiv}N$	$CH_3C{\equiv}N$	
1-Butanol	80	—	—	1-Aminobutane, 4
2-Methyl-1-propanol	73.5	1.5	0.2	1-Amino-2-methylpropane, 3.6
2-Butanol	—	3.9	2.0	—
t-Butyl alcohol	—	—	—	—
Butanone	—	2.6	1.0	—
1-Butanal	69.7	0.4	0.2	1-Aminobutane, 4.9
Ethyl acetate	—	—	51	—

Overall, RPFIC are fairly effective in the syntheses of alkylamines, certain simple saturated heterocycles, and nitriles from oxygen-containing compounds. Analysis of the literature data shows that these processes make it possible to attain higher productivities and proceed more stably than the processes involving the synthesis of the above nitrogen-containing compounds by other known preparative methods in the presence of other heterogeneous catalysts (nickel, copper–chromium, etc.). The reaction mixtures obtained as a result of the amination of individual oxygen-containing compounds in the presence of RPFIC are fairly simple in composition and as a rule contain the target products at a high concentration, which makes it possible to isolate them by means of the usual fractionation.

VI. Hydrogenation and dehydrogenation, isotope exchange, and other reactions

1. The hydrogenation of aldehydes and ketones to alcohols

Alcohols, especially aliphatic alcohols, are the most important products of preparative and industrial organic synthesis. The preparation of high-quality alcohols is in most cases based on the use of the reaction involving the hydrogenation of aldehydes and ketones.

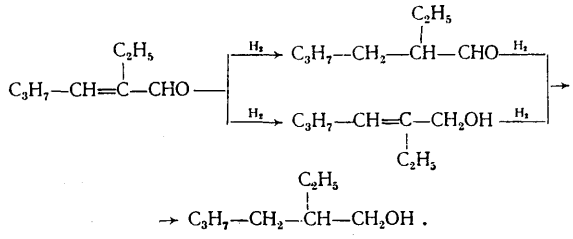
The possibility, in principle, of the formation of alcohols in the hydrogenation of aliphatic aldehydes in the presence of RPFIC has been demonstrated[112,113] but the RPFIC proposed for this purpose ($1MoO_3$ or $2Al_2O_3$) require a hydrogen pressure of 10 MPa and above.

The improvement of the method led to the development of the highly effective RPFIC $(2-5)V_2O_5$, in the presence of which carbonyl compounds were converted into the corresponding alcohols at p_{H_2} = 1–3.5 MPa [114–117] at a high rate and with a high selectivity (Table 7).

Table 7. Hydrogenation of aldehydes and ketones in the presence of a RPFIC (space velocity of H_2 2 × 10^4 h^{-1}).[114,117]

Initial carbonyl compound	Alcohol obtained	T, °C	p_{H_2}, MPa	Rate of supply, h^{-1}	Conversion, %	Selectivity w.r.t. alcohol, %
Butanol	1-Butanol	180	1.5	2	99.5	99.5
Nonanal	1-Nonanol	180	2.5	4.5	98	98.5
2-Octanal	2-Octanol	150	3.5	3	97.5	99.5
2-Ethylhex-2-en-1-al	2-Ethyl-1-hexanol	135	0.9	1.5	95	99
Cyclopentanone	Cyclopentanol	185	2.1	3.5	97	99
Cyclohexanone	Cyclohexanol	185	2.5	4.5	94	99.5

The hydrogenation of 2-ethylhex-2-en-1-al in the presence of water leads to an increase in the yield of an unsaturated alcohol 2-ethylhex-2-en-1-ol:[116]



Data on the kinetics of the hydrogenation of aliphatic and alicyclic ketones have been published.[117–121] The kinetics of the hydrogenation of 2-octanone and cyclohexanone have been investigated in the presence of the RPFIC $5V_2O_5$ under conditions where the reverse dehydrogenation reaction of the alcohols formed could be neglected. The rate of reaction increases with increase in the ketone and hydrogen concentrations and is independent of the alcohol concentration (the reaction product). A kinetic isotope effect (KIE) was observed following the replacement of H_2 by D_2 in the hydrogenation of 2-octanone.[121] A multistage reaction mechanism was proposed in which the rate-limiting stage is the addition of the first hydrogen atom to the adsorbed ketone molecule. For low conversions of ketones under isothermal conditions, the initial rate is described by a kinetic equation of the type[117,118]

$$W_0 = k \cdot p_{0(R^1COR^2)} \cdot p_{0(H_2)}^{0.5},$$

where k is the apparent reaction rate constant and $p_{0(R^1COR^2)}$ and $p_{0(H_2)}$ are the initial partial pressures of the ketone and hydrogen.

The equation holds satisfactorily over the entire experimental temperature range and the ranges of the ketone and hydrogen partial pressures.

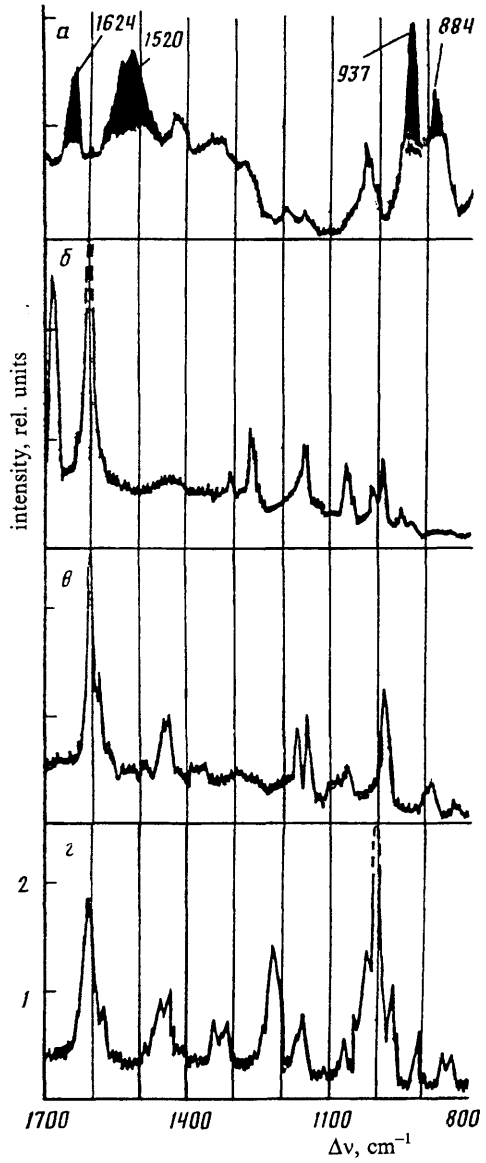


Figure 4. Raman spectra: *a*, the RPFIC surface in the hydrogenation of acetophenone *in situ* (177 °C, p_{H_2} = 0.2 MPa, p_{PhCOCH_3} = 4 kPa); *b*, acetophenone; *c*, methylphenylcarbinol; *d*, ethylbenzene.[16,122]

The kinetics of the non-isothermal hydrogenation of ketones in a tubular flow reactor up to a conversion of 0.8 are described by the equation[120]

$$1/V = (1/A \cdot p_{o(R^1COR^2)} \cdot p^{0,5}_{o(H_2)}) \int_0^x \{[1/(1-x)] \exp E/RT_0(1+\alpha x)\}\, dx,$$

where V is the specific rate supply of the ketone, T_0 the initial reaction temperature, E the apparent activation energy, A the pre-exponential factor, α a coefficient, and x the conversion of the ketone

The mechanism of the addition of hydrogen to ketones during their hydrogenation to alcohols in the presence of RPFIC has been investigated by a combined method involving laser Raman spectroscopy *in situ* and gas–liquid chromatography[16,17,122] and also by reaction chromatograph-linked mass spectrometry (RCMS).[123,124]

The Raman spectrum (Fig. 4*a*) of the surface of the RPFIC $5V_2O_5$ in the hydrogenation of acetophenone (ACP) by hydrogen (ACP conversion 6%, selectivity with respect to methylphenylcarbinol ~70%, selectivity with respect to ethylbenzene ~30%) differs significantly both from the spectrum of the initial ACP (Fig. 4*b*) and from the spectra of the reaction products (Figs. 4*c* and 4*d*). The intense lines in the region of ~1624, ~1520, ~937, ~884 cm^{-1} (Fig. 4*a*) can probably be attributed to intermediates in which there are C=O, C=C, C–C, and C–O bonds and the intermediates themselves can be interpreted as the "keto-" and "enol-forms" of the adsorbed ACP.

The question of the ratio of the "ketone" and "enolic" mechanisms in the hydrogenation of ketones in the presence of RPFIC was solved[123,124] by the RCMS method using a deuterium label and involving the analysis of the isotope composition of the trimethylsilyl ethers of the deuterioalcohols formed. The initial ketones can undergo the following reactions:

ketone mechanism

$$-CH_2-\overset{|}{C}=O \xrightarrow[RPFIC]{D_2} -CH_2-\overset{|}{C}D-OD \xrightarrow{BSTFA} -CH_2-\overset{|}{C}D-OSiMe_3 \quad (E_k)$$

"enolic" mechanism

$$-CH=\overset{|}{C}-OH \xrightarrow[RPFIC]{D_2} -CHD-\overset{|}{C}D-OH \xrightarrow{BSTFA} -CHD-\overset{|}{C}D-OSiMe_3 \quad (E_e)$$

BSTFA = *N,O*-bis(trimethylsilyl)trifluoroacetamide

It is seen from the scheme presented that, depending on the mechanism, trimethylsilyl ethers E_k and E_e with different numbers of D atoms are formed, which can be demonstrated mass-spectrometrically. A typical chromatogram, recorded in an experiment with cyclohexanone, is presented in Fig. 5, while the mass spectra of the cyclohexanone deuteriation products are illustrated in Fig. 6. Calculation of the isotope composition of the trimethylsilyl ethers E_k and E_e, taking into account the isotope composition of the unreacted cyclohexanone and its H/D exchange, established that the hydrogenation of alicyclic ketones to alcohols at 70–210 °C proceeds with equal probability via both the "enolic" and "ketone" mechanisms.

2. Dehydrogenation of alcohols and amines

It is known that the catalysts $1MoO_3$ or $2Al_2O_3 + 0.5V_2O_5 + 1K_2O$ for the hydrogenation of carbonyl compounds to alcohols can be used under appropriate conditions for the reverse alcohol dehydrogenation reaction. 1-Heptanol and ethanol have been hydrogenated in the presence of such catalysts to heptanal and acetaldehyde respectively in 30–40% yield.[113,125] The kinetics and mechanism of the dehydrogenation of alcohols in the presence of the RPFIC $5V_2O_5$ have also been investigated in other studies.[85,125] In the gas-phase dehydrogenation of CH_3CD_2OH, CD_3CH_2OH, and

CH_3CH_2OH [125] in helium at 180 °C, the rates of reaction of these ethanols are in the following proportions:

$$W_{CH_3CH_2OH}/W_{CD_3CH_2OH} \simeq 1;$$
$$W_{CH_3CH_2OH}/W_{CH_3CD_2OH} \simeq 2.5 \pm 0.1.$$

Hence it follows that the slow stage of the reaction is the abstraction of a α-hydrogen atom from the alcohol molecule. The kinetics of the dehydrogenation of the ethanols in the presence of the RPFIC $5V_2O_5$ correspond to the equation

$$W = \frac{k \cdot b_{ROH} \cdot p_{ROH}}{(1 + b_{ROH} \cdot p_{ROH} + b_{ACH} \cdot p_{ACH})^2},$$

where k is the reaction rate constant, p_{ROH} and b_{ROH} are the partial pressure and the adsorption coefficient of the alcohol respectively, and p_{ACH} and b_{ACH} are the partial pressure and the adsorption coefficient of the aldehyde respectively.

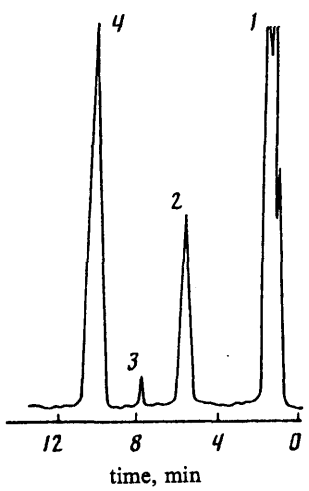
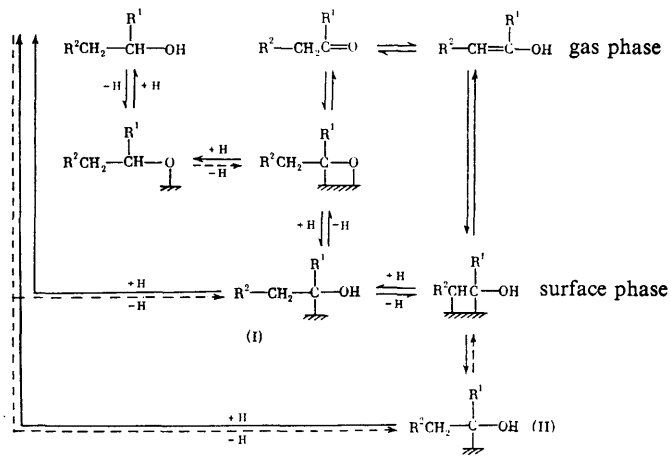


Figure 5. Chromatogram of the reaction mixture obtained in the deuteriation of cyclohexanone in the presence of a RPFIC:[124] *1*, BSTFA and its hydrolysis products; *2*, trimethylsilyl ether of deuteriated cyclohexanol; *3*, trimethylsilyl ether of deuteriated cyclohex-1-enol; *4*, deuteriated cyclohexanone.

The catalysts examined are capable of effecting the dehydrogenation of not only alcohols but also amines. Thus n-butylamine is dehydrogenated to butyronitrile in 78% yield in the presence of the RPFIC $2Al_2O_3$ at 280–320 °C.[111]

The mechanisms of the hydrogenation of carbonyl compounds to alcohols and of the dehydrogenation of the latter to aldehydes and ketones in the presence of RPFIC, based on data in Refs. 123–125, are presented below:

Scheme 2



After deuteriation, the isotope compositions of compounds (I) and (II) are different. The reactions designated by a dashed line occur only in the dehydrogenation of the alcohol.

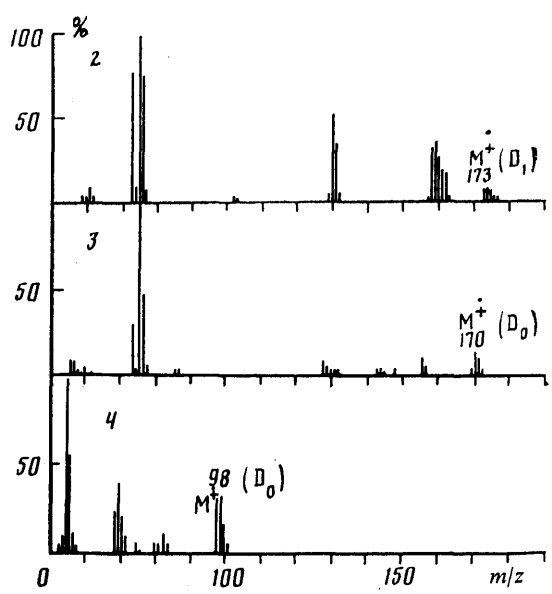


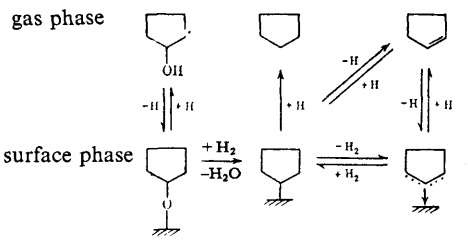
Figure 6. Mass spectra of the chromatographic bands presented in Fig. 5.[123]

3. Hydrodeoxygenation of alcohols, aldehydes, and ketones

The hydrodeoxygenation (HDO) of oxygen-containing compounds to hydrocarbons is used widely in preparative and industrial organic chemistry. Alcohols, aldehydes, and ketones with different structures are hydrodeoxygenated quantitatively to saturated hydrocarbons at 250–350 °C and p_{H_2} = 0.1–0.3 MPa in the presence of the RPFIC

$5V_2O_5$ with retention of the carbon skeleton of the initial oxygen-containing substrate.[126,127] The distribution of deuterium in the saturated hydrocarbons formed on deuteriodeoxygenation of alcohols, aldehydes, and ketones has been investigated[127] by the RCMS method.[128]

Analysis shows that the isotope compositions of the deuteriocyclopentanes obtained in the reaction of cyclopentene and cyclopentanol with deuterium (Fig. 7) are similar,[127] which suggests that the products of the deuteriation of an olefin and of the deuteriodeoxygenation of an alcohol are formed via intermediates having similar structures:



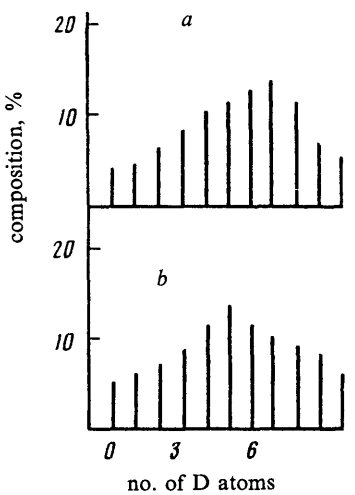
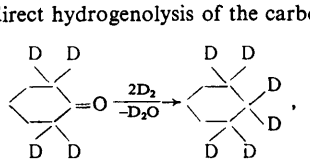


Figure 7. Isotope composition of the deuteriocyclopentanes obtained in the reactions of cyclopentene (*a*) and cyclopentanol (*b*) with D_2 (300 °C, p_{D_2} = 0.15 MPa).[127]

On the other hand, comparison of the isotope compositions of the deuteriocyclohexanes obtained as a result of the deuteriodeoxygenation of cyclohexanone and 2,2,6,6-tetradeuteriocyclohexanone (Fig. 8), according to which about 70% of all the $[D_n]$cyclohexanes is $[D_6]$cyclohexane, provides grounds for the assumption that this reaction proceeds via two pathways, the main one involving the direct hydrogenolysis of the carbonyl group:



while the other involves the hydrogenation initially of the ketone to the alcohol and then of the alcohol to the hydrocarbon.

When benzaldehyde was hydrodeoxygenated, it was observed unexpectedly that, together with toluene, up to 30% of bibenzyl and *trans*-stilbene is formed.[129] It has been suggested that one of the pathways leading to the formation of stilbene is the metathesis of benzaldehyde at the carbonyl group.

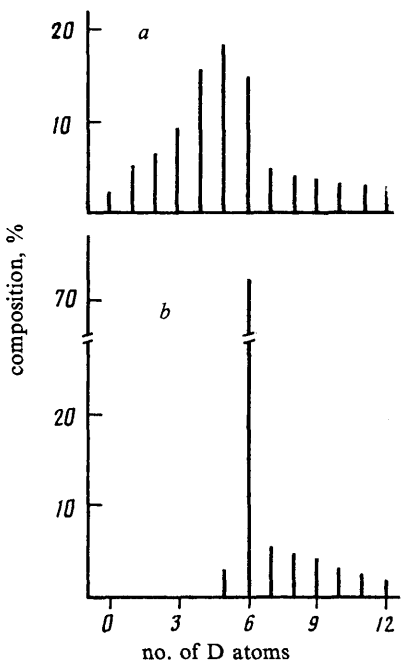
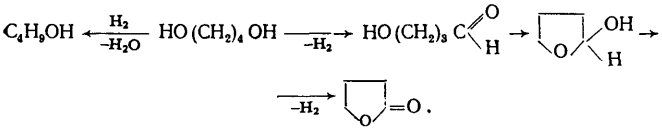


Figure 8. Isotope composition of the deuteriocyclohexanes obtained in the reaction of cyclohexanone (*a*) and 2,2,6,6-tetradeuteriocyclohexanone (*b*) with D_2.[127]

4. Hydrogenolysis of esters, diols, and other oxygen-containing compounds

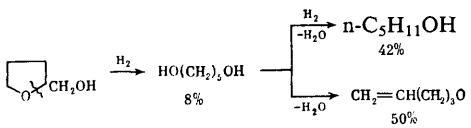
The gas-phase hydrolygenolysis of esters and ethers in the presence of RPFIC has been examined.[106-108] At 200–250 °C, n-heptyl oenanthate gives rise to 1-heptanol and n-heptane in 50 and 25% yields respectively. Only heptane in 18% yield was obtained under the same conditions from di-n-heptyl ether.

On interaction with H_2 in the presence of the RPFIC (4–5)V_2O_5 + 1(Al_2O_3 + SiO_2) at 280–300 °C and p_{H_2} = 2–3 NPa, butane-1,4-diol is converted into γ-butyrolactone and 1-butanol in 20–30% and 10–20 yields respectively:[130]



At 250–300 °C and p_{H_2} = 1–2 MPa, the conversion of tetrahydrofurfuryl alcohol (THFA) is 60–65%.[96] The tetrahydrofurfuryl ring is cleaved only at the C–O bond adjoining the alkoxy-substituent.

The reactions of THFA in the presence of RPFIC are illustrated in the following scheme:



The hydrogenolysis of THFA to pent-4-en-1-ol is an interesting case of the conversion of a heterocyclic alcohol into an unsaturated aliphatic alcohol.

5. Hydrogenation of C=C and C≡C bonds

Only a few studies have been specially devoted to questions concerning the hydrogenation of multiple carbon–carbon bonds in the presence of RPFIC. The possibility of the hydrogenation of hexene to hexane in the presence of the ammonia synthesis catalyst has been reported.[131]

Hept-1-ene and cyclopentene are hydrogenated quantitatively in a microreactor with a fluidised bed of RPFIC $5V_2O_5$ with pulsed supply of the olefin into a stream of H_2 or D_2 at 250 °C.[127]

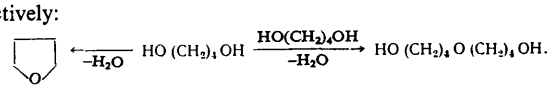
There are data for the hydrogenation of acetylene at 70 °C in the presence of the RPFIC $2Al_2O_3 + 0.5V_2O_5 + 1K_2O$. Isoprene is hydrogenated to a mixture of isopentane and isopentene in the presence of the same catalyst at 165–170 °C.[64]

Benzene is capable of being converted into cyclohexane in the presence of RPFIC, the catalyst having the composition $(5-8)Al_2O_3$ being the most active.[132,133] In its presence, the rate of hydrogenation of benzene is only several times smaller than in the presence of the nickel catalyst.[133]

6. Dehydration and polymerisation reactions

Until recently, the RPFIC was regarded exclusively as a metallic catalyst.[134] The role of stabilisers of the disperse metallic iron phase on the surface and of regulators of the particle size and of the overall surface area was attributed to the promoting agents. However, the RPFIC surface consists mainly of a non-metallic phase (see Section II). In other words, the surface layer of the RPFIC bears a formal similarity to that of traditional bifunctional catalysts, whose composition includes Group VIII metals (1–10%) on Al_2O_3, SiO_2, zeolite, etc. carriers.[135,136] The difference of the RPFIC consists primarily in the fact that, unlike the traditional catalysts, it incorporates 1–10% of promoting agents (Al_2O_3, SiO_2, V_2O_5, etc.) and 90–99% of α-Fe^0. Thus the RPFIC can be regarded as an inverted bifunctional catalyst. The manifestation of both oxidation-reduction (hydrogenation–dehydrogenation processes) and acid–base activities is characteristic of bifunctional catalysts. The efficiency of the RPFIC in oxidation–reduction reactions was demonstrated in previous Sections, but, as will be shown below, some of the results obtained in the presence of RPFIC can be treated from the standpoint of acid–base catalysis.

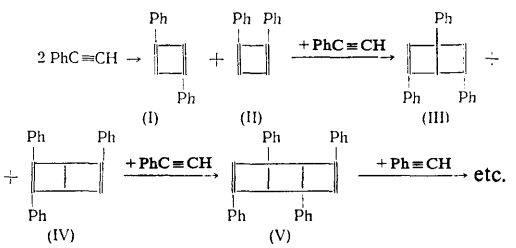
A typical acid–base catalytic reaction is the dehydration of alcohols or diols. The first such reaction carried out in the presence of the RIPMC $(4-5)V_2O_5 + 1(Al_2O_3 + SiO_2)$ was the dehydration of butane-1,4-diol.[130] It underwent both intermolecular and intramolecular dehydration in a H_2 atmosphere at 280–300 °C with formation of dibutylene glycol and tetrahydrofuran (THF) respectively:



Subsequently the intramolecular dehydration of ethylene glycol[137] and the intermolecular dehydration of t-butyl ether of propargyl alcohol[138] were achieved in the presence of RPFIC.

Compounds with the C=C and C≡C multiple bonds can enter into polymerisation reactions in the presence of RPFIC: at 220 to 230 °C, isoprene forms a solid rubber-like product, which consists of polyisoprene.[64]

The development of this approach led to the creation of a procedure for the oligomerisation of phenylacetylene (PA).[139,140] In the presence of the RPFIC $(0.5-1)K_2O + (3-4)(SiO_2 + Al_2O_3 + V_2O_5)$ at 150 °C in a nitrogen atmosphere, PA undergoes linear oligomerisation with formation of PA dimers, trimers, and tetramers and also cyclisation with formation of the diphenylcyclobutadienes (I) and (II), triphenyl-substituted Dewar benzenes (III) and (IV), and the ladder oligomer (V):



The authors[139,140] did not discuss the mechanism of the oligomerisation of PA, but, taking into account the acid–base properties of the RPFIC, presumably one of the possible pathways to the oligomerisation of PA involves a mechanism analogous to that of cationic polymerisation.

7. Isotope exchange reactions

Gaseous deuterium or a deuterium label in the molecule are frequently used in the study of the mechanisms of heterogeneous organic catalysis.[141–143] Certain examples of the employment of gaseous deuterium or a deuterium label, involving the measurement of kinetic isotope effects in syntheses of oxygen- and nitrogen-containing compounds in the presence of RPFIC, were presented above. We shall consider in greater detail a series of isotope exchange reactions occurring in the presence of RPFIC.

In the interaction of CH_3OH with D_2 in a stationary system in the presence of the RPFIC $2K_2O$ at 112 °C, p_{CH_3OH} = 4.5 GPa, and p_{D_2} = 20 GPa, methanol acquires, after 40 min, the following isotope composition (5): CH_3OH 80, CH_3OD 19, CH_2DOD 1, CHD_2OH < 0.1.[144] Hence, it is seen that in the presence of the RPFIC the most vigorous H/D exchange occurs in the hydroxy-group of the alcohol.

The exchange of n-hexane, cyclohexane, cyclohexanol, cyclopentanol, cyclohexanone, and cyclopentanone with D_2 has been investigated in the presence of the RPFIC $5V_2O_5$.[123,127] In alicyclic alcohol molecules (p_{D_2} = 0.1–0.3 MPa), as in CH_3OH molecules, only the H atom of the hydroxy-group is replaced by deuterium at 250 °C. Under these conditions, saturated hydrocarbons hardly undergo the H/D exchange. On the other hand, in ketone molecules protium is vigorously exchanged for deuterium at carbon atoms in the α-position to the carbonyl group.

In a study of deuterium distribution in the products of synthesis from CO and H_2 with added D_2O, it was established that there is no exchange between the hydrocarbons formed and D_2O.[145] On the other hand, the hydrocarbons contain a certain amount of deuterium

which was believed to pass from D_2O to gaseous hydrogen, reacting subsequently with CO. The deuterium content in the alcohols formed in the FT-synthesis is higher than in hydrocarbons.

When $^{14}C^{18}O_2$ is added to the synthesis gas in the presence of a RPFIC, the carbon label is transferred from carbon dioxide to the monoxide mainly via the reaction

$$^{14}CO_2 + H_2 \rightleftarrows {}^{14}CO + H_2O,$$

while the transfer of the oxygen label proceeds via the reaction[146]

$$C^{18}O_2 + C^{16}O \rightleftarrows C^{16}O^{18}O + C^{18}O.$$

A novel one-stage synthesis of aliphatic alcohols labelled with ^{18}O isotope consists in the vapour-phase interaction of alkanols with $H_2{}^{18}O$ in the presence of hydrogen at 150–250 °C over a RPFIC.[147,148] Thus, when a mixture of $H_2{}^{18}O$ methanol vapours is passed through the catalyst bed, $C_2H_5{}^{18}OH$ is formed in 92% yield relative to the equilibrium yield. The authors[147,148] explain the observed $^{16}OH/^{18}OH$ isotope exchange by the reversible dehydrogenation of the alkanols under the conditions indicated. Taking into account the acid-base properties of the RPFIC, such oxygen exchange can be described by the following multistage scheme in which RMC represents reduced FeH metallic centres and ABC represents POH acid–base centres (P = V, Al, Si):

$$C_2H_5OH \xrightarrow[-H_2]{RMC} CH_3CHO,$$
$$CH_3CHO + H_2^{18}O \xrightarrow{ABC} CH_3CH^{18}O + H_2O,$$
$$CH_3CH^{18}O + H_2 \xrightarrow{RMC} CH_3CH_2^{18}OH.$$

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Thus reduced promoted fused iron catalysts exhibit a high (frequently unexpected) efficiency in a whole series of hydrogenation syntheses. In some cases they are superior to the familiar catalytic systems in terms of a series of most important technological parameters such as productivity, selectivity, and stability (Fischer–Tropsch syntheses modified by ammonia or lower amines, hydroamination and hydrogenation of certain oxygen-containing compounds, etc.). In other cases, they may prove preferable, despite their lower efficiency, because of their availability, low cost, and the simplicity of their preparation. Such an unusually broad spectrum of the catalytic activity of RPFIC is probably associated with its bifunctional nature, which is manifested in the syntheses of organic compounds of different classes via a combination of oxidation-reduction (hydrogenation-dehydrogenation) and acid–base catalytic properties. By varying easily within wide limits the chemical composition of the RPFIC and hence also the nature of the catalytically active surface on which a wide variety of reactions of the initial reactants take place, it is possible to achieve deliberately the necessary ratio of these properties. This is in fact why experimental search on a broad front makes it possible in most cases to select a RPFIC best corresponding to the purposes of the synthesis of the organic compounds. The latter factor makes it extremely likely that new examples of the successful employment of RPFIC in organic synthesis will appear in the future.

Finally, the wide-scale application of RPFIC and other universal catalysts may prove a useful alternative to the approach, dominant at present in chemical research, according to which a new catalyst is developed for each specific synthesis of an organic compound.

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