Russian Chemical Reviews **74** (6) 577 – 586 (2005) © 2005 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2005v074n06ABEH001170

Bimetallic cobalt catalysts for the synthesis of hydrocarbons from CO and H_2

A L Lapidus, M V Tsapkina, A Yu Krylova, B P Tonkonogov

Contents

I.	Introduction	577
II.	General information on the Fischer – Tropsch process	577
III.	Bimetallic cobalt catalysts	578
IV.	Mechanisms of promotion of cobalt catalysts by noble metals and rhenium	583

Abstract. The mechanisms of promotion of cobalt catalysts used in the synthesis of hydrocarbons from CO and H_2 by Group VIII metals and rhenium are considered. The properties of the catalytic systems thus prepared are analysed. The bibliography includes 75 references.

I. Introduction

Catalytic processes form the groundwork of petrochemistry and are widely employed in chemical technologies. Further perfection of the existing processes and enhancement of their efficiencies are impossible without application of novel catalysts with higher reactivities and selectivies to production. The solution of these practical tasks requires detailed analysis of structures and properties of catalytic systems, the methods for their preparation and activation, *etc*. Elucidation of relationships between the structures of active surfaces and properties of various catalysts and development of fundamentals of the selection of catalysts are central problems on the agenda of the present-day science of catalysis.

A search for reasonable alternative raw materials to crude oil, such as natural gas, coal, biomass, *etc*., has received wide consideration in recent decades. Conversion of these basic raw materials into a carbon monoxide – hydrogen mixture (the so-called synthesis gas) and its use in preparation of hydrocarbon derivatives by the Fischer – Tropsch synthesis is one of their most promising applications. This trend competes favourably with conventional oil processing technologies used in liquid fuel production and organic synthesis. Today, the development of highly efficient and highly selective catalysts able to optimise the Fischer – Tropsch synthesis is a task of paramount importance.

At present, synthesis gas is employed for the preparation of aliphatic hydrocarbons on iron and cobalt catalysts. Co-containing systems are used as selective catalysts in the synthesis of linear alkanes. However, many currently known Co-catalysts manifest low activities in the synthesis of n-paraffins.

Bimetallic cobalt catalysts have a number of advantages over monometallic systems, being wide-ranging with regard to activity and selectivity. One of the ways to increase the efficiency of Co-catalysts in the synthesis of hydrocarbons from CO and H_2 is doping by Group VIII transition metals. In turn, rationalisation of a search for highly reactive bimetallic catalysts puts forward the necessity to establish a correlation between the physicochemical and catalytic properties of catalytic systems, *i.e*., their activities and selectivities in the processes under consideration.

This review covers the data published over the past 10 – 15 years devoted to cobalt-containing catalytic systems employed in the synthesis of liquid hydrocarbons from carbon monoxide and hydrogen. A separate chapter is devoted to the mechanisms of promotion of these catalysts by noble metals and rhenium.

II. General information on the Fischer – Tropsch process

The conversion of synthesis gas can in general be described in terms of reductive oligomerisation of carbon monoxide on a heterogeneous catalyst:

$$n\,CO + m\,H_2 \longrightarrow C_xH_yO_z.$$

Depending on the nature of the catalyst, reagent ratios and reaction conditions (temperature, pressure, *etc*.), the Fischer – Tropsch process yields hydrocarbons (alkanes, alkenes) and/or oxygen-containing products (alcohols, aldehydes, ketones, acids, esters, *etc*.).[1] As a rule, this synthesis does not afford individual products but, rather, a vast array of substances differing in the length of their alkyl chains typical of polymerisation reactions. The molecular mass distribution of these conversion products is well described by simple equations for polymerisation reactions which take into account the probability of chain growth and chain termination.

As regards the thermodynamics of the Fischer – Tropsch process, the hydrocarbons synthesised from CO and H_2 may possess any chain length, degree of saturation (with the exception of acetylene) and structures.[1] The Fischer – Tropsch synthesis normally yields alkenes as primary products; their subsequent hydrogenation affords alkanes.

Classical Fischer – Tropsch syntheses make use of metal catalysts (the latter are often referred to as 'contacts') based on iron, cobalt, nickel and ruthenium. The former two catalysts have found wide application in various industrial processes.

A L Lapidus, M V Tsapkina, A Yu Krylova N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, 119991 Moscow, Russian Federation. Fax (7-095) 135 53 28, tel. (7-095) 938 36 42, e-mail: albert@ioc.ac.ru (A L Lapidus), mvtsap@yandex.ru (M V Tsapkina), tel. (7-095) 730 61 01, e-mail: KrylovaAY@yukos.ru (A Yu Krylova)
B P Tonkonogov I M Gubkin Russian State Oil and Gas University, Leninsky prosp. 65, 119991 Moscow, Russian Federation. Fax (7-095) 135 88 56, tel. (7-095) 135 89 56 (B P Tonkonogov)

Received 24 September 2004
Uspekhi Khimii **74** (6) 634 – 645 (2005); translated by R L Birnova

The use of iron-based catalysts usually affords hydrocarbon mixtures with a high content of alkenes and branched paraffins as well as oxygen-containing products.[1–3] Cobalt-containing systems are considered to be the most efficient catalysts for the production of hydrocarbons from carbon monoxide and hydrogen, since they enable highly selective synthesis of saturated long-chain linear hydrocarbons:

$$n\,CO + (2n+1)\,H_2 \longrightarrow C_nH_{2n+2} + n\,H_2O.$$

The Fischer–Tropsch synthesis involves some side reactions, *viz.*,:

1) hydrogenation of carbon monoxide to methane:

$$CO + 3\,H_2 \longrightarrow CH_4 + H_2O,$$

2) the Bell–Boudouard reaction (disproportionation of CO):

$$2\,CO \longrightarrow CO_2 + C,$$

3) water gas equilibrium:

$$CO + H_2O \longrightarrow CO_2 + H_2.$$

Synthesis of paraffins from CO and H_2 may be accompanied by secondary reactions over the whole range of temperatures used and includes the formation and hydrogenation of lower alkenes, partial hydrocracking and dehydrogenation of alkanes formed, hydrogen-transfer rearrangements, *etc*.

The actual composition of the products prepared from CO and H_2 differs substantially from the theoretical equilibrium composition. This reaction is kinetically controlled and the final composition of its target products is determined by the nature of the catalyst and the reaction conditions. In turn, the properties of Co-catalysts used in the Fischer—Tropsch syntheses strongly depend on the nature of substrates, percentage of the active metal components and sample activation conditions.

III. Bimetallic cobalt catalysts

1. Promotion by iron-subgroup metals

Recently, the attention of investigators has become focused on bimetallic catalysts for the Fischer–Tropsch synthesis. First, by varying the metal ratios, one can change their catalytic properties.[4–7] Second, combination of several active components in a catalyst makes it more stable and resistant against poisoning and coking.[8]

The Fischer–Tropsch synthesis involves preliminary reduction (or activation) of heterogeneous catalysts. All the catalysts undergo chemical transformations (so-called phase changes) upon reduction and subsequent synthesis of hydrocarbons from CO and H_2. For example, reduced Fe-samples interact with synthesis gas to yield carbides and oxides; the activity of a catalyst increases upon preliminary carbide formation on its surface. On the contrary, cobalt catalysts are much less prone to form carbides and carbide formation prior to the synthesis markedly decreases their activity. Nevertheless, simultaneous introduction of iron and cobalt into the catalyst allows conversion of synthesis gas into hydrocarbons.[9,10]

The activity and selectivity of cobalt catalysts is enhanced upon promotion by Group VIII transition metals and rhenium. The Fischer–Tropsch synthesis (250 °C, 10 atm) in the presence of various catalysts was studied by Ishihara *et al.*[11] It was shown that 10% Co/SiO_2 and 10% Fe/SiO_2 manifested unusually lower activities in comparison with those reported by other authors (see Refs 12–16): the conversion of carbon monoxide on these catalysts was as low as 5.2% and 0.2%, respectively. Introduction of two metals (Fe and Co) into the catalyst increased its activity in comparison with the monometallic systems, being dependent on the metal ratio. A decrease in the mass ratio Fe : Co from 3.0 to 0.35 (at the total metal content in the catalyst of 10%) resulted in an increase in CO conversion from 7.7% to 21.5%, in the selectivity of formation of hydrocarbons containing no less than two carbon atoms (C_{2+}) from 49.8% to 71.6% and a decrease in the methane content in the reaction products from 50.2% to 28.4%. It is noteworthy that the increased yields of paraffins C_2–C_5 and decreased yields of hydrocarbons C_{6+} was concomitant with a decrease in the relative content of Fe in the bimetallic contact.

The same authors[11] investigated also the properties of 10% Co–Ni-containing systems manifesting higher activities in the Fischer–Tropsch synthesis than the monometallic catalysts Co/SiO_2 and Ni/SiO_2. It was found that with an increase in the mass ratio Co : Ni from 0.35 to 3.0 at the total metal content of 10%, the extent of CO conversion increased showing a maximum (32.3%) at Co : Ni = 1. All the samples of this series manifested similar selectivities in the synthesis of hydrocarbons C_{2+} (67%–71%). However, the compositions of the products prepared on Co–Ni-contacts differed from those synthesised on Fe–Co, *viz.*, the former contained less alkenes and more hydrocarbons C_{6+}. Heavier (in comparison with the monometallic samples) hydrocarbons were synthesised in the presence of a Co–Ni-catalyst.

X-Ray phase analysis has shown[11] that the surfaces of reduced monometallic catalysts Co/SiO_2, Ni/SiO_2 and Fe/SiO_2 contained oxide phases. In the case of bimetallic samples, reduction brought about alloying of cobalt with iron or nickel. This favoured the reduction of iron and cobalt oxides to metals so that no oxide phases remained on the surface of the cobalt catalysts. Alloying of Co with Ni also facilitated their reduction which resulted in the increase in the amount of the activated reagents (hydrogen and carbon monoxide) (data from thermoprogrammed desorption of CO and H_2) in parallel with the increase in the catalyst activities. It has been found[17,18] that alloy particles present on the surface of Fe–Co-contacts differ in size. Under the conditions used, no carbide phases are formed from these metals, and the metals manifested enhanced hydrogenating activities in comparison with surface sites containing the carbide phase.

Studies of Co–Ni-catalysts supported on ZrO_2 have shown[19] that the increase in the Co content due to the increase of the mass ratio Co : Ni from 0.3 to 2.4 resulted in a twofold decrease in the content of the light hydrocarbons C_1–C_4 in the products, while that of paraffins C_{5+} increased from 35% to 63%. The degree of CO conversion did not change under these conditions and constituted 4%–5% at 250 °C and ambient pressure. Using thermoprogrammed reduction (TPR, see below), it was found that Ni promotion of Co/ZrO_2 catalysts induced a marked shift of the TPR signals towards the low-temperature region. Based on these data, it was suggested that nickel favours the reduction of cobalt oxide due to hydrogen spillover effect. As nickel is reduced earlier than cobalt, it begins to adsorb and activate hydrogen as a result of which the latter migrates towards cobalt oxide.

These examples clearly demonstrate that introduction of a second metal into Co-based catalysts not only increases their activities, but also allows control over their selectivities in the formation of a vast array of hydrocarbons.

2. Promotion by noble metals and rhenium

Introduction of a tenth and even a hundredth of percent of noble metals into cobalt catalysts changes significantly their physicochemical and catalytic properties. It was found[20,21] that Co-catalysts promoted by Pt, Rh, Pd, Ru and Re manifest high activities and selectivities in the syntheses of aliphatic hydrocarbons with various structures (both liquid and solid), which allows these processes to be conducted at relatively low temperatures (190–200 °C).

a. Studies of bimetallic cobalt catalysts by physicochemical methods

Promotion of cobalt catalysts was studied using various physicochemical methods, in the first place, by thermoprogrammed reduction (TPR). This method is used in the analysis of reducing potentials of catalysts as well as for establishing the compositions of non-reduced catalysts.

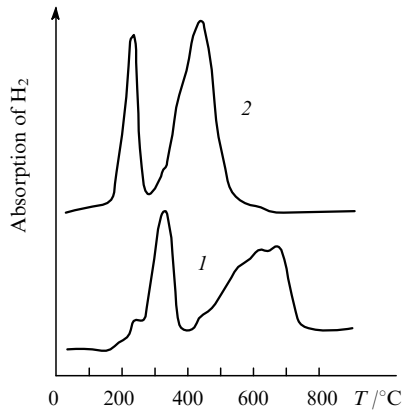


Figure 1. TPR spectra of the catalysts Co/Al_2O_3 (*1*) and $Co-Ru/Al_2O_3$ (*2*) recorded after calcination of the samples (300 °C, 14 h).[22]

The TPR spectrum of 20% Co/Al_2O_3 prepared by impregnation of the support with cobalt nitrate is shown in Fig. 1 (curve *1*).[22] The addition of 0.5% Ru (from the corresponding nitrosyl nitrate) to this catalyst favoured its easier reduction as can be evidenced from the nearly 100 °C shift of the TPR signal of the Co – Ru contact towards lower temperatures (see Fig. 1, curve *2*). Cobalt oxide in the composition of the bimetallic sample was almost completely reduced to Co^0, while the degree of reduction of a non-promoted catalyst was only 60%. It was supposed [22] that ruthenium formed upon reduction of its oxide prior to cobalt adsorbs and activates hydrogen. Hydrogen migrates towards Co_3O_4 by a spillover mechanism and thus favours its easier reduction. Quite probably, ruthenium also either inhibits the formation of cobalt compounds that are difficult to reduce , *e.g.*, by preventing the interaction of cobalt oxide with Al_2O_3 to yield a Co – Al spinel, or favours their partial reduction. The absence of high-temperature peaks at >450 °C in the TPR spectrum of the Co – Ru-catalyst and the presence of a signal with T_{max} = 600 °C in the TPR spectrum of the monometallic cobalt sample corroborates this hypothesis. According to hydrogen chemisorption data, the number of metallic cobalt atoms on the surface of a cobalt catalyst increases threefold upon promotion with ruthenium.

In the TPR spectra of palladium- or ruthenium (0.3%)-promoted Co samples, two signals were also shifted towards the low-temperature region in comparison with the monometallic catalyst (10% Co/Al_2O_3).[23] In the ruthenium-promoted catalyst, the first signal was shifted by 46 °C, while the shift of the second signal was 9 °C. The shifts were even more pronounced (195 and 72 °C, respectively) for the Co – Pd contact.

The effects of palladium additives to the catalyst Co/SiO_2 prepared by the sol – gel method (Fig. 2) have been studied by Guczi *et al.*[24] The presence of a very broad peak in the TPR spectrum of a monometallic Co-contact (curve *1*) points to a high degree of dispersion of cobalt particles. Introduction of Pd and subsequent reduction of the catalyst increases the content of metallic cobalt in the sample. At the mass ratio Co : Pd = 2 (see Fig. 2, curve *2*), the peak corresponding to the reduction of cobalt oxide was shifted from 450 °C to 375 °C (Fig. 2, curve *1*). It is noteworthy that the reduction of the monometallic catalyst 5% Pd/SiO_2 occurred at 150 °C (Fig. 2, curve *5*). With a further increase in the Pd content, the shift of the characteristic peak was even more pronounced, *viz.*, up to 350 °C (Fig. 2, curves *3*, *4*). In the authors' opinion, a shoulder at 220 °C suggests the formation of bimetallic particles Co – Pd; this conclusion was confirmed by X-ray photoelectron spectroscopic (XPS) data.

The formation of bimetallic particles under TPR conditions was also observed in the analysis of rhodium-containing Co-catalysts.[25–27] The samples for this study were prepared on different oxide supports, *e.g.*, SiO_2, Al_2O_3, TiO_2. (A more detailed description of characteristic features of these catalytic systems will be given below).

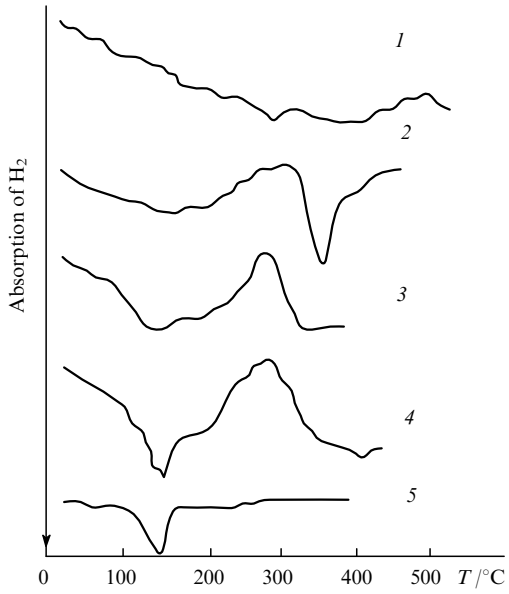


Figure 2. TPR spectra of the samples Co/SiO_2 (*1*); $Co-Pd/SiO_2$ (*2*–4); Pd/SiO_2 (*5*).[24]
The Co : Pd atomic ratios are equal to 2 (*2*), 1(*3*) and 0.5 (*4*).

As a case in point, let us consider the results of a TPR analysis of Co/SiO_2 and Rh/SiO_2 samples and a bimetallic catalyst ($Co-Rh/SiO_2$) prepared by impregnation with cobalt nitrate and rhodium chloride (total metal content was 4.9%, the atomic ratio Co : Rh was 1 : 1) (Fig. 3).[25] In this study, complete reduction of the catalyst Rh/SiO_2 occurred at 140 °C. The reduction of $Co-Rh/SiO_2$ occurred at a lower temperature (237 °C) than reduction of the the monometallic cobalt sample (327 °C), which suggests that cobalt nitrate and cobalt oxide are reduced at higher rates in the presence of rhodium. It was found also [25] that the reduced catalyst $Co-Rh/SiO_2$ contains bimetallic particles, their inner part is enriched with metallic rhodium, while the outer layer is enriched with cobalt (see below, Section IV).

The addition of platinum to Co-containing systems also facilitates the reduction of cobalt oxides.[28–30] The results of a TPR study of the promoting effect of platinum on Co-catalysts are shown in Fig. 4.[28] A comparison of the TPR spectra of the monometallic sample (9% Co/Al_2O_3) (Fig. 4, curve *2*) and the catalyst (9% Co – 0.4% Pt/Al_2O_3) (Fig. 4, curve *3*) shows that in

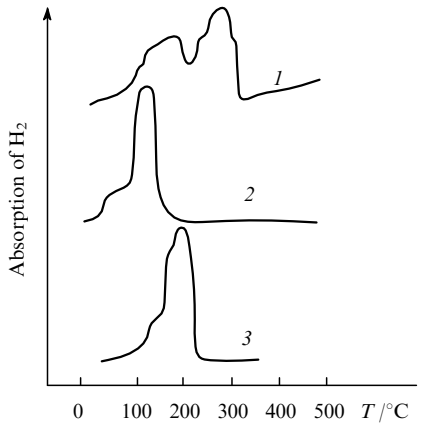


Figure 3. TPR spectra of the catalysts Co/SiO_2 (*1*), Rh/SiO_2 (*2*) and $Co-Rh/SiO_2$ (*3*).[25]

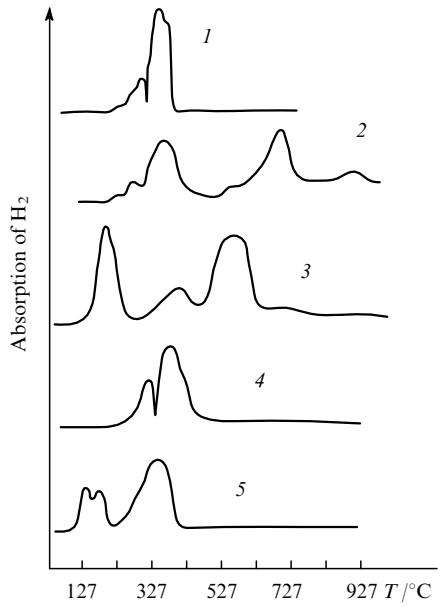


Figure 4. TPR spectra of the samples Co_3O_4 (*1*), 9% Co/Al_2O_3 (*2*), 9.2% Co–0.4% Pt/Al_2O_3 (*3*), 8.9% Co/SiO_2 (*4*), 8.7% Co–0.4% Pt/SiO_2 (*5*).[28]

the latter case the peaks corresponding to the reduction of Co oxide phases are shifted towards the low-temperature region by more than 100 °C. The peak corresponding to the reduction of Co_3O_4 is shifted from 377 to 207 °C, while the peak corresponding to the mixed cobalt–aluminium oxide is shifted from 717 to 587 °C. The TPR spectrum of the Co–Pt sample contained an additional signal (at 417 °C), which was assigned [28] to the reduction of Co_3O_4 without involvement of platinum. Similar dependences were observed when SiO_2 was used as a substrate, *viz*., the peak corresponding to the platinum-promoted reduction of Co^{3+} to Co^{2+} was shifted from 327 to 147–177 °C (see Fig. 4, curves *4* and *5*), while the shift of the peak assigned to the reduction of Co^{2+} to Co^0 was less pronounced (from 397 to 357 °C).

As with platinum, promotion of the cobalt catalyst (20% Co–1% Re/Al_2O_3) by rhenium shifted the signals in the TPR spectra towards the low-temperature region in comparison with the monometallic sample (Fig. 5).[31] However, in contrast to platinum, which favours the reduction of the dominant cobalt oxide phases on the surface of a bimetallic contact at lower temperatures, rhenium brings about the reduction of both the highly dispersed surface phase of Co (T_{max} = for 727 °C for the monometallic sample, the TPR signal was shifted by 200 °C) and the spinel $CoAl_2O_4$. In the presence of rhenium, the latter was reduced practically completely as can be evidenced from the absence of signals at temperatures above 800 °C. It is noteworthy that the TPR spectrum of a monometallic Re sample displays a single signal at 425 °C.

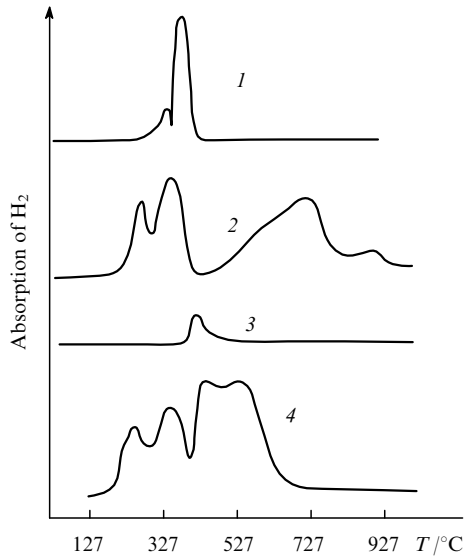


Figure 5. TPR spectra of the samples Co_3O_4 (*1*), Co/Al_2O_3 (*2*), Re/Al_2O_3 (*3*) and Co–Re/Al_2O_3 (*4*).[31]

Promotion of the catalyst 8.7% Co/Al_2O_3 by platinum and rhenium increases the degree of reduction (R_{CO}) and dispersity (D) of metallic cobalt.[32] The former value reflects the number of metallic cobalt atoms with respect to the total content of cobalt atoms in the catalyst, while the latter indicates the number of surface metal atoms with respect to the total number of metallic cobalt atoms.

Additive	Without additive	1% Pt	1% Re
R_{CO} (%)	52	79	78
D (%)	6.7	13.9	16.5

These data confirm the promoting effects of Pt and Re on the reduction of cobalt oxides.

However, some authors hold the opinion [33] that unlike noble metals, rhenium does not influence the reduction of cobalt catalysts. The extent of cobalt reduction was not changed upon addition of 0.6% Re to 5% Co/Nb_2O_5 and constituted 48%. The TPR spectra of monometallic Co and a rhenium-promoted catalyst were also virtually identical. It should be noted however that the addition of rhenium to a Co-catalyst increased the dispersity of metallic cobalt from 8% to 12.5% in parallel with a decrease in the size of cobalt crystallites from 12 to 8 nm.

The TPR method was used to study the formation of bimetallic catalysts Co–M/SiO_2 (M = Pt, Ru, Rh, Pd).[34] The samples were prepared by repeated impregnation of the support with the salts $Co(NO_3)_2 \cdot 6H_2O$, $RhCl_3 \cdot 4H_2O$, $RuCl_3$, $PdCl_2$ or the $Pt(acac)_2$ complex. After each (except for the last) impregnation, the samples were calcined at 450 °C. The results of these studies are presented in Figs 6 and 7 where the TPR spectra are superimposed for convenience. It was found that cobalt nitrate and cobalt oxide were present on the surface of the non-reduced catalyst Co/SiO_2 (see Fig. 6, curve *1*). The former underwent reductive decomposition (T_{max} = 235, 278 °C), while the stepwise reduction of the latter to Co^0 ($Co_3O_4 \rightarrow CoO \rightarrow Co^0$) occurred at T_{max} = 330 and 412 °C. Co–support compounds that are difficult to reduce (T_{max} = 479 °C) were also found on the surface. The addition of platinum, palladium or rhodium (see Fig. 6, curves *2*–*4*) to a monometallic catalyst resulted in an appreciable shift of the overall TPR spectrum towards the low-temperature region and the appearance of isolated signals at temperatures

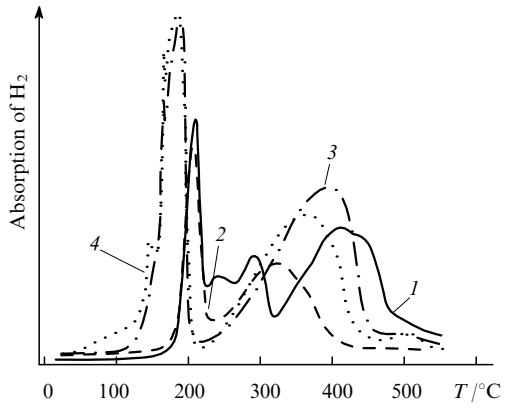


Figure 6. TPR spectra of the samples Co/SiO_2 (*1*) and Co–M/SiO_2, where M = Rh (*2*), Pd(*3*) and Pt (*4*).[34]

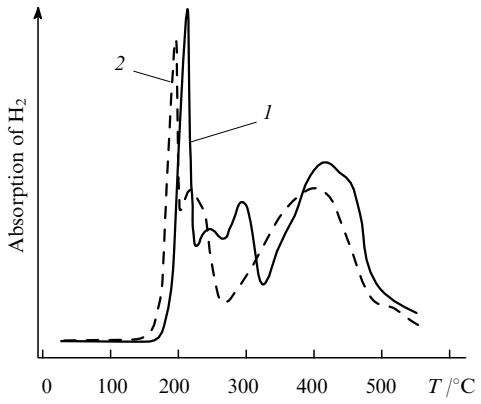


Figure 7. TPR spectra of the samples Co/SiO_2 (*1*) and $Co-Ru/SiO_2$ (*2*).[34]

below 200 °C in the former two cases (Pt and Pd). This peak corresponds to the reduction of platinum (palladium) oxide or mixed Co–Pt(Pd) oxides. The presence of a noble-metal phase on the surface of a substrate led the authors to postulate its role in the autocatalytic reduction of Co samples. Ruthenium formed no individual phase on the surface of a bimetallic contact and had virtually no effect on the reduction of the dominant cobalt phases as can be judged from the similarity of the TPR spectra of Ru-containing and Ru-free samples (see Fig. 7). Presumably, the properties of reduced bimetallic cobalt-containing catalysts depend on the nature of the promoter. Based on these data, the authors proposed a model of formation of active sites for a series of $Co-M/SiO_2$ catalysts (M = Pt, Ru, Rh, Pd) (see below).[34]

Thus, introduction of Pd, Rh, Ru, Pt and Re into cobalt catalysts results in considerable changes in their physicochemical properties. In the presence of noble metals, the reduction of cobalt oxides on the surface of a catalyst occurs more easily in the stage of activation due to hydrogen spillover. The number of active sites on the surface of cobalt catalysts increases with the increase in the degree of cobalt reduction rate and dispersity. This effect contributes significantly to the enhancement of activity of catalytic systems.

b. Studies of bimetallic cobalt catalysts in the Fischer–Tropsch synthesis

Changes in the physicochemical properties of cobalt catalysts upon introduction of noble metals or rhenium result in changes in their catalytic properties. The use of such modified systems in hydrocarbon syntheses from CO and H_2 makes it possible to increase the activity of catalysts and the selectivity of formation of liquid hydrocarbons (C_{5+}).

The effects of platinum and rhenium additives on the activities of Co-catalysts in the Fischer–Tropsch synthesis with 10% Co/Al_2O_3 and 10% Co/SiO_2 as the original systems have been studied.[28,29,32] The catalysts were prepared by co-impregnation, drying and calcination in a flow of air (400 °C, 2 h) with subsequent reduction by hydrogen (14–16 h, T = 350 °C). The specific activities of Al_2O_3-based catalysts in the hydrocarbon synthesis from CO and H_2 (220 °C, 1 atm) at the molar ratio $H_2:CO = 7.3$ were shown to increase substantially upon addition of 1% platinum or rhenium [from 18.4 for the monometallic sample to 36.8 and 38.3 μmol CO (g Co s)$^{-1}$, respectively].[32] According to other authors,[29] the addition of 1% Pt to 10% Co/Al_2O_3 increases the catalytic activity from 11 to 19 μmol CO (g Co s)$^{-1}$ (200 °C, 1 atm, $H_2:CO = 2$). A 3–5-fold increase in the catalytic activity was also observed after addition of 0.4% Pt to 9% Co/Al_2O_3 (SiO_2) (210 °C, 1 atm, $H_2:CO = 7$).[28]

The addition of small amounts of palladium or ruthenium (0.1%–0.7%) to 10% $Co/Al_2O_3(SiO_2)$ prepared by impregnation with cobalt nitrate allows one to increase the extent of conversion of carbon monoxide and the yield of hydrocarbons C_{5+} in the Fischer–Tropsch synthesis. Thus the extent of CO conversion on a Co–Pd-contact (200–210 °C, 1 atm, $H_2:CO = 2$) was > 80%, and the yield of hydrocarbons C_{5+} reached 95–97 g m^{-3} (see†) (*cf.* 70% and 55 g m^{-3}, respectively, for a non-promoted Co-catalyst). The selectivity of the synthesis of liquid hydrocarbons in the presence of Co–Ru-catalysts exceeded 80%.[23,35–38] The effects of minor concentrations of Pt (0.1%–0.7%) on the activity of a cobalt catalyst (10% Co/SiO_2) have been studied.[39] It was found that the contact 10%Co–0.7%Pt/SiO_2 manifested the highest activity in the hydrocarbon synthesis from CO and H_2 (200 °C, 1 atm, $H_2:CO = 2$). With this catalyst, the yields of the liquid hydrocarbons increased to 92 g m^{-3} at the degree of CO conversion rate of 87%, while the selectivity of their formation was 71%. The fractional compositions of the reaction products did not depend on the concentrations of Pd, Ru and Pt added to the Co-catalyst, *viz.*, the content of hydrocarbons C_5-C_{10} was 65%–70%, that of hydrocarbons $C_{11}-C_{18}$ was 27%–32%, while that of the C_{19+} fraction was insignificant (1%–4%).[36–39]

The activities of Co/SiO_2 catalysts promoted by the platinum-group metals in the Fischer–Tropsch synthesis have been compared.[34] In all cases, the introduction of a second metal (Pt, Rh, Pd, Ru) resulted in a significant increase of the activities and selectivities of the bimetallic catalytic systems. Catalysts of this series manifested the following properties in the hydrocarbon synthesis from CO and H_2 (190–200 °C, 1 atm, $H_2:CO = 2$):

1) the yields of liquid hydrocarbons (g m^{-3}) decreased in the following order:

Co–Pt (139) > Co –Ru (129) > Co–Rh (124) > Co (118) > Co–Pd (82);

2) the selectivities of the formation of liquid hydrocarbons (%) decreased in the following order:

Co–Pt (81) > Co–Ru (77) > Co (76) > Co–Rh (72) > Co–Pd (60).

The liquid products obtained in the presence of the bimetallic catalysts contained predominantly saturated hydrocarbons with normal structures (64%–74%).

There is a large body of evidence in the current literature concerning Co–Ru catalysts of the Fischer–Tropsch synthesis.[22,40–51] The synergism of catalytic effects of cobalt and ruthenium reported by most investigators suggests that bimetallic contacts exceed their monometallic counterparts in both activity and selectivity.

The addition of ruthenium to the catalyst 11.6% Co/TiO_2 (SiO_2) changed the atomic ratio Ru : Co from 0.001 to 0.014.[43] In all cases, the rate of hydrocarbon synthesis‡ (200 °C, 20 atm, $H_2:CO = 2$) showed a tendency to increase. Thus for Ru : Co = 0.0067, this increased twofold, *i.e.*, from 3.9×10^{-4} to 6.4×10^{-4} s^{-1}. Under these conditions, the degree of carbon monoxide conversion increased from 49% to 51%, while the selectivity of liquid hydrocarbon synthesis reached 85%–86%. Calcination of a bimetallic Co–Ru-catalyst prior to reduction (1 h, 300 °C) brought about a further twofold increase in the reaction rate: the degree of conversion of CO and the selectivity of the synthesis of the hydrocarbons C_{5+} amounted to 61% and 91%, respectively. These parameters were compared[43] to those obtained under similar conditions with 1.1% Ru/TiO_2.[44] The extent of CO conversion on Ru/TiO_2 was 35%, *i.e.,* lower than on the bimetallic contact with nearly the same selectivity (93% and

† The activities of the catalysts of the Fischer–Tropsch synthesis are usually estimated by the yields of the hydrocarbons [g per 1 m^3 of synthesis gas (CO + 2 H_2) corrected to normal conditions (n.c.)]. The theoretical yield of the hydrocarbons is 208.5 g m^{-3} (n.c.).

‡ In this case, the synthesis rate is expressed by a value termed as 'reaction turnover number', *i.e.*, the number of reaction acts per unit time.

91%). It is of note that the dispersity of the cobalt catalyst was not changed upon promotion by ruthenium.

Based on the data from electron microscopy, X-ray absorption spectroscopy and thermogravimetric analysis, it was suggested[43] that more rapid reduction of cobalt oxide requires a contact between Co and Ru to yield a mixed oxide upon calcination of bimetallic samples prior to reduction. Such treatment triggers the migration of ruthenium and cobalt oxides over the catalyst surface resulting in the formation of mixed Co–Ru oxides ($Co_{3-x}Ru_xO_4$, where $0 < x < 1$). The presence of ruthenium decelerates deactivation of the catalyst due to coking. As a consequence, the activity of the Co–Ru-contact and the selectivity of formation of liquid hydrocarbon increase.

The properties of mono- and bimetallic catalysts containing 6% Co and/or 2% Ru supported onto SiO_2 or Al_2O_3 were examined under differential, static and flowing regimes.[45,46] In all the three cases, the bimetallic catalysts manifested the highest selectivities in the Fischer–Tropsch synthesis, the highest selectivity (69%) of the synthesis of hydrocarbons C_{2+} in a flow reactor (240–280 °C, 1 atm, $H_2:CO = 1$) being manifested by the bimetallic contact Ru–Co/Al_2O_3. In addition, in this case the highest yield of alkenes (19%) was achieved. The activities of the catalysts Ru/Al_2O_3 and Ru–Co/Al_2O_3 appeared to be similar as could be judged from the extent of conversion of carbon monoxide: the extent of CO conversion (K_{CO}) was 14% and 16%, respectively, which markedly exceeded that for Co/Al_2O_3 (K_{CO} = 8.2%). The degree of cobalt reduction in the bimetallic contact was higher in comparison with the corresponding monometallic catalyst, which can be attributed to the activation of H_2 on the surface of ruthenium and its subsequent spillover to cobalt oxide as well as to the formation of Ru and Co alloys as can be evidenced from the appearance of signals corresponding to mixed clusters $RuCo^+$ in the mass spectra of secondary ions.

Co–Ru-Catalysts prepared on mixed oxide supports (ThO_2–Al_2O_3 and La_2O_3–Al_2O_3) also exceeded monometallic Co-samples in activity; the selectivity of formation of liquid hydrocarbons reached 79%.[47–49] The activity and selectivity of a bimetallic Co–Ru-sample increased noticeably after calcination and subsequent reduction.

It is of note that the temperature of preliminary calcination of a cobalt-containing catalyst influences the extent of cobalt reduction and, as a consequence, its catalytic activity. The properties of a contact 20% Co–0.5% Ru/Al_2O_3 employed in the synthesis of hydrocarbons from CO and H_2 (220 °C, 1.8 atm, $H_2:CO = 10$) have been investigated.[50] With an increase in the calcination temperature from 250 to 400 °C, the peaks in the TPR spectra were shifted towards higher temperatures (Fig. 8), while the extent of Co reduction decreased from 77% to 59%. This was accompanied by a decrease in the extent of carbon monoxide conversion (from 11% to 5%), reaction rate [from 50 to 23 μmol CO (g Co s)$^{-1}$] and selectivity of methane synthesis (from 84% to 73%).

Besides, catalytic properties of bimetallic contacts strongly depend on the method of preparation and the nature of the substrates and the starting metal salts. Thus the catalyst 20% Co–0.5% Ru/Al_2O_3 was prepared from different ruthenium derivatives, *viz*., Ru(NO)$(NO_3)_3$ and $RuCl_3$, using combined or sequential impregnation.[22] The Fischer–Tropsch synthesis was carried out at 220 °C, 1 atm and the $H_2:CO$ ratio = 2. The catalyst prepared by co-impregnation with $Co(NO_3)_2 \cdot 6H_2O$ and $RuCl_3$, drying (5 h, 115 °C) and calcination (2 h, 300 °C) manifested the highest activity. The reaction rate on this catalyst was 0.342 g [-CH_2-] (g of catalyst h)$^{-1}$.

Samples containing 5% Co on SiO_2, Al_2O_3 or alumosilicate ($SiO_2 \cdot Al_2O_3$) were prepared by impregnating the support with a solution of cobalt carbonyl in n-hexane. The addition of 0.5% Pd to such a catalyst increased its activity and the yield of liquid hydrocarbons.[51] The bimetallic contact with $SiO_2 \cdot Al_2O_3$ as a support manifested the highest activity in the Fischer–Tropsch synthesis (210 °C, 1 atm, $H_2:CO = 2$) which increased from

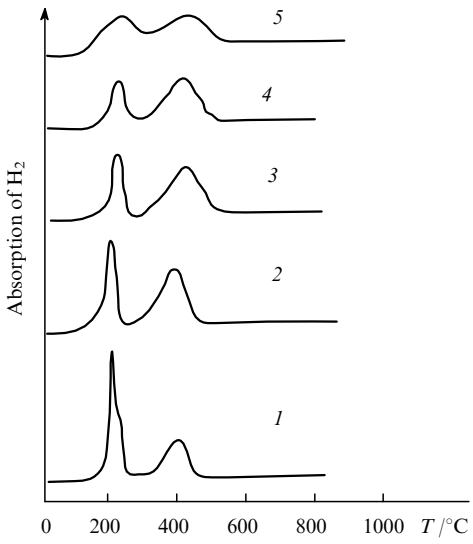


Figure 8. TPR spectra of the sample Co–Ru/Al_2O_3 calcined at different temperatures: non-calcinated (*1*); 250 °C (*2*); 300 °C (*3*); 350 °C (*4*); 400 °C (*5*).[50]

6.6×10^{-3} to 8.7×10^{-3} mmol CO (g of Co s)$^{-1}$ in comparison with the monometallic Co-sample. The yield of liquid hydrocarbons increased from 57 to 72 g m^{-3}, while the selectivity of their formation increased from 33% to 42%. The extent of cobalt reduction increased from 55% to 62%. Presumably,[51] Co–Pd-clusters are formed on the surface of this catalyst and autocatalytic reduction of Co occurs by spillover of hydrogen adsorbed on palladium.

It has been found[24] that the rate of hydrocarbon synthesis from CO and H_2 (250 °C, 1 atm, $H_2:CO = 2$) increased 35-fold upon addition of palladium to a catalyst Co/SiO_2 (the atomic ratio Pd : Co = 1 : 2, total metal content = 5%). This was accompanied by a sharp (from 91% to 59%) decrease in the methane content, a marked (from 1% to 26%) increase in the n-paraffin (C_{2+}) content in the reaction products and an increase in the hydrocarbon chain length (the probability coefficient for the chain growth, α, increased from 0.29 to 0.78). Methane was the only product formed on a monometallic Pd-sample (yield 100%).

Ion exchange of solutions of $Co(NH_3)_6Cl_3$ and $RuCl_3$ in 8% NH_4OH was employed for the preparation of a series of catalysts (3% Co/SiO_2, 3% Co–3% Ru/SiO_2 and 3% Ru/SiO_2) for the Fischer–Tropsch synthesis (250 °C, 21 atm, $H_2:CO = 2$).[52] The activity of the Co–Ru contact exceeded that of the non-promoted Co-sample 4.6-fold and was nearly twice as low as that of the monometallic Ru-sample (K_{CO} were 9.6%, 2.1% and 18.7%, respectively). Methane (71%) was formed predominantly on Co-catalysts; the reaction products contained 25% of hydrocarbons C_{2+} and 4% of alcohols. Upon addition of Ru, the amount of methane formed decreased twofold (36%), while that of hydrocarbons C_{2+} increased 1.7-fold. Other reaction products included alcohols (MeOH, EtOH, Pr^nOH); their total content was 20%. The Ru/SiO_2 sample manifested the highest selectivity in the synthesis of paraffins (63%), virtually no alcohols were formed.

Hydrocarbons C_{2+} were predominantly formed on catalysts prepared by spraying carbonyls $Co_{4-n}Ru_nH_n(CO)_{12}$ ($n = 0–4$) or $Co_2Ru_2(CO)_{13}$ onto SiO_2 under identical conditions (250 °C, 21 atm, $H_2:CO = 2$) (see Ref. 53). These catalysts differed from those prepared by ion exchange[52] in lower methane yields (13%–25%) and higher selectivities with respect to hydrocarbons C_{2+} (64%–79%). The content of oxygen-containing reaction products and CO_2 was insignificant (0.2%–5%).

Ion-exchange and impregnation were used for the preparation of Pt–Co-catalysts on zeolite NaY.[54] Synthesis of hydrocarbon from CO and H_2 was carried out at 232 °C, 10 atm and

$H_2:CO = 2$. In the former case, methanol was the major product (50%). Methane (51%) and hydrocarbons C_{2+} (49%) were formed on a catalyst prepared by impregnation, oxygen-containing products were formed in trace amounts. The difference in the reaction of the target products are usually attributed to the difference in the sizes of the bimetallic Co–Pt-particles formed in the course of the preparation procedure. If ion-exchange is used, the size of the particles is less than 2.5 nm, which can be attributed to the small size of zeolite NaY pores. If the catalysts are prepared by impregnation, their particles have a larger size ($\sim$ 20 nm) and are localised on the zeolite surface.

It has been found [55] that a catalyst prepared by co-precipitation of cobalt and cerium oxides manifested high activity in the Fischer–Tropsch synthesis. The reaction products comprised lower alkenes and higher n-alkanes; the amount of CO_2 was negligible. The activities of such a catalyst increased threefold upon promotion by 0.3% Ru [from $Ru_3(CO)_{12}$] and remained virtually unchanged over 100 h, the degree of CO conversion being > 40%. However, the selectivity of the synthesis catalysed by a promoted sample did not change. TPR studies have shown [55] that the temperature of CeO_2 reduction decreased in the presence of Co_3O_4 on the surface of a non-promoted catalyst, while the addition of Ru decreased the reduction temperatures of both Co_3O_4 and CeO_2 due to hydrogen spillover. As a result, the surfaces of Ru-promoted contacts contained more Co^0 particles than non-promoted samples, which increased their catalytic activities.

It has been shown [56] that introduction of 0.2% ruthenium, platinum or palladium strongly affected the catalytic and physicochemical properties of 10% Co/SiO_2 prepared from a cobalt acetate–cobalt nitrate mixture. According to the extent of carbon monoxide conversion (%) in the methanation reaction (240 °C, 1 atm, $H_2:CO = 2$), all the catalysts of this series can be arranged in the following order: Co–Ru (72) > Co–Pd (58) > Co–Pt (50) > Co (34) > Ru (3). It is noteworthy that the turnover number of the most reactive Co–Ru-sample (12.7×10^{-2} s^{-1}) exceeded that of the monometallic Co-catalyst (9.3×10^{-2} s^{-1}). For the Co–Pt- and Co–Pd-contacts, the turnover numbers are equal to 4.2×10^{-2} and 5.9×10^{-2} s^{-1} respectively.

The higher activity of the Co–Ru-contact in comparison with a monometallic sample was attributed [56] to the increase in the extent of cobalt reduction (from 50% to 100%) upon promotion by Ru and the increase in the size of Co crystallites from 12 to 13 nm. In Pt- and Pd-promoted cobalt catalysts, the extent of cobalt reduction also increased to 56% and 53%, respectively, but the size of crystallites decreased to 4 and 6 nm. IR spectroscopic studies have shown that CO adsorption on Co–Ru-catalysts is of a bridging type (an intense band at 1950 cm^{-1}). It was suggested [56] that the bridge form exceeds the linear form in reactivity. High catalytic activity of the Co–Ru-contact can be explained by the increase in the number of bridging-type CO-absorbing sites. In the bridge form, carbon monoxide readily dissociates into carbon and oxygen.

Nb_2O_5 prepared by calcination of niobic acid in an air flow (550 °C, 2 h) was used as a support for cobalt-containing catalysts.[33] Samples containing 5% Co and 0.6% ruthenium or rhenium were prepared by co-impregnation of niobium oxide with aqueous solutions of cobalt nitrate and the corresponding metal chlorides. Hydrocarbons were synthesised at 220 °C, 1 atm and $H_2:CO = 2$. Promotion of Co-catalysts by ruthenium or rhenium increased the selectivity of synthesis of liquid hydrocarbons C_{5+} from 55% to 60% and 81%, respectively. The selectivity of methane formation on a Co–Ru-contact decreased from 10% to 3.5% in comparison with the monometallic sample. However, the introduction of Pd, Pt and Rh into the catalyst Co/Nb_2O_5 increased its activity in the Fischer–Tropsch synthesis in parallel with the increase in the selectivity of formation of liquid hydrocarbons and lower alcohols (MeOH, EtOH).[57] TPR and XPS studies of this effect revealed that promotion by noble metals favours the reduction of Co^{3+} and Co^{2+} phases on the catalyst surface.

It is important to note that cobalt catalysts promoted by noble metals can be regenerated directly in the reactor in the course of operation.[58,59] At 200 °C, 5.5 atm and the volume velocity of synthesis gas of 1200 h^{-1} (volume velocity is the volume of a gas that has passed through a unit of catalyst volume per unit time), the extent of conversion of carbon monoxide on $Co–Ru/TiO_2$ was 26% for the atomic ratio Co:Ru of 10–400, while the selectivity with respect to liquid hydrocarbons was 85.7%. Regeneration of the deactivated catalyst with hydrogen was performed in the same reactor at 190–260 °C which provided a 90%–100% recovery of the catalytic activity. This is of considerable practical importance, since large capacities of modern reactors for conducting large-scale Fischer–Tropsch syntheses create inevitable problems connected with the loading/unloading of the catalysts in the course of their regeneration.

It may be concluded from these data that introduction of noble metals into Co-catalysts significantly increases their activities and selectivities in the Fischer–Tropsch synthesis. Physicochemical studies have shown that introduction of noble metals (or Re) into bimetallic cobalt catalysts facilitates reduction of surface oxide phases and increases the extent of reduction and/or dispersity of cobalt independently of the preparation procedure (impregnation or ion exchange),[50–52] cobalt source (carbonyl, nitrate, acetate, *etc.*),[60,61] the nature of supports and activation conditions.[47,62]

The mechanism of this promoting effect is not clearly understood yet. Neither do the above-described data provide explicit evidence in favour of one of the two mechanisms underlying this effect, *viz.,* hydrogen spillover from a noble metal to cobalt (see Refs 19–24, 28, 31 and 32) or direct interaction between metals resulting in the formation of bimetallic particles.[25–27] Let us consider these mechanisms in more detail.

IV. Mechanisms of promotion of cobalt catalysts by noble metals and rhenium

The phenomenon of hydrogen spillover on Al_2O_3 and SiO_2 coated with platinum, rhodium, rhenium and nickel is well established.[63–66] Spillover represents migration of hydrogen atoms from one adsorption site to another across the surface. Depending on conditions, the migrating hydrogen exists as H^+, H^- and $H^\bullet$. There is evidence that the spillover rate of activated hydrogen atoms depends on the state of the surface which is the hydrogen acceptor. In particular, this depends on the degree of hydroxylation of the support surface and increases markedly following preliminary adsorption of water. It is believed that the surface OH-groups form bridges through which the atomic hydrogen migrates to the adsorption sites of a support. Alternatively, it is water molecules that create the active sites enabling additional spillover.

The effect of rhenium on the reduction of a catalyst Co/Al_2O_3 was studied using TPR.[31] Treatment of $Co–Re/Al_2O_3$ with water and drying at 97 °C favours its reduction owing to hydrogen spillover from rhenium to cobalt oxide. In the authors' opinion, the magnitude of the promoting effect of Re depends on the efficiency of hydrogen transport from the reduced promoter to cobalt oxide. To test this hypothesis, Co/Al_2O_3 and Re/Al_2O_3 mixtures were prepared by two different methods, *viz.*, mechanical mixing of sample powders and fine grinding to a state where the particle size was smaller than the size of the original particles. TPR analysis showed that the extent of cobalt reduction increased upon direct interaction of metal particles which can be achieved if the second preparation procedure is used. The TPR spectrum of the bimetallic catalyst prepared by mechanical mixing was similar to that of the monometallic catalyst except that the former contained an additional peak at 447 °C corresponding to the reduction of rhenium oxides. Thus, rhenium has no effect on the extent of cobalt reduction.

The promoting effect of rhenium was observed for the catalysts prepared by fine grinding. The TPR spectra of mono- and bimetallic samples differed in that the peak at 727 °C of a Co/Al_2O_3 sample corresponding to reduction of the cobalt–aluminate surface phase was shifted by 200 °C towards the low-temperature region upon addition of Re, while the 927 °C peak characteristic of $CoAl_2O_4$ reduction was absent. This suggests that cobalt reduction on modified catalysts occurs more smoothly due to hydrogen spillover from metallic rhenium to cobalt oxide. [31]

However, other investigators (see Refs 25–27, 67–70) explain also the promoting effects of noble metals on Co-catalysts by the formation of reactive bimetallic particles on the catalyst surface. Let us consider the mechanism of formation of some bimetallic Co catalysts promoted by Group VIII metals .

A series of Co–Rh-catalysts on various supports (Al_2O_3, SiO_2 and TiO_2) were examined using TPR and thermoprogrammed oxidation (TPO).[25–27] Bimetallic catalysts prepared by co-impregnation of supports with the corresponding metal salts are reduced at lower temperatures in comparison with their monometallic counterparts independently of the nature of the support and of whether they underwent preliminary calcination or not. Thus, rhodium catalysed the reduction of both the salt and cobalt oxide, although the nature of the support is also important. Thus the catalyst Co/Al_2O_3 forms spinel-like compounds of the $CoAl_2O_4$ type that are difficult to reduce; in Co/SiO_2 catalysts, complete reduction of cobalt ions occurred; the formation of a mixed oxide $CoRh_2O_4$ was recorded on TiO_2. Notwithstanding, van't Blik *et al.*[25–27] have developed a general model of structural changes in these catalysts under different pretreatment regimes (Fig. 9). This model has got the name 'a cherry pit model'.

Within the framework of this model, after impregnation of a support (TiO_2, SiO_2 or Al_2O_3) with salts [$RhCl_3$ or $Co(NO_3)_2$] cobalt and rhodium ions occupy adjacent positions. The outer layers of bimetallic Co–Rh-particles formed upon reduction are enriched with Co^0, whereas the kernels ('cherry pits') consist predominantly of metallic rhodium. If Al_2O_3 is used as a support, cobalt partly reacts with Al_2O_3 before Co–Rh-particles are formed; the resulting spinel $CoAl_2O_4$ is not reduced even at 500 °C.

Although the structures of bimetallic particles remain unchanged upon passivation of the reduced catalysts, Co^0 is oxidised to a significantly greater extent than rhodium as a result of which a rhodium-enriched 'cherry pit' appears to be covered with cobalt oxide. Thus, passivated Co–Rh-particles consist of a rhodium core and a cobalt oxide shield (see Fig. 9). Complete oxidation of the catalyst brings about structural changes in bimetallic particles, resulting in the formation of adjacent metal oxides. Thus, Rh_2O_3 localised on the catalyst surface becomes fully exposed.

Unlike rhodium, the ruthenium component of bimetallic catalysts may come into contact with cobalt to yield alloys. Studies by XPS and mass spectrometry of Co–Ru-catalysts and secondary ions revealed [67] that the state of metals, their surface concentrations and distribution across the layer depend on the nature of the support used (Al_2O_3 or SiO_2). This can be explained by different dispersities of the metal particles and different types of interactions, metal–support and metal–metal. For example, mass spectra of samples on an Al_2O_3 support contain peaks with the mass numbers (m/z) 86, 102 and 129, which correspond to the clusters $CoAl^+$, $CoAlO^+$ and $CoAl_2O^+$, thus suggesting the formation of surface aluminates. The reduced cobalt reacts with Ru^0 to form Ru–Co microcrystallites as can be judged from the appearance in their mass spectra of a peak with m/z 160 assigned to the cluster $RuCo^+$. Based on these data, the authors have developed a layer-by-layer model for the Co–Ru-catalyst: [67]

$$Ru–Co\text{-alloy}/Ru^0/Co^0, Co_3O_4, CoAl_2O_4/Al_2O_3.$$

An alternative model for the formation of bimetallic catalysts has been proposed.[68–70] The structures of the contacts $Pt–Co/Al_2O_3$ and their catalytic activities in the Fischer–Tropsch synthesis were studied by TPR and XPS. The catalysts prepared by impregnation of alumina with $Co(NO_3)_2$ and H_2PtCl_6 possessed variable compositions $Pt_{1-x}Co_x/Al_2O_3$ (total metal content was 10%) and were active as regards the synthesis of hydrocarbons and alcohols from CO and H_2. Methanol was mainly formed on samples where the platinum content exceeded that of cobalt (Pt > Co); for Co > Pt, hydrocarbons and higher alcohols were the main reaction products.

Studies of monometallic Co-catalysts revealed that mild (297 °C, 1 h) calcination of cobalt nitrate results in its conversion into [Co(III) and Co(II)] oxides. Part of CoO formed a highly dispersed difficult-to-reduce phase on the surface of the support (Al_2O_3), predominantly as a monolayer. With an increase in the cobalt content in the catalyst, Co_3O_4 crystallites are predominantly formed.

Hydrogenation of a monometallic Co-sample at 300 °C yields only CoO. Reduction of a platinum-promoted catalyst under similar conditions converts Co_3O_4 into Co^0. The cobalt surface phase (CSP), which is firmly bound to Al_2O_3, is not reduced even in the presence of Pt.

Two mechanisms of surface conversions at different molar ratios of Pt and Co (Pt > Co and Co > Pt) have been pro-

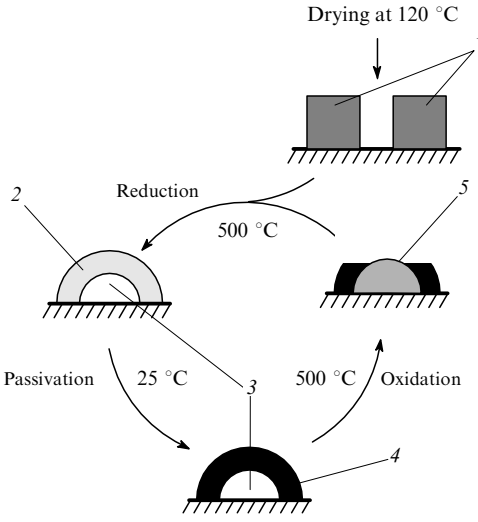


Figure 9. A model of formation of a Co–Rh-catalyst.[25, 27]
(*1*) $RhCl_3 + Co(NO_3)_2$, (*2*) Co-enriched shell, (*3*) Rh-enriched core, (*4*) Co_3O_4, (*5*) Rh_2O_3.

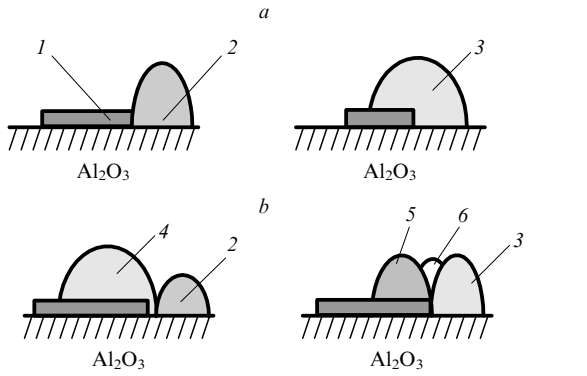


Figure 10. Conversion of Pt- and Co-phases on the surface of the contact $Pt–Co/Al_2O_3$ upon its reduction at different ratios of the metals: Pt > Co (*a*) and Co > Pt (*b*).[68, 70]
(*1*) CPS, (*2*) Pt ions, (*3*) Pt^0, (*4*) cobalt oxide, (*5*) Co^0, (*6*) bimetallic phase $Co^0–Pt^0$.

posed [68–70] (Fig. 10). In the first case, the surface Co monolayer is formed upon calcination (CSP), whereas platinum ions exist as particles of a fairly large size. CSP is not reduced upon treatment of the catalyst with hydrogen (300 °C, 1 h), but becomes partly covered by Pt^0 formed upon conversion of platinum ions.

In the second mechanism (Co > Pt), calcination of the catalyst yields CSP, platinum ions and Co_3O_4. Under mild conditions (300 °C), no reduction of CSP takes place, but Pt ions and cobalt oxide are reduced to Pt^0 and Co^0, respectively, and the metal particles interact. It was supposed [68–70] that partial shielding of Pt by metallic cobalt and formation of a bimetallic phase (Co^0–Pt^0) occurs.

The formation of Co–Pt particles was confirmed by EXAFS (Extended X-Ray Absorption Fine Structure) and X-ray diffraction analysis of $Pt_{0.6}Co_{0.4}$ samples.[71] The size of Co–Pt-particles in this catalyst was 15 nm (*cf.* ~11 nm in the $Pt_{0.5}Co_{0.5}$ contact). Additional evidence in favour of formation of Co–Pt-particles on the surface of the $PtCo_x/Al_2O_3$ catalysts ($x = 0–0.67$) was obtained using XPS.[72]

As a matter of fact, the two models of formation of the Co–Rh catalysts, which imply appearance of different types of bimetallic particles, are essentially similar. Whereas the 'cherry pit' model [25–27] suggests the presence of a core consisting of metallic rhodium and an outer shell enriched with cobalt, in the second model metallic cobalt particles partly shield reduced platinum to form a Co^0–Pt^0 interface (see Refs 69 and 70).

A model for active sites formation in the catalysts Co/SiO_2 promoted by noble metals (Pd, Pt, Rh, Ru) has been developed by Lapidus *et al.*[34] According to the previously postulated mechanism of hydrocarbon synthesis from CO and H_2 in the presence of Co-catalysts,[16, 73, 74] the synthesis of liquid hydrocarbons occurs on a bifunctional active site, *i.e.*, a polymerisation site. This site is localised at the interface between metallic cobalt and the oxide (the latter behaves as a a Lewis acid). The electron density of cobalt ions in such a site is shifted towards the oxide, as a result of which the metal acquires a partial positive charge ($\delta+$).

Some characteristics of oxide phases on the surfaces of reduced catalysts were obtained by TPR of samples following preliminary reduction under isothermal conditions (TPRPR) (Table 1). As can be seen, the TPR spectrum of a Co/SiO_2 sample following reduction at 450 °C contains four signals with $T_{max} = 127$, 210, 388 and 561 °C. The second and the third peaks correspond to the reduction of underreduced Co^{2+} ions and Co_3O_4, respectively. It is known that the latter manifests the properties of a Lewis acid. The high-temperature peak corresponds to the reduction of mixed Co–support oxides, while the low-temperature signal with $T_{max} = 127$ °C corresponds to the easily oxidisable species $Co^{\delta+}$, which represents a constituent of the polymerisation site. Its oxidation can occur under the action of, *e.g.,* water released in the course of reduction. Thus, the polymerisation site is predominantly localised at the $Co^{\delta+}$–Co_3O_4 interface on the surface of a reduced catalyst Co/SiO_2.[34]

The addition of platinum increases the concentrations of both $Co^{\delta+}$ (manifested in the appearance of an additional peak in the low-temperature region I) and Co_3O_4, the acidic component of the bifunctional centre (see Table 1), that is, increases the number of polymerisation sites. The yield of liquid hydrocarbons increases from 118 (in the case of a non-promoted sample) to 139 g m^{-3}, while the selectivity of their formation in the Fischer–Tropsch synthesis increases from 76% to 81%.[34, 75]

The content of Co_3O_4 in Co–Pd-catalysts decreased (the peak at 406 °C was characterised by $S = 28\%$). In this case, the oxide phases were largely represented by Co^{2+} and $CoO \cdot xH_2O$ species, which did not manifest the properties of Lewis acids. This circumstance might account for the relatively low activity of these catalysts in the synthesis of liquid hydrocarbons C_{5+} (the yields of C_{5+} decreased to 82 g m^{-3} and the selectivity, to 60%).

The introduction of rhodium into the contacts Co/SiO_2 had no effect on the content of $Co^{\delta+}$ (the total area of the low-temperature peaks in their TPR spectra was 10%, see Table 1), whereas that of Co_3O_4 increased from 33 (in the case of the non-promoted sample) to 40%. The ratios of metallic and oxide phases in the bifunctional centre changed thereby with a concomitant increase in the catalytic activity. However, the oxide phases of Co–Rh contain predominantly Co(II) and $CoO \cdot xH_2O$ (the total area of the peaks in regions II and III is 49%). This may be the reason for the lower selectivity of this catalyst as regards synthesis of liquid hydrocarbons (72%) in comparison with the monometallic sample (Co/SiO_2).

The concentration of $Co^{\delta+}$ on the surface of Co–Ru-samples ($S = 5\%$) is twice as low as that in monometallic Co-catalysts (12%). Nevertheless, it is quite probable that high content of Co_3O_4 (53%) significantly increases the probability of formation of catalytic sites of the type $Co^{\delta+}$–Co_3O_4. As a consequence, the yields of liquid hydrocarbons on Co–Ru-catalysts were only somewhat higher (129 g m^{-3}), while the selectivity of their formation was virtually the same (77%) in comparison with monometallic samples.

It may thus be concluded that the introduction of noble metals into monometallic cobalt catalysts changes the mode of formation of their active surfaces.[16, 34] Hydrogenation of Co–M/SiO_2 (M = Pt, Pd, Rh, Ru) brings about the formation, on their surface, of bifunctional centres ($Co^{\delta+}$–Co_3O_4), which play the role of polymerisation sites in the Fischer–Tropsch syntheses.

* * *

The data presented above provide an illustrative example of the interest of investigators in the study of bimetallic Co-containing catalysts for the synthesis of hydrocarbons from CO and H_2 and in the elucidation of mechanisms of their promotion by noble metals and rhenium.

In summary, the following conclusions can be made. The introduction of platinum-containing metals into Co-catalysts facilitates the reduction of cobalt derivatives and increases their catalytic activities. There is still no concensus, however, concerning the reasons for the promoting effect of rhenium for Co-catalysts. Some authors hold the opinion [31, 32] that, similar to noble metals, rhenium facilitates reduction of the cobalt oxide phases on the surface of the catalysts by hydrogen spillover from rhenium to cobalt, while other authors suggest [33] that Re increases

Table 1. Temperatures of the peaks (T) and their relative areas (S) obtained by deconvolution of the TPR spectra of the reduced catalysts Co–M/SiO_2 (I–V are the temperature regions where hydrogen adsorption takes place).

Promoter	I						II		III		IV		V	
	T/°C	S(%)	T/°C	S(%)	T/°C	S(%)	T/°C	S(%)	T/°C	S(%)	T/°C	S(%)	T/°C	S(%)
Without promoter	–	–	127	12	–	–	210	27	–	–	388	33	561	28
Pt	47	9	128	7	–	–	186	11	274	23	381	49	–	–
Pd	78	1	110	2	147	18	201	15	248	33	406	28	499	4
Rh	70	1	117	2	144	7	198	16	257	33	431	40	516	1
Ru	–	–	118	5	–	–	209	39	–	–	415	53	553	3

the dispersity of cobalt and diminishes the size of Co crystallites without any effect on reduction.

Thus, there are several viewpoints concerning the mechanisms of action of Group VIII metal-promoted cobalt catalysts in the synthesis of hydrocarbons from CO and H_2. This problem may be solved in the near future through wide purpose-oriented application of modern physicochemical methods.

References

1. J Falbe (Ed.) *Chemierohstoffe aus Kohle* (Stuttgard: Georg Thieme, 1978)
2. A L Lapidus, S D Pirozhkov, V D Kapkin, A Yu Krylova, in *Tekhnologiya Organicheskikh Veshchestv (Itogi Nauki i Tekhniki)* [Technology of Organic Compounds (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1987) Vol. 13, p. 158
3. S M Loktev *Khim. Prom-st (Moscow)* (5) 270 (1983)
4. V Ponec *Catal. Rev. Sci. Eng.* **11** 41 (1975)
5. J H Sinfelt *Adv. Catal.* **23** 19 (1973)
6. W M H Sachtler *Catal. Rev. Sci. Eng.* **14** 193 (1976)
7. J R Anderson *Structure of Metallic Catalysis* (New York: Academic Press, 1975)
8. J H Sinfelt *Bimetallic Catalysis Discoveries. Concepts and Applications* (New York: Wiley, 1983)
9. R S Mann, T R Lien *J. Catal.* **15** 1 (1969)
10. G C A Schultz, L L van Rijen *Advances in Catalysis and Related Subjects* (New York, London: Academic Press, 1958)
11. T Ishihara, K Eguchi, H Arai *Appl. Catal.* **30** 225 (1987)
12. A Feller, M Claeys, E van Steen *J. Catal.* **185** 120 (1999)
13. B Rebenstorf *Acta Chem. Scand., Sect. A* **31** 208 (1977)
14. A L Lapidus, Khoang Chong Iem, A Yu Krylova *Izv. Akad. Nauk SSSR, Ser. Khim.* 148 (1983) [a]
15. M K Niemela, A O I Krause, T Vaara, J Lahtinen *Top. Catal.* **2** 45 (1995)
16. A L Lapidus *Izv. Akad. Nauk SSSR, Ser. Khim.* 2683 (1991) [a]
17. J A Amelse, L H Schwartz, J B Butt *J. Catal.* **72** 95 (1981)
18. J A Amelse, J B Butt, L H Schwartz *J. Phys. Chem.* **82** 558 (1978)
19. L A Bruce, G J Hope, J F Mathews *Appl. Catal.* **8** 349 (1983)
20. T Mallat, J Petro, S Szabo *React. Kinet. Catal. Lett.* **29** 353 (1985)
21. G E Batley, A Ekstrom, D A Johnson *J. Catal.* **34** 368 (1974)
22. A Kogelbauer, J G Goodwin Jr, R Oukaci *J. Catal.* **160** 125 (1996)
23. A L Lapidus, A Yu Krylova, M P Kapur, E V Leongardt, A B Fasman, S D Mikhailenko *Izv. Akad. Nauk SSSR, Ser. Khim.* 60 (1992) [a]
24. L Guczi, Z Schay, G Stefler, F Mizukami *J. Mol. Catal. A* **141** 177 (1999)
25. H F J van't Blik, D C Koningsberger, R Prins *J. Catal.* **97** 210 (1986)
26. H F J van't Blik, R Prins *J. Catal.* **97** 188 (1986)
27. J H A Martens, H F J van't Blik, R Prins *J. Catal.* **97** 200 (1986)
28. D Schanke, S Vada, E A Blekkan, A M Hilmen, A Hoff, A Holmen *J. Catal.* **156** 85 (1995)
29. A Hoff, E A Blekkan, A Holmen, D Schanke, in *Proceedings of the 10th International Congress on Catalysis. New Frontiers in Catalysis, Budapest, 1992* p. 2067
30. G W Huber, C H Bartholomew, in *Proceedings of the 6th Natural Gas Conversion Symposium, Alaska, 2001* Article 46
31. A M Hilmen, D Schanke, A Holmen *Catal. Lett.* **38** 143 (1996)
32. S Vada, A Hoff, E Adnanes, D Schanke, A Holmen *Top. Catal.* **2** 155 (1995)
33. F Mendes, F B Noronha, R R Soares, in *Proceedings of the 6th Natural Gas Conversion Symposium, Alaska, 2001* Article 29
34. A L Lapidus, A Yu Krylova, M V Tsapkina, A V Reizin, S V Roslyakov *Khim. Tv. Topliva* (3) 32 (2003)
35. A V Zaitsev, V Yu Borovkov, A Yu Krylova, M P Kapur, V B Kazanskii, A L Lapidus, in *Khimicheskie Sintezy na Osnove Odnouglerodnykh Molekul (Tez. Dokl. III Vsesoyuz. Konf.), Moskva, 1991* [Chemical Syntheses Based on Monocarbon Molecules (Abstracts of Reports of the IIIth All-Union Conference), Moscow, 1991] p. 91
36. A L Lapidus, A Yu Krylova, B P Tonkonogov, D O Ch Izzuka, M P Kapur *Khim. Tv. Topliva* (4) 48 (1995)
37. M P Kapoor, A L Lapidus, A Yu Krylova *Stud. Surf. Sci. Catal.* **75** 2741 (1993)
38. A L Lapidus, A Yu Krylova, B P Tonkonogov, D O Ch Izzuka, M P Kapur *Khim. Tv. Topliva* (3) 90 (1995)
39. D O Ch Izzuka, Candidate Thesis in Chemical Sciences, I M Gubkin State Academy of Petrol and Gas, Moscow, 1995
40. E Iglesia, S L Soled, R A Fiato, G H Via *Stud. Surf. Sci. Catal.* **81** 433 (1994)
41. E Iglesia *Appl. Catal., A* **161** 59 (1997)
42. E Iglesia, in *Natural Gas Conversion IV* Vol. 107 (Amsterdam: Elsevier, 1997) p. 153
43. E Iglesia, S L Soled, R A Fiato, G H Via *J. Catal.* **143** 345 (1993)
44. E Iglesia, S L Soled, R A Fiato, G H Via, in *Natural Gas Conversion II* Vol. 101 (Amsterdam: Elsevier, 1994) p. 433
45. E S Shpiro, O P Tkachenko, V N Belyatskii, Yu Rudnyi, N S Telegina, S Yu Panov, V M Gryaznov, Kh M Minachev *Kinet. Katal.* **31** 950 (1990) [b]
46. G V Antoshin, E S Shpiro, V N Belyatskii, O P Tkachenko, Kh M Minachev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1913 (1983) [a]
47. US P. 4 585 798; *Chem. Abstr.* **105** 136 905 (1986)
48. US P. 4 413 064; *Chem. Abstr.* **100** 9846 (1984)
49. US P. 4 493 905; *Ref. Zh. Khim.* 22 L 239P (1985)
50. A R Belambe, R Oukaci, J G Goodwin Jr *J. Catal.* **166** 8 (1997)
51. A L Lapidus, A Yu Krylova, G V Kozlova, L T Kondrat'ev, T N Myshenkova, L V Babenkova, Yu G Kul'evskaya, S D Sominskii *Izv. Akad. Nauk SSSR, Ser. Khim.* 521 (1990) [a]
52. M Reinikainen, M K Niemela, N Kakuta, S Suhonen *Appl. Catal., A* **174** 61 (1998)
53. M Reinikainen, J Kiviaho, M Kröger, M K Niemela, S Jaaskelainen *J. Mol. Catal. A: Chem.* **118** 137 (1997)
54. L Guczi, D Bazin *Appl. Catal., A* **188** 163 (1999)
55. L A Bruce, M Hoang, A E Hughes, T W Turney *Appl. Catal., A* **100** 51 (1993)
56. S Sun, N Tsubaki, K Fujimoto *Chem. Lett.* 176 (2000)
57. F B Noronha, A Frydman, D A G Aranda, C A Perez, R R Soares, B Morawek, D Casnter, C T Campbell, R Frety, M Schmal *Catal. Today* **28** 147 (1996)
58. US P. 4 822 824; *Ref. Zh. Khim.* 22 N 230P (1990)
59. US P. 4 738 948; *Chem. Abstr.* **109** 9225 (1988)
60. M Niemela, M Reinikainen, in *Natural Gas Conversion V* Vol. 119 (Amsterdam: Elsevier, 1998) p. 161
61. M Kraum, M Baerns *Appl. Catal., A* **186** 189 (1999)
62. L Guczi, A Sarkany, Z Koppany *Appl. Catal., A* **120** 1 (1994)
63. W C Conner, G M Pajonk, S J Teichner *Adv. Catal.* **34** 1 (1986)
64. N E Lobashina, N N Savvin, I A Myasnikov *Dokl. Akad. Nauk SSSR* **268** 1434 (1983) [c]
65. R B Levy, M Boudart *J. Catal.* **32** 304 (1974)
66. W J Ambs, M M Mitchell Jr *J. Catal.* **82** 226 (1983)
67. E S Shpiro, G V Antoshin, O P Tkachenko, V N Belyatskii, S Yu Panov, Kh M Minachev *Dokl. Akad. Nauk SSSR* **278** 155 (1984) [c]
68. Z Zsoldos, T Hoffer, L Guczi *J. Phys. Chem.* **95** 798 (1991)
69. L Guczi, T Hoffer, Z Zsoldos, S Zyade, G Maire, F Garin *J. Phys. Chem.* **95** 802 (1991)
70. Z Zsoldos, L Guczi *J. Phys. Chem.* **96** 9393 (1992)
71. S Zyade, F Garin, G Maire *Nouv. J. Chim.* **11** 429 (1987)
72. Z Zsoldos, F Garin, L Hilaire, L Guczi *J. Mol. Catal. A: Chem.* **111** 113 (1996)
73. Kh M Minachev, A L Lapidus, A Yu Krylova *Khim. Tv. Topliva* (6) 7 (1993)
74. A Lapidus, A Krylova, J Rathousky, A Zukal, M Janchalkova *Appl. Catal., A* **80** 1 (1992)
75. A L Lapidus, A Yu Krylova, M V Tsapkina, A B Erofeev, A V Reizin *Khim. Tv. Topliva* (5) 52 (2004)

[a] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[b] — *Kinet. Catal. (Engl. Transl.)*
[c] — *Dokl. Chem. (Engl. Transl.)*