Russian Chemical Reviews **79** (11) 1027 – 1046 (2010) © 2010 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2010v079n11ABEH004160

Enhancement of water – gas shift reaction efficiency: catalysts and the catalyst bed arrangement

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Abstract. The results of studies devoted to the search for catalysts of water – gas shift (WGS) reaction that are highly active in a wide temperature interval are generalized. New compositions based on traditional and alternative, as regards the chemical composition, catalysts of high- and low-temperature WGS reaction are considered in detail. The single-stage arrangement of WGS reaction ensuring small temperature gradients in the radial direction of the catalyst bed are discussed. The bibliography includes 179 references.

I. Introduction

Conversion of natural gas containing methane as the major component is the main industrial method of production of hydrogen, which is used in the synthesis of ammonia, in the hydrogenation of petrochemicals (hydrotreament, hydrocracking, *etc.*) and other organic compounds, and recently as fuel in environmentally benign power generation using fuel cells.[1,2] The method of methane conversion determines the amount of carbon monoxide in the hydrogen-containing gas. Highly concentrated gas containing up to 30 vol.% – 34 vol.% of CO is produced by partial oxidation of methane. In the case of steam reforming of methane, the content of CO in the gas is 10 vol.% – 15 vol.%.[3]

Being a stage of hydrogen production process, the water – gas shift (WGS) reaction (an exothermic reaction) to a great extent determines its efficiency. An adiabatic WGS reaction is accompanied by heating (10 – 12 °C per 1 vol.% of CO converted to CO_2).[3] The conversion of CO is determined by the thermodynamic equilibrium in the reaction system and depends on the temperature within the catalyst bed (the WGS reaction cannot be conducted if no catalyst bed is available). The temperature dependence of the equilibrium degree of conversion of CO in the WGS reaction and the optimum temperature profile within the hypothetical catalyst bed, which is thermally stable in the whole temperature range, are shown in Fig. 1.[4] The temperature distribution within the catalyst bed was considered optimum if it provided a maximum rate of CO conversion at each point of the bed. Clearly, the necessary conversion of CO is attained at a minimum catalyst load.

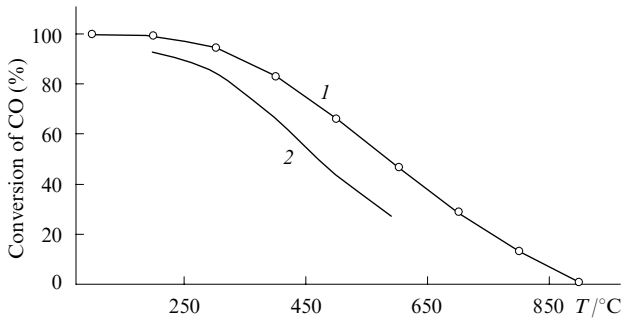


Figure 1. Temperature dependence of the conversion of CO in the WGS reaction under continuous heat removal along the catalyst bed.[4] The curve of the equilibrium conversion of a gas containing CO (6.3 vol.%), CO_2 (4.7 vol.%), H_2 (44 vol.%) and H_2O (45 vol.%) (*1*) and the optimum temperature profile of the catalyst bed for a catalyst that is thermally stable in a wide temperature range (*2*).

The optimum temperature profile was not implemented industrially for two reasons. First, the temperature intervals of stable operation of the known industrial catalysts the WGS reaction are limited and do not intercept, namely, the Fe – Cr-containing catalysts of high-temperature (HT) WGS reaction are active at temperatures above 330 °C, while the Cu – Zn-containing catalysts are thermally stable up to 280 – 320 °C. Second, carrying out an energy intensive exothermic process in immobilized catalyst bed faces diffi-

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Received 19 July 2009
Uspekhi Khimii **79** (11) 1112 – 1133 (2010); translated by A M Raevskiy

culties in heat transfer, which causes large temperature gradients in the radial direction of the reactor (tube). In this connection, industrial processes traditionally involve two adiabatic stages and an intermediate heat removal stage. A conventional two-stage design with adiabatic reactors is quite a bulky. An important requirement for the designs of fuel cell power generation in is compact arrangement of components of the power plant, in particular, equipment for the WGS reaction. The mass and dimensional characteristics can be improved by carrying out the WGS reaction in a single-stage tubular reactor with controlled temperature profile along the catalyst bed. This is possible if one uses catalysts that are highly active in a wide temperature interval. Also, some characteristics of the process can be improved upon increasing the thermal conductivity of the catalyst bed, especially, in the radial direction.

This review generalizes the results obtained in studies carried out since 1995 and devoted to the search for catalysts that retain their activity and operational stability in such a temperature interval that allows the WGS reaction to be conducted in a single stage. We also analyze publications concerned with the design of single-stage WGS reaction as well as the R&D activity in the field of catalysts ensuring low temperature gradients in the radial direction.

II. Studies devoted to search for catalysts that are highly active in a wide temperature interval

Recent studies on the search for highly active catalysts are mainly aimed at

— improving the activity of catalysts based on iron oxide compounds;

— improving the thermal stability of catalysts based on copper oxide compounds; and

— searching for catalysts based on other metal oxides (including noble metal oxides) that are active and stable in a wide temperature range (250–450 °C).

1. Catalysts based on iron oxide compounds

The HT stage of the WGS reaction involves the use of iron–chromium catalysts. There is a large number of patents devoted to various methods of preparation of such catalysts and improvement of their efficiency by modifying them with various metal oxides. These catalysts are characterized by stable operation at high temperatures, but their activity at temperatures below 350 °C is low. In the text below we will analyze the studies aimed at achieving high activity of an iron–chromium catalyst at low temperatures, in particular, investigations of the effect of the starting reactants and synthesis conditions, the phase and chemical compositions of precursors or promoters on the activity, stability and selectivity of catalysts, and the possibility of preparation of corresponding catalysts containing no chromium oxide.

In discussing various factors affecting the catalyst activity, the structural type of iron oxide that is formed in the course of preparation of Fe_2O_3/Cr_2O_3-catalysts attracted the attention of researchers.[5] The authors of that study considered the crystalline phases (α, γ and amorphous phase) of Fe_2O_3 as component of iron–chromium catalysts of HT WGS reaction, obtained by codeposition of a mixture of solutions of $Fe(NO_3)_2$ and $Cr(NO_3)_3$ prepared in different manner. It was shown that the initial structural type of Fe_2O_3 explicitly affects the activity of the Fe_2O_3/Cr_2O_3-catalysts. With respect to such properties, as the developed surface, particle size, thermal stability and stable catalytic activity, the crystalline phases of Fe_2O_3 can be arranged as follows:

amorphous phase of Fe_2O_3 > α-Fe_2O_3 > γ-Fe_2O_3.

A significant effect of the crystal structure of precursors on the catalyst activity was also reported in studies [6, 7] of the properties of the catalysts prepared by heat treatment of the hydroxo compounds of iron(III) and chromium(III) with the goethite, hematite (α-Fe_2O_3) and hydrohematite [ferrihydrite, $FeO_{(1.5-0.5x)}(OH)_x$] structures. It was shown that the ferrihydrite-based catalyst of the WGS reaction is much more active than the catalysts based on the hydroxo compounds with the goethite or hematite structures (Table 1).

Table 1. Rate constants for the WGS reaction on the 0.25–0.5 mm fraction of catalysts.[7]

Precursor	Structure	Rate constant (s^{-1}) at temperature		
		300 °C	330 °C	450 °C
Fe–Cr	Goethite	1.8	3.9	56
	Hematite	0.2	1.0	21
	Ferrihydrite	2.2	5.5	62
Fe–Cr–Cu (2%)	Goethite	4.0	17.0	73
Fe–Cr–Cu (2%)	Ferrihydrite	14.0	24.0	127
Fe–Cr–Cu (20%)	the same	18.0	38.0	92
Fe–Cr–Cu (2%)	Hematite (comparison)	1.0	2.2	60

Note. Reaction conditions: dry gas mixture composition (vol.%): CO — 9.6, CO_2 — 7.9, H_2 — 82.5; steam : gas = 0.8, pressure 1 atm.

Ferrihydrite promoted by copper ions ensures even higher activity.[7] There is a considerable literature on the promotion of iron–chromium catalysts with various metal compounds. For instance, the WGS reaction on chromium-promoted iron oxide catalysts deposited on SiO_2, TiO_2 and MgO at atmospheric pressure in the temperature interval 350–450 °C was studied.[8] The catalytic activity changed as follows

$$Fe–Cr–O < Fe–Cr–O/SiO_2 < Fe–Cr–O/TiO_2 \ll \ll Fe–Cr–O/MgO.$$

Based on the data from power X-ray diffraction analysis (XRD) and temperature-programmed reduction (TPR) in hydrogen flow, one can suggest that the catalytic activity depends on the extent of the interaction between the iron oxide and support.

Iron–chromium catalysts containing manganese, copper, cobalt and zinc oxide additives (5 mass %) were studied.[9, 10] The vanadium and nickel oxides were used as promoters for enhancement of the stability of the iron–chromium catalysts. Experiments were carried out in a flow reactor in the temperature interval 340–480 °C at a pressure of 2 MPa using a reaction mixture containing CO (14.7 vol.%), CO_2 (9.3 vol.%), H_2 (64 vol.%) and N_2 (12 vol.%). The volume rate of moist gas was 3000 h^{-1} and the steam : gas ratio was equal to 0.7. It was shown that the Fe_3O_4/Cr_2O_3 catalyst doped with copper or cobalt oxides exhibits enhanced activity [conversion of CO was

85% and 95% at 350 °C, respectively, and the reaction rate was 0.45 and 0.5 mol CO (g h)$^{-1}$ at 340 °C, respectively]. The authors noted that the addition of nickel to the iron–chromium catalyst causes undesired methanation under the reaction conditions, whereas the addition of cobalt or copper may be practically valuable for production of active catalysts of HT WGS reaction.

The addition of promoters into the iron–chromium catalyst prepared by codeposition causes the apparent activation energy to change (Table 2).[11] At equal content of promoters (2 mass %), the activity of the catalysts of conversion of a gas mixture containing H_2 (50 vol.%), CO (12.5 vol.%) and N_2 (37.5 vol.%) in the temperature range 350–440 °C decreases as follows:

Hg > Ag, Ba > Cu > Pb > unpromoted catalyst > B.

Unfortunately, no information on the precursor prepared by codeposition was reported.

Table 2. Effect of promoters on the characteristics of the Fe_3O_4/Cr_2O_3 catalysts of the WGS reaction.[11]

Promoter	Conversion of CO (%) [a]	E_a /kJ mol^{-1} (see [b])
–	18.8	112
B	18.7	108
Pb	25.0	90
Cu	27.9	81
Ag	32.9	74
Ba	33.5	83
Hg	37.4	82

[a] Conversion of CO at 400 °C, 27.6 atm, volume rate of the reaction mixture 1.2×10^6 h^{-1}. [b] To an accuracy of ±4 kJ mol^{-1}.

TPR studies[12] showed that promotion of iron–chromium catalysts by ceria (CeO_2) leads to an increase in the catalyst surface area and to a decrease in the reduction temperature. The reduced Fe–Ce–Cr–O-catalyst can be oxidized by water and CO_2 at 300–400 °C. It was assumed that the mechanism of the WGS reaction on these catalysts can be treated as a kind of redox mechanism. Based on the results of FT IR studies of catalyst samples with adsorbed H_2O and CO_2 molecules, exposed to specified volumes of a H_2O–CO (1:1) reaction mixture, it was assumed that the ceria-promoted iron–chromium catalysts are sensitive to particular structural modifications and exhibit a high activity and selectivity under the reaction conditions.

The results of a study of Fe–Cr-catalysts promoted by bismuth oxide and ceria were reported.[13] The authors studied the crystal structure of the catalysts before and after reduction and assumed that no replacement of iron atoms by atoms of the promoters occurs in the unit cells. Promoters have different functions in the catalysts, *viz*., Cr_2O_3 and Bi_2O_3 enhance the catalytic activity and stability and preclude the growth of γ-Fe_2O_3 particles; CeO_2 is mainly on the iron oxide surface and has little effect on the growth of the γ-Fe_2O_3 particles.

Enhancement of the stability of the iron–chromium catalyst is achieved[14] by co-promotion by the Mn, Mg and Ca oxide compounds as well as by Ce, La, Nd and Pr oxides. The catalyst activities were determined at 350 °C in the steam reforming of a gas mixture containing CO and N_2 (50:50 by volume) at a steam:gas ratio of 3.0. The promoted catalyst is highly active and more stable, *viz*., the ratio of the catalyst activity after overheating of the sample in a H_2O–H_2 (2.26:1) mixture at 500 °C for 4 h to the activity of the initial catalyst is 1.22 (*cf*. 0.8 for a reference catalyst).

A considerable enhancement of the activity of the Fe–Cr oxide catalyst can be achieved by introducing small amounts of rhodium (1 mass %).[15,16] The catalyst activity in conversion of a gas mixture containing H_2O (9 vol.%), CO (9 vol.%) and N_2 (82 vol.%) was measured in the temperature interval 350–500 °C. It was shown that the activity of the promoted catalyst samples enhances by almost five times at 350 °C and by 1.5 times at 500 °C compared to that of the unpromoted sample. A drawback of this catalyst is a high cost of rhodium.

Considerable attention is given to promotion of the iron–chromium catalyst by copper oxide. The state of copper (0.17 mass %–1.5 mass %) was analyzed using the results of an X-ray absorption fine structure spectroscopy (XAFS), X-ray absorption near edge structure (XANES) and X-ray diffraction (XRD) study.[17] Two samples of the iron–chromium catalyst were studied, one being a reduced freshly prepared sample and the other was a sample prestored under the reaction conditions. In the latter sample, Cu(II) ions are reduced to Cu(I) in the temperature range 120–150 °C, whereas in the freshly prepared sample reduction occurs at temperatures above 250 °C simultaneously with transformation of the Fe(III) and Cr(III)/Cr(VI) oxide phases to a Cr-containing magnetite phase. Mention was made that the addition of chromium atoms leads to formation of a solid solution based on the phase with the magnetite structure (Fe_3O_4) and to stabilization of the catalyst structure. Copper ions are also constituents of the solid solution.[18] The introduction of copper atoms enhances the catalyst activity.

The effect of activation on the structure of the $Fe_2O_3/Cr_2O_3/CuO$ catalyst of high-temperature WGS reaction was studied.[19] Initially, the catalyst has the hematite structure; activation leads to formation of a phase with the magnetite structure and the Fe^{2+}:Fe^{3+} ratio close to the expected value of 0.5. In the nonreduced samples, Cu(II) ions occupy distorted octahedral sites while after activation some copper ions are reduced to metal by a rather complex mechanism.

The role of copper atoms as promoters in the iron-chromium catalysts of HT WGS reaction was demonstrated.[20] A TPR study of the Fe_3O_4/Cr_2O_3 and $Fe_3O_4/Cr_2O_3/CuO$ catalysts in two gas mixtures (H_2 + He and H_2 + CO) showed that introduction of copper atoms enhances the catalytic activity and reduces the apparent activation energy to 75–80 kJ mol^{-1}. These results were obtained from calculations carried out assuming a zero-order reaction with respect to H_2O and a first-order reaction with respect to CO. For the unpromoted catalyst, the apparent activation energy was 118 ± 9 kJ mol^{-1}, which is in agreement with the known value. The authors recommended to use the copper-containing catalyst for conversion of CO-enriched gas.

A decrease in the apparent activation energy of the WGS reaction on copper-containing iron–chromium catalysts was also revealed in a more recent study.[7] The decrease in the apparent activation energy and enhancement of catalyst activity at low temperatures (below 350 °C) was associated with the formation of an iron–chromium–copper hydroxo compound with the ferrihydrite structure as precursor. The results of tests of the catalytic activity of

catalyst samples prepared by thermal decomposition of precursors with different structures are presented in Table 1. The authors of Ref. 7 analyzed the synthesis conditions of the desired precursors.

The nature of reactants and the conditions for their interaction in the course of synthesis of catalysts was considered.[21,22] In particular, it was reported that preferred use of copper nitrate in the preparation of the catalyst enhances its activity at low temperatures. According to XRD, BET (Brunauer–Emmet–Teller) method, H_2-TPR and X-ray photoelectron spectroscopy (XPS) studies, the introduction of CuO improves the reducibility of the catalyst, *viz*., the temperature of its reduction decreases by about 100 °C.[21] Catalysts of high-temperature WGS reaction containing Fe_2O_3 (60 mass % – 95 mass %), Cr_2O_3 (0 mass % – 20 mass %) and CuO (0 mass % – 10 mass %) prepared from high-purity iron and promoted by rare-earth metal compounds are highly active and stable. By thoroughly choosing solutions of iron and chromium salts as well as methods of synthesis one can significantly enhance the stability of iron–chromium catalysts modified by Mo, Co, Cu, Al, Ni, Ce, La, Mn and K oxides.[23]

The effect of the method of preparation on the physicochemical properties of an iron-containing oxide precursor of the catalyst was studied.[24] The authors proposed a method for preparation of an iron–chromium–copper catalyst with high concentration of surface hydroxyl groups, which ensures high catalytic activity.

Thus, the main avenues of search for methods of improvement of iron–chromium catalysts include promotion by various metal oxides and establishment of the dependence of the catalyst properties on the structure of precursors, the nature of promoters and the catalyst synthesis conditions. Despite the fact that the results obtained by different authors can hardly be assessed from a uniform position (one deals with different conditions for catalytic activity tests and different operating characteristics of catalysts), one can suggest that the properties of iron–chromium catalysts can be significantly improved. In particular, one can enhance their stability at high temperatures and activity at low temperatures and, therefore, reduce the initial operating temperature.

However, iron–chromium catalysts may contain toxic chromium(VI) compounds due to specific features of the preparation procedure. There is a considerable literature on the preparation of chromium-free catalysts. It was proposed[25] to use aluminium instead of chromium in the catalysts of HT WGS reaction based on iron and copper oxides. The catalysts had the hematite structure and were tested under more severe reaction conditions (steam : gas < 0.6) compared to the industrial operating conditions. It was shown that replacement of toxic chromium by aluminium may improve the catalytic properties of the samples studied. It was established[26] that the catalyst thus modified can operate in the kinetic regime in the temperature interval 300–400 °C. Aluminium and copper atoms present in the catalyst enhance its activity and selectivity in the WGS reaction. Aluminium acts as texture promoter, whereas copper 'operates' as structural promoter.

Replacement of chromium ions by aluminium ones were also reported in another study.[27] The catalyst was prepared by hydrolysis of solutions of iron nitrate and aluminium nitrate and tested in the WGS reaction (sream : gas = 0.6). It was reported that the precursor with the structure of Al-doped hematite is promising as environmentally safe catalyst of HT WGS reaction. However, catalysts with the hematite-type precursor structure are low active at temperatures below 350 °C. An iron-containing catalyst containing aluminium instead of chromium and promoted by first-row transition metal additives was studied.[28] Tests using an HT WGS reaction (400 °C, $H_2O : CO = 1$) and the XRD and TPR studies of catalyst samples suggest that the introduction of aluminium atoms improves the sintering stability of magnetite particles while the doping with copper atoms enhances the catalytic activity.

Studies on the preparation of catalysts of high-temperature WGS reaction containing no toxic chromium compounds were presented at an ACS symposium.[29,30] An industrial chromium-free catalyst NBC-1 prepared by codeposition and promoted by aluminium and cerium ions exhibited a rather high activity in the WGS reaction.[30] The results of comparative studies of the activity and stability of the NBC-1 catalyst and the commercially available Fe-catalyst C12-4 in tests in a reactor with fixed catalyst bed (350 °C, pressure 1 atm, steam : gas = 1, the volume rate of dry gas 3000 h^{-1}) are presented in Table 3. The results of studies of the chemical composition and structure of the NBC-1 catalyst by different physical methods were also reported in detail in Ref. 31.

Table 3. Compositions, properties and activity of the catalysts NBC-1 and C12-4.[31]

Parameter	NBC-1	C12-4
Composition [a]	$(88.6)Fe_2O_3-(2.0)Al_2O_3-(0.5)CeO_2$	$(81.2)Fe_2O_3-(8.8)Cr_2O_3$
Surface area /$m^2\ g^{-1}$		
before operation	72.8	70.3
after operation	35.2	40.4
X_{CO} (%) [b]	53.0 [c]	53.8 [c]

[a] 100 mass % including graphite and H_2O. [b] X_{CO} (%) is the conversion of CO calculated as follows: 100 × (mol CO at the inlet – mol CO at the outlet)/mol CO at the inlet. [c] Calculated under the following conditions: 350 °C, 1 atm, H_2O : gas = 1 : 1, volume rate of reaction mixture 3000 h^{-1} [dry gas composition (vol.%): CO — 26, CO_2 — 8, H_2 — 40, N_2 — 26], the catalysts were kept at 530 °C for 15 h in the reaction gas flow.

Promotion of the iron-containing catalyst by aluminium and copper significantly enhances its activity in the temperature interval 300–400 °C ($H_2O : CO = 1$).[29] The method of preparation of Fe–Al–Cu-catalysts was patented.[32] The catalysts were tested in the WGS reaction under the following conditions: a $CO-H_2O$ (1 : 1) reaction mixture and the temperature range 250–400 °C. The results of comparative studies are presented in Fig. 2.

Cobalt-promoted catalysts based on iron oxide doped with copper oxide and alumina, prepared using different order of the addition of the initial reactants in the course of neutralization and deposition were studied.[33] The catalyst has the hematite structure before activation and the magnetite structure after activation. The order in which the solutions of promoters are added during the neutralization

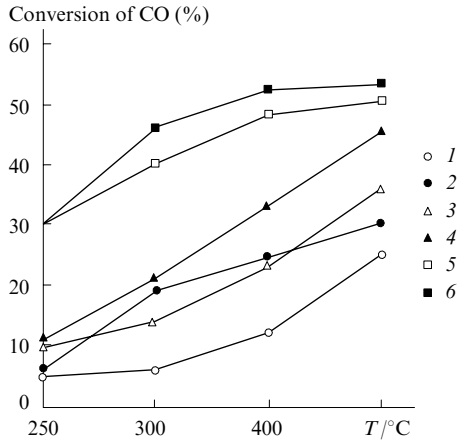


Figure 2. Conversion of CO on Fe–Al–Cu catalysts and on commercially available Fe–Cr catalyst plotted *vs.* temperature.[32]
Catalyst: Fe (*1*), Fe–Cu (*2*), Fe–Cr (commercially available) (*3*) and Fe–Al–Cu (*4–6*) at Fe : Cu = 20 (*4*), 10 (*5*) and 5 (*6*).

and deposition affects the surface area of magnetite and the particle size.

The use of thorium instead of chromium in the magnetite-type Fe–Cr–Cu-catalyst of HT WGS reaction to some extent improves its catalytic properties;[34] however, thorium is a radioactive element and its use seems to be not environmentally safe. The reaction mixture contained CO (10 vol.%), CO_2 (10 vol.%), H_2 (50 vol.%) and N_2 (30 vol.%). At a steam : gas ratio of 0.6 and a reaction temperature of 370 °C, the activity of the catalyst with the average composition (62.5) Fe–(30.7) Th–(6.9) Cu† was somewhat higher than that of the commercially available catalyst of HT WGS reaction. The results of tests are presented in Fig. 3 and in Table 4.

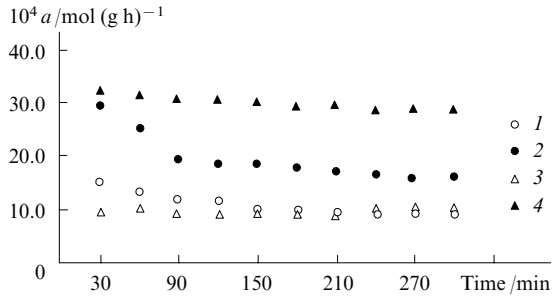


Figure 3. Activities (*a*) of catalysts in HT WGS reaction plotted *vs.* time.[34]
Fe_3O_4 (*1*), Fe_3O_4–Cu (*2*), Fe_3O_4–Th (*3*) and Fe_3O_4–Cu–Th (*4*).

It was proposed[35–37] to consider a series of low-chromium (or even chromium-free) iron-containing catalysts of high-temperature WGS reaction. The activities of two kinds of catalysts, *viz.*, α-Fe_2O_3 and γ-Fe_2O_3 supported on the spinel $MgAl_2O_4$ and on activated carbon, were comparable with the activity of the commercially available

† Hereafter the numbers in parentheses denote the mass % of metal in the catalyst.

Table 4. Catalytic activities of catalysts in the WGS reaction.[34]

Sample	$(a \pm 0.1) \times 10^4$ / mol (g h)$^{-1}$	$(a \pm 0.1) \times 10^5$ / mol (m^2 h)$^{-1}$
Fe_3O_4	8.8	8.8
Fe_3O_4–Cu	16.1	16.1
Fe_3O_4–Th	9.2	2.9
Fe_3O_4–Cu–Th	28.9	11.0
Commercially available iron–chromium catalyst	24.7	18.7

catalyst of HT WGS reaction.[35] The samples supported on $MgAl_2O_4$ (see Ref. 36) contained about 0.7% of Cr_2O_3 (CO conversion was 92% at 400 °C and 84% at 350 °C at a vapor : gas ratio of 1 and a volume rate of 2000 h^{-1}), while the samples supported on activated carbon contained 4% of Cr_2O_3 (CO conversion was 88% at 400 °C and 80% at 350 °C).

A chromium-free iron-containing catalyst promoted by transition metal oxides (NiO, V_2O_5 and CuO) was prepared by adsorption of colloidal γ-Fe_2O_3 on the surface of $MgAl_2O_4$. It showed a rather high activity in the WGS reaction (CO conversion was 95% at 400 °C and 80% at 350 °C) at a volume rate of the reaction mixture of 2000 h^{-1} (steam : gas = 1). The samples retained high catalytic activity under more severe reaction conditions (steam : gas = 0.6 and a volume rate of 3000 h^{-1} (Ref. 37). Further enhancement of the catalytic activity (CO conversion 98% at 400 °C) and stability of the catalyst under the same reaction conditions was attained by doping with La_2O_3 and Pr_6O_{11}. A catalyst prepared[38] by adsorption of colloidal γ-Fe_2O_3 on the surface of $MgAl_2O_4$ was promoted by ruthenium (in the form of metallic clusters) and lanthanum oxide. The catalyst containing Fe_2O_3 (14 mass %), Ru (0.4 mass %) and La_2O_3 (0.7 mass %) showed a high activity at low steam : gas ratio (0.6) and high volume rate of the reaction mixture (3000 h^{-1}). The authors believed this was due to high dispersion of the active component on the catalyst surface and to the presence of La_2O_3 as promoter (Fig. 4 and Table 5).

The use of a chromium-free, NiO- and V_2O_5-doped catalyst based on highly disperse iron prepared by colloidal

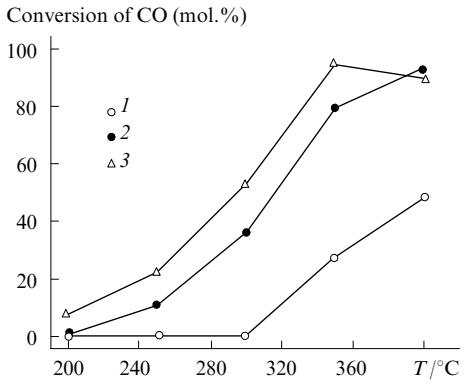


Figure 4. Conversion of CO on catalysts (14)Fe/$MgAl_2O_4$ (*1*), (0.4)Ru–(14)Fe/$MgAl_2O_4$ (*2*) and (0.7)La–(0.4)Ru–(14)Fe/$MgAl_2O_4$ (*3*) plotted *vs.* temperature.[38]
Reaction conditions: steam : gas = 1.0; volume rate of the reaction mixture 2000 h^{-1}.

Table 5. Thermal stabilities of the catalyst La(0.7)–Ru(0.4)–Fe(14)/$MgAl_2O_4$ (I) and the commercially available iron–chromium catalyst B117 (II) before and after high-temperature treatment.[38]

Parameter	I	II
Conversion of CO (mol.%)		
before treatment		
350 °C	94	80
400 °C	89	92
after treatment		
350 °C	84	57
400 °C	83	82
Surface area /$m^2\ g^{-1}$		
before treatment	246	24
after treatment	196	15

Note. Treatment conditions: 530 °C, 15 h; test conditions: steam : gas = 1 : 1; volume rate of the reaction mixture 2000 h^{-1}.

adsorption on the Al–Mg support did not enhance the catalytic activity in the WGS reaction (steam : gas = 1, volume rate of the reaction mixture 2000 h^{-1}), *viz*., the CO conversion at 400 and 350 °C was 95% and 80%, respectively.[39]

Two patents[40,41] concern methods of synthesis of chromium-free catalysts of HT WGS reaction. One patented catalyst[40] contains Fe_2O_3 (80 mass %–95 mass %), NiO (0.5 mass %–5 mass %), Bi_2O_3 (2 mass %–10 mass %) and one or more oxides from the following list: Al_2O_3, MgO, CaO, MnO_2 (1 mass %–5 mass %) or CuO (0.5 mass %–5 mass %). The catalyst was prepared by deposition of a mixture of solutions of the iron, nickel and bismuth nitrates with NaOH in air stream. The material treated in some way was impregnated by a solution of a copper salt. The catalyst thus prepared is highly active in the conversion of a reaction mixture containing CO (14 vol.%), CO_2 (8.1 vol.%), H_2 (55.3 vol.%) and N_2 (22 vol.%) under the following conditions: steam : gas = 0.45, volume rate of 2500 h^{-1}, 375 °C and a pressure of 40 atm (4.0 MPa); the CO conversion was on the average 76%–83%. Yet another catalyst contains Fe_2O_3 (60 mass %–90 mass %), MnO_2 (1 mass %–20 mass %), NiO (0.5 mass %–5 mass %), CuO (0.5 mass %–5 mass %) and K_2O (0.5 mass %–15 mass %). Samples are prepared by codeposition of solutions of manganese and nickel salts followed by the addition of CuO and K_2O. High mechanical strength and high catalytic activity of the samples thus obtained was reported, namely, CO conversion was 80%–87% at 350 °C.

A catalyst for production of hydrogen-enriched gas (hydrogen fuel) using a design including the WGS reaction in the temperature interval 150–450 °C was patented.[42] The noble metal-free catalyst composition contains bulk or supported nickel and one of the following metals (or the corresponding oxide): Ge, Cd, In, Sn, Sb, Te, Pb, Cr, Mn, Cu. The role of support can be played by alumina, zirconia, titania, ceria, as well as by magnesium, lanthanum, niobium and cobalt oxides, yttria, zeolites, perovskites, silica clay or iron oxide.

Studies of a series of modified ferrites prepared by doping iron oxide with various metal ions (Cr, Mn, Co, Ni, Cu, Zn and Ce) have demonstrated interrelations between the activities of these catalysts and their TPR profiles.[43] According to TPR data, incorporation of promoter metal cations into the crystal structure of hematite

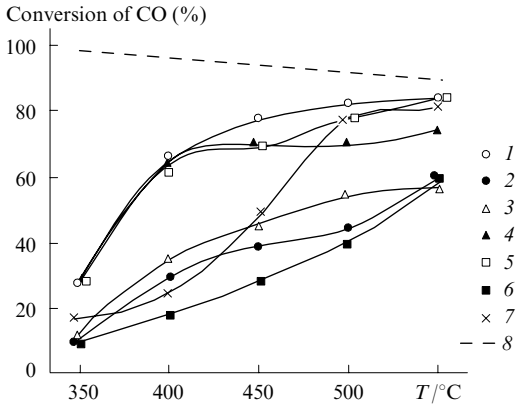


Figure 5. Conversion of CO on Fe/M catalysts plotted *vs*. temperature.[43]
Fe : M = 10 : 1, M = Cr (*1*), Mn (*2*), Co (*3*), Ni (*4*), Cu (*5*), Zn (*6*) and Ce (*7*); equilibrium conversion (*8*). Reaction conditions: H_2O : CO = 3.5; volume rate of the reaction mixture 60 000 h^{-1}.

changes the reducibility of hematite particles, which in turn depends on the nature of the metal cations. The results of catalytic tests are presented in Fig. 5.

The method proposed in another patent[44] allows one to prepare a chromium-free catalyst which is more active than the traditionally used iron–chromium oxide catalyst requiring fewer process operations giving no waste water or atmospheric pollution by toxic gases. The catalyst is prepared by mechanical activation of a Fe-containing component, *e.g*., metallic iron, with calcium oxide and copper oxide, mixing with water until formation of a plastic mass, extrusion, drying and calcination. Mechanical activation of the components is completed by blowing air enriched with oxygen (from 30% to 100%). The average composition of the catalyst thus obtained is Fe_2O_3 : CaO : CuO = 72 : 25 : 3. A prototype of this catalyst[45] is the composition with the following molar ratio of the components Fe_2O_3 : CaO : CuO = 1 : (1–2) : (0.03–0.2) (percentage ratio from 45 : 45 : 10 to 33 : 66 : 1). It was also prepared by mechanical activation. The catalytic activity of the prototype at 320 °C is about 20% lower than that of the proposed[44] catalyst (reaction conditions: volume rate of the reaction mixture 5000 h^{-1}, steam : gas = 0.6, CO content at the inlet 12%).

The results of some studies on the subject were reported in Chinese and only abstracts are available. They are briefly outlined below.

The effect of a Ce-promoter of the Fe_2O_3-based catalyst on the reduction was reported.[46] Cerium favours an increase in the surface area of the catalyst, which leads to extension of the operating temperature range, *viz*., the initial reduction temperature decreases while the final reduction temperature increases.

A new sulfur- and chromium-free iron-based catalyst was developed.[47,48] Its main components include iron and nitric acid. A study of the crystalline phase of the catalytic matrix by various physical methods showed that it is a highly active oxide γ-Fe_2O_3. It was recommended to use the catalyst in large-scale installations for the synthesis of ammonia operating at atmospheric pressure.

The activity and stability of the catalyst mentioned above was improved by introducing CoO as promoter.[49]

A method of preparation of a chromium-free catalyst of high-temperature WGS reaction was patented.[50] The catalyst is highly efficient, nontoxic and cheap. It contains

Fe_2O_3 (65%–90%), 1%–10% of Al–Fe–Si (6 : 2 : 1) oxide or silica gel (Al : Si = 8 : 2), vanadium oxide (0.5%–2%), MgO (0.5%–3%), NiO (0.5%–3%) and K_2O (0.1%–0.6%).

Catalysts of high-temperature WGS reaction based on chromium-free, perovskite-type iron oxide complexes $La_{(1-x)}Ce_xFeO_3$ doped with K were developed.[51,52] These catalysts show good thermal stability at $x \leqslant 0.5$ (at $x = 0.5$, the CO conversion was about 68% at 530 °C).

Thus, the development of chromium-free catalysts of HT WGS reaction is topical, deserves considerable attention of researchers and leads to success in some cases.

In the text below we will consider a number of studies concerning the Fe_2O_3 catalyst supported on activated carbon.[53–56] A catalyst with the magnetite structure, supported on activated carbon was proposed.[53] It was demonstrated that iron-containing catalysts prepared by deposition on activated carbon are rather efficient in the WGS reaction, especially if the carbon support is characterized by the well-developed surface and a large pore volume. The structures and activities of these catalysts were reported in the next study by the same authors.[54] Catalytic tests were performed with a flow reactor at a pressure of 25 atm. It was shown that, first, the catalytic activity is exhibited by the catalyst supported on pre-treated carbon kept in He at 1900 °C or in He at 1900 °C and then in CO_2 at 900 °C. Second, the degree of dispersion of the active oxide phase (magnetite) is related to the support texture, namely, the smaller the pores in the carbon matrix the higher the degree of dispersion of the iron-containing oxide phase.

A new catalyst prepared by pyrolysis and gasification of iron-containing brown coal from Victoria deposits (Australia) was reported.[55,56] It was shown that nanoparticles of the iron-containing phase with the magnetite structure are formed on the coal surface in the course of preparation of the catalyst. The distribution of magnetite particles of size less that 50 nm within the coal matrix is characterized by large dispersion. Tests of the catalyst in a quartz reactor with immobilized catalyst bed showed that it is comparable in activity with the traditionally used iron–chromium catalyst in the WGS reaction at 300–450 °C.

A particular group includes Fe_2O_3 catalysts modified with noble metals or noble metal alloys doped with iron. The effect of modifiers on the catalytic activity and stability of the catalysts containing gold deposited on the oxide composite ($Au/Fe_2O_3-MO_x$) in the WGS reaction was studied.[57] The catalytic properties of $Au/Fe_2O_3-MO_x$ (M = Zr, Mg, Ca, Ni, La, Cu, Zn, Al, Ba, Cr, Co, Ce, Mo, Bi, Ti, Mn) samples are improved significantly upon addition of ZrO_2 and to a lesser extent when modified with MgO, CaO, NiO, La_2O_3, Cr_2O_3 and CuO. Titania, bismuth oxide and manganese oxide additives cause the catalytic activity to reduce, while the Zn, Ba, Co and Mo oxides as well as alumina and ceria do not directly affect the catalytic activity and stability of the catalyst samples (Fig. 6). Based on the results obtained by physical methods, it was concluded that the activity of the $Au/Fe_2O_3-MO_x$ catalysts depends not only on the dispersion of gold particles, but also on the reduction properties of the composite oxide support.

A method of preparation of this type of catalyst containing Al_2O_3, ZrO_2, Nb_2O_5 in a molar ratio (0–0.6) : (0–0.6) : (0.1–0.6) at an Au : Fe_2O_3 : composite oxide support molar ratio of 1 : (10–35) : (2–8) was proposed in a patent.[58] The results of studies on the effect of

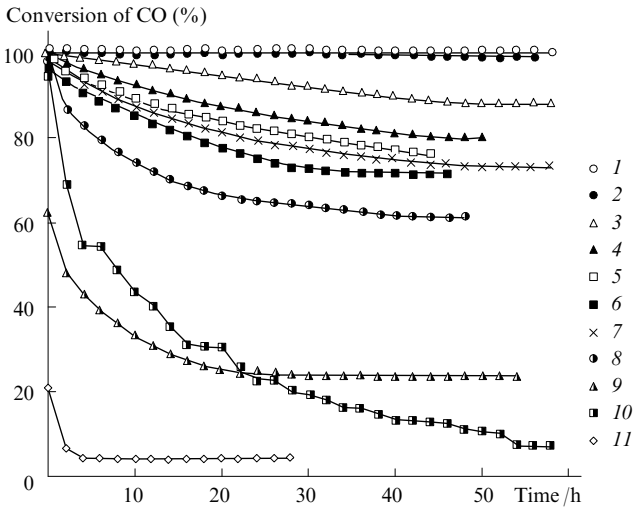


Figure 6. Activities and stabilities of oxide-promoted Au/Fe_2O_3 catalysts in the WGS reaction.[57]
Reaction conditions: 200 °C, gas composition: 10 vol.% of CO in nitrogen, steam : gas = 1 : 1, volume rate of the reaction mixture 10 000 h^{-1}.
Equilibrium curve (*1*); oxides: Zr (*2*), Mg (*3*), La (*4*), Cu (*5*), Cr (*6*), Zn (*7*), unpromoted sample (*8*); Bi (*9*), Ti (*10*) and Mn (*11*).

gold nanoparticles codeposited on the texture of these catalysts, as well as the regimes of crystallization and temperature-programmed desorption of CO from the iron oxide surface were also reported.[59]

The activities of Au/CeO_2 and Au/Fe_2O_3 catalysts used for the oxidation of CO and in the WGS reaction were compared.[60] The authors of that study analyzed the preparation of the catalysts and showed that the activity of the Au/Fe_2O_3 samples subjected to calcination, leaching and preliminary keeping in H_2 at 400 °C in the former reaction significantly enhances (Fig. 7).

The effect of the preparation conditions of the catalysts Au/Fe_2O_3 and Au/TiO_2 on their activities in the CO oxidation by oxygen and in the WGS reaction was discussed.[61] It was shown that these catalysts are highly active in both reactions. Attempts were made to relate the catalytic activity to the sample preparation procedure (impregnation,

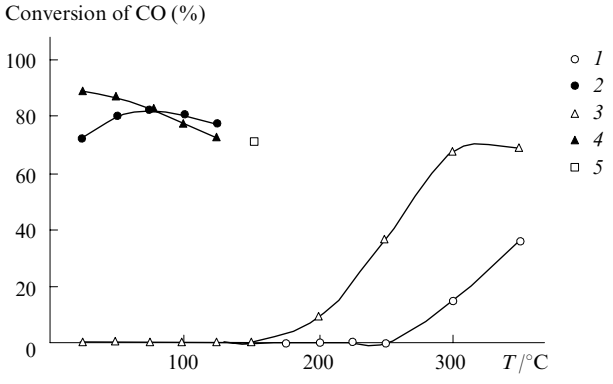


Figure 7. Conversion of CO on Au–Fe oxide catalysts in the oxidation of CO.[60]
Fe_2O_3 (*1*), (2)Au/Fe_2O_3 (*2*), (0.7)Au/Fe_2O_3 (*3*), (0.7)Au/Fe_2O_3 (reduced, *4*), (0.7)Au/Fe_2O_3 (*5*) (cooled). Gas composition: 2% CO and 1% O_2 in helium; volume rate of the reaction mixture 100 000 h^{-1}.

decomposition–deposition), to the content of dopants (alkali metal ions) and to the calcination temperature of the catalysts. It was shown that the Au/Fe_2O_3 catalyst is more active in the oxidation of CO by oxygen while the Au/TiO_2 catalyst is more active in the WGS reaction.

The mechanism of deactivation of the Au/Fe_2O_3 catalyst under conditions of the WGS reaction was analyzed.[62] It was shown that the decrease in the surface area of the support is almost the only reason for reduction of the catalytic activity.

The catalytic activities of iron-containing aerogels doped with palladium (1% and 2%) were studied.[63] Tests were carried out in a six-channel reactor with immobilized catalyst bed at atmospheric pressure in the temperature range 150–350 °C. The gas mixture contained CO (11 vol.%), H_2O (21 vol.%) and N_2 (68 vol.%) and the volume rate of the reaction mixture was 28 000 h^{-1}. It was reported that the activity of the catalyst containing 2% of Pd is 50% higher than that of the sample containing 1% of Pd.

The results of studies of iron-promoted Pd/Ce, Pt/Ce and Rh/Ce catalysts were reported.[64] The Pd–Fe-catalyst supported on $Ce_{0.5}Zr_{0.5}O_2$ showed the highest activity in tests (Table 6). XRD studies of the samples kept in the reaction conditions revealed the formation of an iron/palladium alloy.

Table 6. Activity characteristics of catalysts supported on $Ce_{0.5}Zr_{0.5}O_2$ in the WGS reaction.[64]

Catalyst [a]	Reaction rate at 180 °C (see [b])	E_a / kJ mol^{-1}
$Pd/Ce_{0.5}Zr_{0.5}O_2$	0.34	49
$Pd–Fe/Ce_{0.5}Zr_{0.5}O_2$ (see [c])	1.97	58
$Pt/Ce_{0.5}Zr_{0.5}O_2$	0.30	50
$Pt–Fe/Ce_{0.5}Zr_{0.5}O_2$ (see [c])	0.26	47
$Rh/Ce_{0.5}Zr_{0.5}O_2$	0.21	47
$Rh–Fe/Ce_{0.5}Zr_{0.5}O_2$ (see [c])	0.19	55

[a] The content of Pd, Pt and Rh was 1 mass %.
[b] 10^{18} molecules $(s\ g_{cat})^{-1}$. [c] 2.9 mass % Fe_2O_3.

High catalytic activity of iron oxide-based catalysts promoted by platinum group metals was reported.[65] Iron oxides from the series B and D were prepared from iron oxohydroxides β- and δ-FeOOH, respectively. Iron oxide from the series B contained no Na^+ ions, while iron oxide from the series D contained 0.03 mass % of Na^+. Iron oxide from the series K contained 3.6 mass % of K^+. The WGS reaction conditions were as follows: gas contained pure CO (99.9%) and steam, $H_2O:CO = 2.5$, volume rate of the reaction mixture 14 000 h^{-1}, reaction temperature 350 °C. From the data in Table 7 it follows that the best characteristics have the ruthenium-promoted catalysts.

Table 7. Activities of M/Fe_2O_3 catalysts in the WGS reaction.[65]

Iron oxide of series	Conversion of CO (mol.%) on catalysts					
	Fe_2O_3	Ru/Fe_2O_3	Rh/Fe_2O_3	Pd/Fe_2O_3	Ir/Fe_2O_3	Pt/Fe_2O_3
B	0	9	0	0	3	7
D	13	92	4	8	72	80
K	1	95	96	72	81	89

A positive effect of the alkali metal additive in the iron oxides was reported.

A series of studies of the catalyst based on Ru/Fe_2O_3 was reported.[66–69] They were aimed at optimizing the procedure for preparation of the Ru/Fe_2O_3 system to ensure high activity, selectivity and stability of the catalyst. The effects of the support preparation procedure, support doping with lithium group metal ions and lanthanide cations, of various solvents for the decomposition of ruthenium precursors, various routes of their decomposition on the support, ruthenium concentration and the activation temperature of the systems thus prepared were studied. The ruthenium catalyst supported on SiO_2, Al_2O_3 and La_2O_3 showed low selectivity in the WGS reaction, *viz*., the process was accompanied by intense methanation reaction. The Ru/Fe_2O_3 catalyst was more active than the Fe–Cr catalyst; 96-h tests of the catalyst revealed a constant level of its activity.

The properties and role of promoters for the Fe_2O_3-, Ru/Fe_2O_3- and $Ru(Na)/Fe_2O_3$-catalysts prepared by different methods were studied. The catalysts were tested using in WGS reaction in a flow reactor ($H_2O:CO = 2.5$). It was shown that the catalytic activity depends on the nature of the iron oxide produced (preparation procedure). Ruthenium atoms present in the catalyst play a key role in the enhancement of its activity. The activity of the catalyst in the LT WGS reaction also enhances if it contains alkali metal ions.

The effect of potassium as alkaline promoter on the regime of reduction and on the catalytic properties of Fe_2O_3, Ru/Fe_2O_3 and $Ru(K)/Fe_2O_3$ samples was considered.[69] It is characterized by stabilization of the highly disperse ruthenium phase on the iron oxide surface. The reduction kinetics of the catalyst noticeably changes in the presence of ruthenium(IV) oxide, *viz*., the reduction of $Ru(K)/Fe_2O_3$ is significantly different from that of Fe_2O_3, being governed by the reduction of the $KFeO_2$ phase.

The use of a platinum-free Ru–Co-catalyst for production of hydrogen-enriched gas using a design involving the WGS reaction at temperatures below 450 °C was patented.[70] Possible supports include alumina, zirconia, titania, ceria, yttria, as well as magnesium, lanthanum and niobium oxides, zeolites, perovskites, silica clay or iron oxide. The catalyst contains ruthenium and its oxides, cobalt, molybdenum and their oxides, as well as one of the following metals: Li, Na, K, Rb, Cs, Ti, Zr, Cr, Fe, La, Ce, Eu or the corresponding oxide.

Thus, our survey of studies devoted to the search for catalysts capable of replacing traditional catalysts of HT WGS reaction showed that the catalytic activity at low temperatures can be improved and thus a wide range of operating temperatures can be ensured by using iron-containing catalysts which usually contain noble metals or their oxides.

2. Catalysts based on copper oxide compounds

A traditionally used highly active industrial catalyst of low-temperature WGS reaction (LT WGS reaction) is a composition based on Cu–Zn modified by aluminium and/or chromium. Therefore, studies on the preparation of active catalysts that are stable at elevated temperatures mainly involve the search for compounds based on Cu–Zn and Cu–Zn–(Al and/or Cr).

In most cases, Cu–Zn-catalysts of the WGS reaction is prepared by codeposition under specified conditions. An alternative is provided by the Raney method of preparation

Table 8. Specific activities of copper-containing catalysts and the kinetic parameters of the WGS reaction.[74]

Catalyst	Component ratio	T/K	P_{H_2O}/Torr	P_{CO}/Torr	TOF [a] centre^{-1} s^{-1}	E_a/ kcal mol^{-1}	n	m
Cu(111)		563–683	10	26	0.02–0.4	17.0	0.5–1	0
Cu/ZnO	33 : 67	501	304	214	0.07	16.0	0.7	0
Cu/ZnO	33 : 67	563	10	26	0.02	—	—	—
Cu/ZnO	50 : 50	—	—	—	—	14.0	—	—
$Cu/ZnO/Al_2O_3$	23 : 67 : 10	523	< 750	< 750	0.002	—	—	—
Cu	—	523	< 750	< 750	0.001	—	—	—
Cu/Al_2O_3	—	673	236	182	12.0	13.3	—	—
	—	403	—	—	—	—	0.38	0.3

Note. TOF $= A \exp\left(-\frac{E_a}{RT}\right) P^n_{H_2O} P^m_{CO}$, where n is the reaction order with respect to H_2O and m is the reaction order with respect to CO.

[a] At 10^{15} centres per cm^2.

of the Cu-containing catalyst, which involves leaching of the Cu–Zn alloy of preset composition.[71–73] The initial activities of the catalysts thus prepared were comparable with that of the industrial catalyst; however, a rapid loss of activity due to the sintering of copper was observed.[71] It was proposed to stabilize the operation of the catalyst by increasing the content of zinc.[72] Indeed, this led to significant, although insufficient, enhancement of the catalyst stability. The best catalyst tested at 200 °C, a volume rate of 1000 h^{-1} and dry gas composition CO (10 vol.%)–N_2 (90 vol.%) at $CO : H_2O = 1 : 22.5$ showed a 10.2% reduction of its activity after 900 h.

There are two studies on the doping effect. The case in point is an Al-doped Cu–Zn-compound[74] and copper compounds doped with Al, Mn, Cr, Y, Fe and La.[75] The main goal of these studies was to prepare thermally stable catalyst (Table 8, Fig. 8).

Comparative tests of two catalysts with the spinel structure ($CuAl_2O_4$ and $CuMn_2O_4$) and the Cu–Zn–Al and Pt/Al_2O_3 catalysts[75] revealed high activity of $CuMn_2O_4$ which was comparable with that of the Cu–Zn–Al catalyst at temperatures above 225 °C. The $CuAl_2O_4$ catalyst appeared to be much less active; it was comparable in activity with the Cu–Zn–Al catalyst only at temperatures above 300 °C. The activities of the catalysts studied were higher than that of Pt/Al_2O_3.

The activities of the catalysts $Cu/Al_2O_3-MO_x$ (M = Zn, Al, Cr, Mn, Mg) in the WGS reaction were investigated.[76] The catalysts were tested at 200 and 250 °C. The highest activity was obtained on the Cu–Al–Zn-catalyst and reduced in the order Zn > Al > Cr > Mn > Mg. The same results were obtained earlier.[74,77] Unfortunately, no catalyst stability data were reported in the studies cited.

It was reported[78] that Cu–Ce-catalysts are non-pyrophoric and show operational stability and low degree of deactivation in the fast on–off regime. The catalyst $Cu_{0.2}Ce_{0.8}O_{2-y}$ prepared by codeposition contains 7.5 mass % of Cu and its activity in the WGS reaction is comparable with that of the conventional catalyst of LT WGS reaction, which contains 42 mass % of Cu. The reaction gas mixture contained CO (1.8 vol.%), H_2O (1.8 vol.%) and He (96.4 vol.%); the volume rate of the gas mixture was 5000 h^{-1}. The results obtained are presented in Fig. 9.

Investigations[79–84] of the catalytic properties of copper-containing spinels including chromites, ferrites, copper aluminates and their solid solutons in the WGS reaction

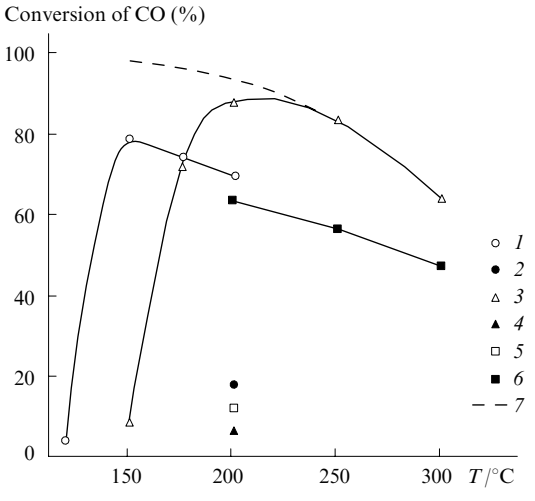


Figure 8. Conversion CO on Cu-containing mixed oxide catalysts plotted *vs*. temperature.[75]
Cu/Al_2O_4 (*1*), Cu/Cr_2O_4 (*2*), Cu/Mn_2O_4 (*3*), Cu/Y_2O_5 (*4*), Cu/Fe_2O_4 (*5*), Cu/La_2O_4 (*6*) and the equilibrium conversion (*7*). Gas mixture composition (vol.%): H_2 — 37.5, CO — 1.25, H_2O — 25.0, CO_2 — 12.5 and O_2 — 1.25; volume rate of the reaction mixture 6400 h^{-1}.

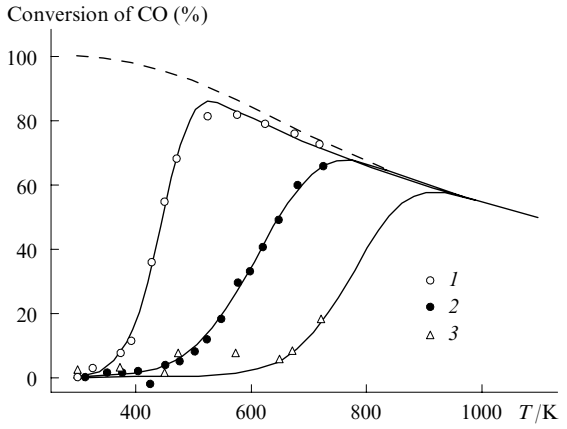


Figure 9. Conversion of CO in the WGS reaction on catalysts $CuO-ZnO-Al_2O_3$ (*1*), $Cu_{0.2}Ce_{0.8}O_{2-y}$ (*2*) and $Cu_{0.1}Ce_{0.9}O_{2-y}$ (*3*) plotted *vs*. temperature.[78]

revealed enhancement of the catalytic activity of the spinels upon partial (less than 40% atoms) replacement of Cu(II) ions by Zn(II), Co(II) or Mg(II) ions.

All catalysts based on the copper-containing spinels are highly active in the WGS reaction, being insignificantly less active than the commercially available Cu–Zn–Al catalyst. At the same time, these catalysts are more stable at high temperatures. For instance, the Cu–Zn aluminate containing 3 at.%–5 at.% of Cr ensures stable operation of the catalyst to 350 °C.

A number of catalysts of the WGS reaction, containing hydroxocarbonates including $(Cu_xZr_yZn_{1-x-2y})_5(CO_3)_2.(OH)_6$ (with the hydrozincite and/or aurichalcite structures) and/or $(Cu_xZr_yZn_{1-x-2y})_2(CO_3)(OH)_2$ (with the rosasite structure), or a product of their heat treatment of the general formula $Cu_xZr_yZn_{1-x-2y}O$ (with the würtzite structure), where $x < 0.7$, $y = 0.01-0.33$ were patented.[85] The thermal stability was improved by introducing zirconium cations into the structure of the copper–zinc hydroxycarbonate phase or the copper–zinc oxide phase. It is desired that this phase be a copper–zinc–zirconium hydroxycarbonate with the hydrozincite and/or aurichalcite structure. This phase decomposes under the reaction conditions or upon heat treatment with the formation of the Cu–Zn–Zr oxide with the würtzite structure. In addition, under these conditions copper cations in the ternary oxide are reduced to metallic copper while the oxide with the würtzite structure including zirconium cations remains unchanged. The advantages of this catalyst include operational stability in the WGS reaction in a wide temperature range from 150 to 400 °C, the possibility of conducting a single-stage WGS reaction instead of traditional industrial two-stage process and the lack of environmentally hazardous components.

Experimental data on changes under the catalytic activity during long-term tests of catalysts under the reaction conditions in a flow reactor are presented in Fig. 10. As can be seen, the known Cu–Zn–Al catalyst rapidly loses its activity during the first 90 h of operation at 380 °C. Under these conditions, deactivation of the catalyst Cu–Zn–Al–Cr proceeds at a constant rate. Catalyst *3* also loses its activity during the tests because most zirconium cations present in it form an individual phase ZrO_2. Unlike these catalysts, the catalysts *1* and *2* containing zinc and zirconium cations as components of a chemical compound show a rather high constant activity after 100 h of operation (up to 150 h).

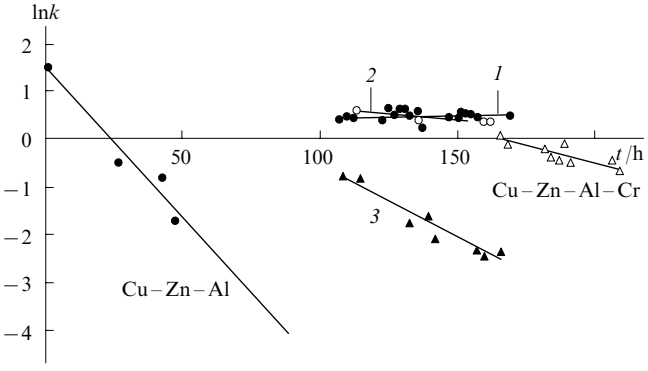


Figure 10. Experimental data on changes in the catalytic activity in long-term tests of catalysts (5 × 5 mm cylindrical pellets) under reaction conditions in a flow reactor at a pressure of 20 atm and a temperature of 380 °C.[85]
Gas mixture composition (vol.%): CO — 13, CO_2 — 7, H_2 — 51 and H_2O — 29.
The catalysts $Cu_{0.4}Zn_{0.5}Zr_{0.1}$ (*1*) and $Cu_{0.4}Zn_{0.45}Zr_{0.15}$ (*2*) heat-treated at 400 °C are monophase and have the würtzite structure; the catalyst $Cu_{0.4}Zn_{0.5}Zr_{0.1}$ (*3*) heat-treated at 400 °C contains a phase with the würtzite structure and an individual phase of zirconia ZrO_2. k is the rate constant for the reaction and t is the duration of tests.

3. Alternative catalysts

There is considerable literature concerned with investigations of catalysts that could provide an alternative to the traditionally used catalysts based on Fe–Cr and Cu–Zn oxide compounds and operating in a wide temperature range (200–500 °C).

A single-bed catalyst of the WGS reaction should efficiently operate in the temperature range 200–400 °C. This means that it should be highly active and thermally stable. In addition, it is desired that activation and passivation of the catalyst be conducted under conventional conditions.

High thermal stability of the catalyst is required for its potential operation in the WGS reaction to produce a hydrogen-enriched gas mixture for fuel cell applications. Considerable literature on noble metal-based catalysts is available.

In the last decade, catalysts containing noble metals (mainly Pt, Rh, Ru, Au, Pd) supported on partially reducible oxides (Ce, Zr, Ti oxides and mixtures of Ce and Ce–Zr oxides) have been intensively studied in connection with the design of a compact fuel processor for transportation vehicles. These catalysts exhibit a rather high activity in the temperature interval 250–400 °C. Typical representatives of such catalysts including Au/CeO_2, Au/TiO_2, Ru/ZrO_2, Rh/CeO_2, Pt/CeO_2, Pt/ZrO_2, Pt/TiO_2 and Pd/CeO_2 have been a subject of a comprehensive review.[86] The authors of Ref. 86 also considered some noble metal-free catalysts, namely, Cu/CeO_2, Ag/TiO_2, Cu/TiO_2 and Cu/ZrO_2.

Catalysts of the WGS reaction based on platinum group metal compounds are highly active; however, they are of limited use in industry owing to high cost.

Matsushita Electric Works (Japan) patented[87] a WGS reaction using a platinum catalyst supported on a metal oxide to remove CO from the hydrogen-containing gas for fuel cell applications. Toyota Motor Corporation (Japan) developed[88] a thermally stable catalyst of the WGS reaction (platinum supported on porous TiO_2 containing Al, Si, P, S and V oxide). The authors of yet another patent[89] refined the porous structure of the support and suggested to use a support with a mesoporous structure (pore diameters ranging from 3 to 100 nm).

Data on the activity of platinum and platinum-rhenium catalysts supported on different modifications of TiO_2 were reported.[90] It was concluded that the platinum–rhenium catalysts on TiO_2 (rutile) are highly active in the WGS reaction. At 250 °C, they are comparable in activity with the commercially available Cu–Zn-catalyst.

To carry out a LT WGS reaction, Nissan Motor Corporation (Japan) developed[91] a catalyst containing Pt and Zr supported on monolithic zirconia. The reaction can be conducted in the temperature interval 150–250 °C. A similar catalyst of the WGS reaction was patented.[92] The

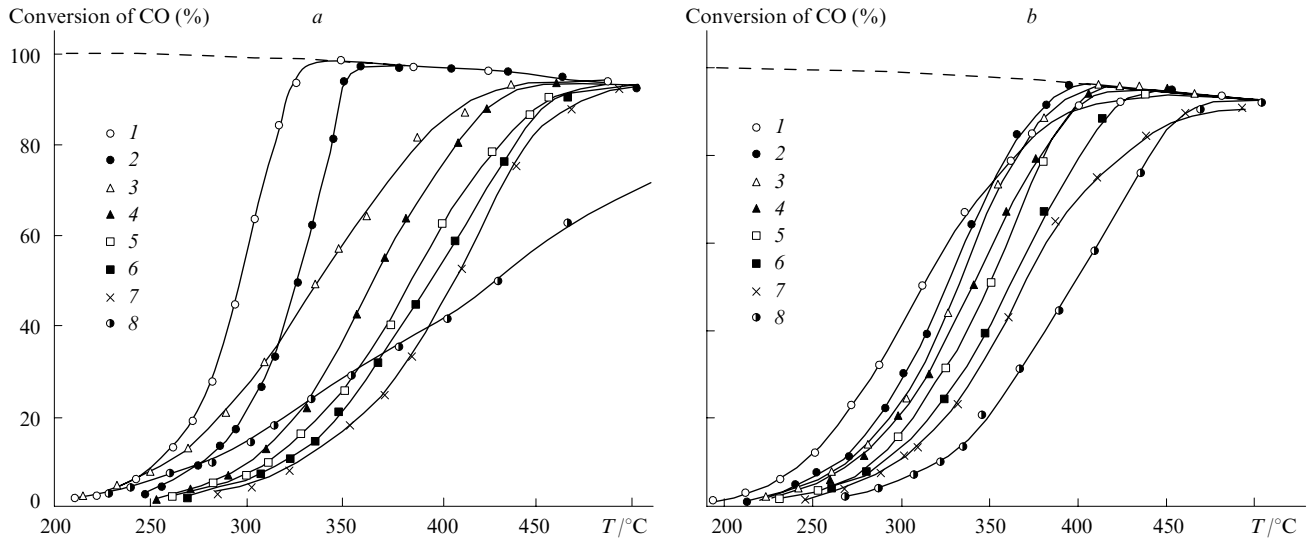


Figure 11. Conversion of CO on the catalysts 0.5% $Pt/MO_x-Al_2O_3$, where M are transition metals (*a*) and rare-earth elements (*b*), plotted *vs.* temperature.[99]
The curve for the catalyst 0.5% Pt/Al_2O_3 is shown for comparison. The MO_x content is 10 mass %. The dashed line denotes the equilibrium conversion. Gas mixture composition (vol.%): CO — 3, H_2O — 10 and He — 87; pressure 1 atm, volume rate of the reaction mixture 120 000 h^{-1}, particle size 0.18–0.25 mm. (*a*): Co (*1*), Ni (*2*), Ti (*3*), Fe (*4*), Cr (*5*), Pt/Al_2O_3 (*6*), Mn (*7*), Cu (*8*); (*b*): Ce (*1*), Ho (*2*), Nd (*3*), La (*4*), Tm (*5*), Sm (*6*), Eu (*7*) and Pt/Al_2O_3 (*8*).

catalyst is thermally stable and has the operating temperature range 200–650 °C.

A ruthenium-based catalyst, namely, alkali-modified ruthenium on zirconia is highly efficient in the WGS reaction.[93,94] The catalyst operates in the temperature interval 200–420 °C.

The authors of many patents recommend to introduce oxides of readily oxidizable and reducible metals into noble metal-based catalysts. For instance, a number of patents[95,96] are concerned with combinations of noble metal-based catalysts of the WGS reaction containing Pt, Pd, Rh, Ru and Ir with readily reducible and oxidizable metal (Ce, Zr, Ti, V, Mn, Fe) oxides supported on Al_2O_3, SiO_2, TiO_2, on rare-earth element oxides or on zeolites.

The mechanism of the WGS reaction on Pt–Re and Pd–Re catalysts supported on TiO_2 was studied.[97] It was shown that the activity of $Pd-Re/TiO_2$ is comparable with those of the low-temperature copper-containing catalysts and depends on the content of rhenium, whereas the activity of $Pt-Re/TiO_2$ to a lesser extent depends on the content of rhenium, being mainly affected by the reduction temperature of the catalyst. The activity of $Pd-Re/TiO_2$ and $Ir-Re/TiO_2$ was found to be sufficiently high and directly related to the rhenium content.[98]

Comparative studies of the activities of Pt-containing catalysts with platinum supported on simple (MO_x) and mixed ($MO_x-Al_2O_3$, MO_x-TiO_2) oxides (M = Ti, V, Cr, Mn, Co, Ni, Cu, Y, Zr, La, Ce, Nd, Sm, Eu, Cd, Ho, Er, Tm) were reported.[99] Tests were performed in the temperature interval 150–500 °C using a gas mixture containing CO (3%), H_2O (10%) and He (87%) at a volume rate of gas of 120 000 h^{-1} (Figs 11 and 12).

It was shown that the mixed catalysts $Pt/MO_x-Al_2O_3$ and Pt/MO_x-TiO_2 are promising for the use in the WGS reaction as a stage of a fuel processor. Unfortunately, no durability tests were carried out.

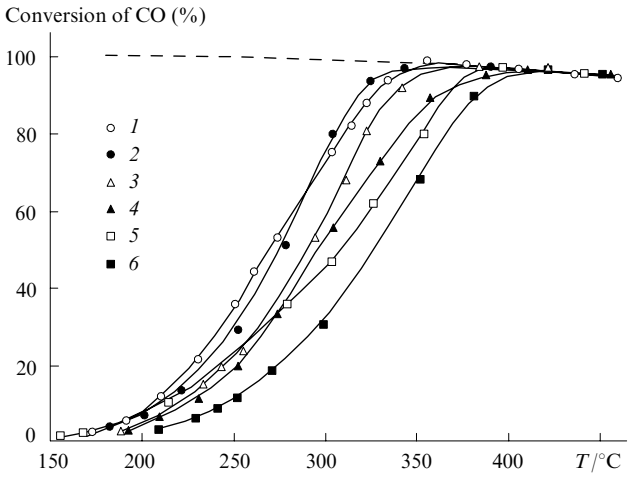


Figure 12. Conversion of CO on catalysts 0.5% Pt/MO_x-TiO_2, where M = Ce (*1*), Gd (*2*), Nd (*3*), Ho (*4*) and Y (*5*), plotted *vs.* temperature.[99]
The curve for the catalyst 0.5% Pt/TiO_2 (*6*) is shown for comparison. The MO_x content is 10 mass %. The dashed line denotes the equilibrium degree of conversion. Gas mixture composition (vol.%): CO — 3, H_2O — 10, He — 87; pressure 1 atm, volume rate of the reaction mixture 120 000 h^{-1}, particle size 0.18–0.25 mm.

The activity of the Cu–Zn–Al catalyst was compared with that of Pt/Al_2O_3.[100] It was shown that at low CO concentrations the Cu–Zn–Al catalyst is comparable in activity with the platinum catalyst, being much more active than the latter at high CO content.

A catalyst of the WGS reaction for conversion of gas containing H_2 and CO was patented.[101] The catalyst contains magnesium oxide and zirconia and, possibly, Cu, Ag,

Au, Pd, Pt, Group III–VIII transition metal and lanthanide oxides. The composition of the reaction mixture matches that of the gas after autothermal steam reforming or after gasification of hydrocarbons or carbon.

It should be noted that most studies on the use of readily reducible and oxidizable metals in combination with noble metals in the WGS reaction are concerned with ceria. A review [102] is devoted to the catalytic properties of CeO_2 and CeO_2-containing materials and to thorough consideration of CO conversion under purification of exhaust gas on these catalysts.

The effect of the Ca, Ce and Ln oxide additives on the alumina-supported platinum catalysts for cleaning of exhaust gas was studied.[103] The highest activity was established for the CeO_2-promoted catalysts. This was explained [104] by the ability of CeO_2 to transfer oxygen for the oxidation of CO from NO being reduced.

High activity of Pt/CeO_2 catalysts in the WGS reaction was reported.[105, 106]

The activity of Pt/CeO_2 catalyst in the WGS reaction is comparable with that of the commercially available Cu-containing catalyst at temperatures above 250 °C.[107, 108] It is believed that the former catalyst is promising for fuel cell applications. The stability tests of the Pt/CeO_2-catalysts of the WGS reaction were carried out for 300 h at 250 °C using 0.1 g of the catalyst and a gas mixture containing CO (7.6 vol.%), CO_2 (11.5 vol.%), H_2 (31.1 vol.%), H_2O (19.9 vol.%) and He (29.9 vol.%) at a flow rate of 251 cm^3 min^{-1} (Ref. 109). It was established that the deactivation rate of the Pt/CeO_2 catalysts depends on the synthesis conditions. The catalysts can be regenerated by calcination in air stream at 350 °C. Deactivation was explained by a decrease in the degree of dispersion of the metal owing to the deposition of carbon. The results obtained in a more recent study [110] show a high activity of the Pt/CeO_2 catalyst at temperatures above 240 °C (Fig. 13).

Engelhard Corporation (USA) developed a group of new catalysts called 'Selectra'.[111] The catalysts represent supported noble metals. Their activities at 220 °C approach that of the commercially available Cu–Zn catalyst. The catalysts are not pyrophoric and retain their activity under the action of air and moisture formed upon condensation of water vapour as the temperature decreases. It was stated that the catalysts are stable, although the duration of tests was not reported. Also, data on the content of noble metal in the catalyst are unavailable. To inhibit the activity towards methanation, an inhibitor is introduced into the catalyst. In this case, a threefold increase in the content of the noble metal is required to retain the catalytic activity. The chemical composition of the catalyst is unknown. It was shown that deactivation of the catalysts based on CeO_2-supported noble metals at temperatures below 150 °C is due to the formation of carbonates on the surface.[112] Deactivated catalysts cannot be regenerated by simply heating in the working gas. Regeneration is only possible by calcination in air at temperatures above 500 °C.

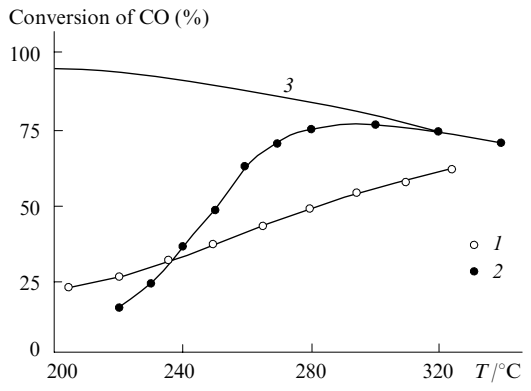


Figure 13. Degree of conversion of CO on industrial copper-containing catalyst (*1*) and (3)Pt/CeO_2 (3 mass %, *2*) under identical test conditions plotted *vs.* temperature.[110]
The volume rate of the reaction gas mixture is about 144 000 h^{-1}; Curve *3* corresponds to the equilibrium.

The kinetics of the WGS reaction on CeO_2-supported Pt, Pd and Rh catalysts was studied.[113] It is believed that these metals cannot be good catalysts of the WGS reaction because they are poorly oxidized by water.

The behaviour of the catalysts Pd/CeO_2 and Rh/CeO_2 in the course of adsorption of CO, NO and H_2 was studied.[114, 115] It was shown that an oxygen atom from ceria migrates to the metal surface and oxidizes carbon monoxide adsorbed on it while partially reduced cerium is readily re-oxidized by water. Therefore, the addition of ceria to platinum group metal-based catalysts enables significant enhancement of their activity in the WGS reaction.

The activities and stabilities of a number of platinum-based catalysts in steam reforming of a gas mixture containing N_2, CO, CO_2, H_2 and H_2O to produce hydrogen for fuel cell applications were studied.[116] Tests were performed over a period of 70 h. The activity of the Pt/CeO_2 catalyst rapidly decreased during the initial few hours and decreased more slowly and uniformly throughout the remaining test period. After 100 h of operation, the catalyst activity decreased by 50%, *i.e.*, the deactivation rate was high; therefore, these catalysts are inappropriate for practical use. The authors of that study explained deactivation of the catalysts by the high degree of equilibrium reduction of ceria in the real reaction mixture. They believe such a deactivation is characteristic of all noble metal-based catalysts supported on CeO_2. The amount of catalyst (Pt content 1.5 mass %) necessary for operation of a 50-kW power plant calculated from the initial activity is nearly 50 kg, which corresponds to 750 g of platinum. The corresponding reactor volume is too large to be used in, *e.g.*, cars, while the need for such a large amount of platinum makes them much more expensive (by about US $33 000, as to August 2008).

There are a few studies on Ce-containing catalysts of HT WGS reaction.[117–120] The activities of the catalysts Pd/CeO_2, Ni/CeO_2, Fe/CeO_2, Co/CeO_2 and $Ce–Pd/SiO_2$ were determined [117] from the dependence of the rate of CO conversion on the reaction temperature using $Cu/ZnO–Al_2O_3$ as the reference. Having specified a particular interval of the rates of CO conversion for all samples, the catalyst that meets this condition at the lowest reaction temperature is treated as the most active. Pd/CeO_2 was the most active in the series of catalysts

$$Pd/CeO_2 \approx Ni/CeO_2 > Co/CeO_2 > Fe/CeO_2 > Pd/SiO_2 > CeO_2.$$

Its activity approaches that of Ni/CeO_2, being higher than those of Co/CeO_2 and Fe/CeO_2. Studies by various physical methods showed that cerium in the Pd/CeO_2-catalyst is in

the reduced state and is coated with carbon particles in the course of the reaction. The carbon particles can be removed only after re-oxidation of the sample.

The activities and stabilities of Cu/CeO_2-catalysts of the HT WGS reaction were demonstrated.[118] These catalysts are stable in the HT WGS reaction in contrast to Fe/CeO_2 characterized by significant deactivation in the CO_2-enriched gas. The iron–cerium oxide catalysts are also less active than the Cu/CeO_2 catalysts. It is believed that the surface properties of cerium play the decisive role in high catalytic activity and sensitivity of the catalysts to dopants. Kinetic measurements for the catalyst of the composition 10 at.% Cu/Ce(30 at.%) LaO_x were carried out in the temperature interval 300–450 °C. The apparent activation energy of the catalyst stabilized under the reaction conditions at 450 °C was 70 kJ mol^{-1}. An initial decrease in the catalyst activity was followed by stabilization of the state of the catalyst. The initial loss of activity was explained by a decrease in the surface area of the catalyst (by about 20%) and enrichment of the copper surface with cerium in the course of the reaction at 450 °C. This conclusion contradicts the conclusions drawn in Ref. 116, which revealed irreversible degradation of the CeO_2 support and the loss of activity even at a lower temperature of 250 °C.

Studies [121, 122] of the catalytic properties of copper-, cobalt- or nickel-doped ceria carried out taking Cu_xO/CeO_x and nanocrystalline $Cu/Ce(La)O_x$ and $Ni/Ce(La)O_x$ as examples revealed high activity in the WGS reaction starting with a temperature of 200 °C for $Cu/Ce(La)O_x$ and a temperature of 300 °C for $Ni/Ce(La)O_x$. It was also reported that the catalyst $Cu/Ce(La)O_x$ retains high activity and stability to 600 °C.

The possibility of using ceria-based catalysts promoted by Pt, Au, Ni, Cu, Fe, Co in a fuel cell reformer was considered.[123] These catalysts were tested in a WGS reaction under the following conditions: temperature range 250–350 °C, gas mixture composition: CO (1.6 vol.%), H_2 (41.9 vol.%), H_2O (52.3 vol.%) and N_2 (4.2 vol.%); the volume rate of the reaction mixture was about 33 000 h^{-1}. The results obtained are shown in Fig. 14.

The activities of the catalysts Ni/CeO_2 and $Pt–Ni/CeO_2$ in the WGS reaction in the temperature interval 200–320 °C were compared [124] with the activity of commercially available Cu–Zn–Al oxide catalyst. The activity of the catalyst containing 40 mass % of Ni and 0.1 mass %–0.2 mass % of Pt was found to be higher than that of the commercially available catalyst in the temperature range 280–320 °C (Fig. 15).

A highly active catalyst of the WGS reaction for production of hydrogen from the synthesis gas without methane formation was described in a patent.[119] It was proposed to carry out conversion of the synthesis gas to CO_2 and H_2 in the WGS reaction without methane formation in the temperature range 200–425 °C on a catalyst which may contain noble metals supported on ceria or on ceria/zirconia or ceria/lanthanum oxide mixtures, the content of ceria ranging from 20% to 80% of the overall amount of the oxides. The role of methanation inhibitors can be played by such catalyst components, as the copper, magnesium and iron oxides or by their combinations. The optimum promoters of the catalyst include alkali metal or alkali-earth metal ions. Possible supports include mixtures of ceria with copper oxide or zirconia with copper oxide, with the ceria and zirconia contents varied from 50% to

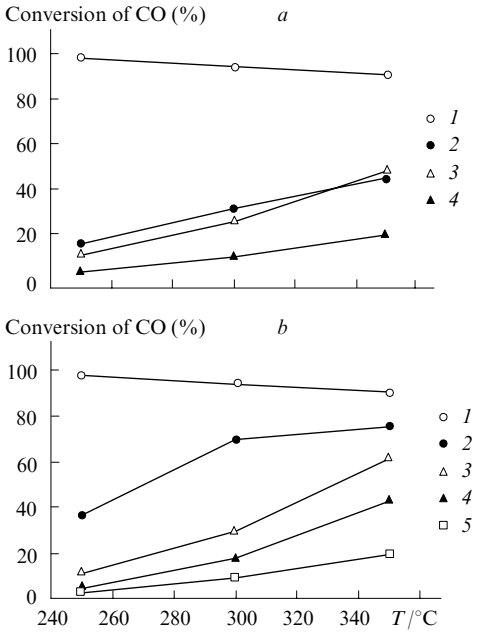


Figure 14. Test results obtained for CeO_2-based catalysts in the reactor with fixed catalyst bed.[123]
(*a*): Pt (*1*), Cu (*2*), Au (*3*), unpromoted sample (*4*);
(*b*): Pt (*1*), Ni (*2*), Fe (*3*), Cu (*4*), unpromoted sample (*5*).

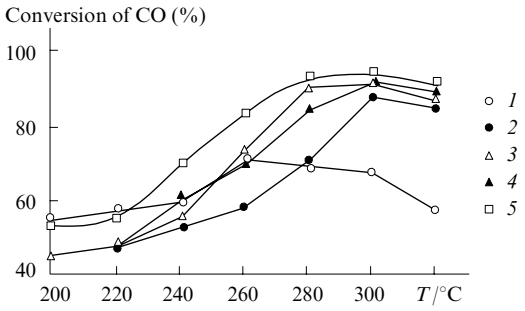


Figure 15. Conversion of CO on the original and commercially available catalysts of LT WGS reaction plotted *vs.* temperature.[124]
$Cu–Zn/Al_2O_3$ (*1*), $(40)Ni/CeO_2$ (*2*), $(1)Pt/CeO_2$ (*3*), $(0.1)Pt–(40)Ni/CeO_2$ (*4*) and $(0.2)Pt–(40)Ni/CeO_2$ (*5*).

80%. The reaction conditions and the results of comparative tests of some groups of catalysts described in that patent are presented in Table 9. As can be seen, two samples given in bold approach the catalyst $Cu/ZnO–Al_2O_3$ in activity and selectivity.

The results of comparative studies of the activities of commercially available catalysts Cu–Zn–Al (LT WGS reaction) and Fe–Cr–Cu (HT WGS reaction) and an original high-temperature, noble metal-free catalyst UFR-C promoted by copper doped with cerium and zirconium were reported.[120] The composition of the original catalyst $CuO/NiO/ZrO_2–CeO_2$ (in mass %) is as follows: CuO — 4.4, NiO — 2.5, ZrO_2 — 46.5 and CeO — 46.5. Its activity can be higher than those of the commercially available catalysts (Table 10).

Table 9. Activities of catalysts in the WGS reaction.[119]

Catalyst	T/°C		
	$X \approx 20\%$	X_{max}	CH_4
Pt/CeO_2	300	400	> 400
$Pt-Cu/CeO_2$	~340	~425	no
$Pt-La_2O_3-CeO_2$	~340	~425	> 425
$Pt-Cu/La_2O_3-CeO_2$	~375	~475	no
CuO_x/CeO_x	**~240**	**~425**	**no**
CuO/ZrO_2	~240	~475 (40%)	no
$Fe-Pt/CeO_2$	~250	~425	> 375
$Fe-Pt/CeO_2-ZrO_2$	**~250**	**~325**	**no**
$Mn-Pt/CeO_2-ZrO_2$	~225	~325	> 350
$Cu-ZnO/Al_2O_3$	~180	~325	no

Note. Reaction conditions: gas mixture composition (vol.%): CO — 8, CH_4 — 1, CO_2 — 10, H_2 — 32.5, H_2O — 30, N_2 —18.5; temperature range 150–600 °C; volume rate of the reaction mixture 67 500 h^{-1}.

Table 10. Catalytic activity of the catalysts Cu–Zn–Al, Fe–Cr–Cu and UFR-C in the WGS reaction.[120]

Catalyst	T/°C	Volume rate of gas mixture /h^{-1}	Conversion of CO (%)
Cu–Zn–Al (LT WGS reaction)	200	2320	63
Fe–Cr–Cu (HT WGS reaction)	480	3500	64
UFR-C	300	3500–9600	5
	400		62
	500		66
	700		72

Note. Reaction conditions: reaction mixture composition (vol.%): CO — 12.5, CH_4 — 1, CO_2 — 0.8, H_2 — 1.3, H_2O — 48, N_2 — 36.6.

Recently, gold-based catalysts have attracted the attention of researchers. Their activities in the LT WGS reaction are rather high.[125] The necessary conditions for high activity of such a catalyst include a small gold particle size (about 4 nm) and the use of transition metal oxides (Fe_2O_3, NiO, MnO_2) as supports.[126] Catalysts based on hemispherical ultrathin gold particles less than 5 nm in diameter are highly active in various reactions.[127]

Studies of catalysts of the WGS reaction containing gold supported on various metal oxides are well documented.

Catalyst	Au/ZrO_2	Au/Co_3O_4	Au/TiO_2	Au/Te_2O_3	Au/CeO_2
Ref.	128	129	130, 131	132–136	137–146

The behaviour of the Au/Fe_2O_3-catalyst was studied.[134–136] Measurements were carried out in a flow reactor at atmospheric pressure using a 0.6–0.8 mm fraction of the catalyst at a volume rate of dry gas (4.5 vol.% of CO in argon) of 4000 h^{-1} (steam : gas = 0.7). The catalyst containing 3 mass % of gold on iron oxide in the WGS reaction was at least comparable in activity with the commercially available Cu–Zn–Al catalyst.[136] The catalyst activity is governed by the preparation procedure.[134, 135] A highly disperse catalyst containing gold nanoparticles was prepared by homogeneous deposition–precipitation. The effect of the support texture on the activities of catalysts Au/ZnO, Au/ZrO_2, Au/Fe_2O_3, Au/Fe_2O_3-ZnO, $Au/Fe_2O_3-ZrO_2$ was studied.[128] Among the supports used, only iron oxide and zirconia were well-crystallized, whereas all other supports were amorphous substances or poorly crystallized. Only samples on the well-crystallized supports showed high activities. This was explained by a large decrease in the pore volume in the catalysts on the poorly crystallized supports in the course of operation.

Ceria was used as support for both gold-based and other noble metal-based catalysts.[113, 133, 137–146] Such catalysts are highly active in the high-temperature WGS reaction. Nanocrystalline Au/CeO_2 catalysts containing 5 mass %–8 mass % of gold are highly active in LT WGS reaction.[137] A highly active and stable Au/CeO_2-catalyst containing 3 mass % of gold showed a constant activity when operated over a period of three weeks under the following conditions: gas mixture composition: 4.5 vol.% of CO in argon, partial steam pressure 31.1 kPa and the temperature range 150–350 °C.[139] However, stability analysis of the catalysts based on noble metals supported on ceria[116] showed that these data are insufficient for characterization of the catalyst stability under real conditions of hydrogen production for fuel cell applications.

A new modified deposition–precipitation technique and the preparation conditions of Au/CeO_2 catalysts significantly affect their activities and operating stability.[147–149] The kinetics and mechanism of the WGS reaction on an Au/CeO_2 catalyst (the content of gold was varied from 0.8 mass % to 12 mass %) were studied[146] using an idealized gas mixture (1 kPa CO, 2 kPa H_2O) at 180 °C. It was concluded that the Au/CeO_2 catalyst prepared by the new modified deposition–precipitation technique and reduced at 200 °C is highly active in the oxidation of CO under the conditions specified. The optimum content of gold in the catalyst was 5 mass %. Mention was made that the catalyst shows high stability and is characterized by a 20% exponential deactivation with respect to the initial activity after 1000 min of operation. No data on stabilization of the catalytic activity were reported.

Based on assessment of the possibilities of the use of noble metal-based catalysts, one can suggest that the catalysts containing readily reducible oxides, in particular, CeO_2 are the most interesting. Their advantages include non-pyrophoric character and stability at high temperatures (to 400 °C). The activities of such catalysts become comparable with those of the Cu/ZnO catalysts only at temperatures above 250 °C. Long-term operation causes deactivation of the catalysts. Irrespective of the reasons for deactivation, the catalysts can be regenerated only upon calcination in air at high temperatures; this complicates their use.

In the text below we will consider oxide catalysts containing transition elements. The effect of the preparation procedure and modifiers on the activity of Cu–Mn oxide catalysts with the spinel structure in the WGS reaction was studied.[150] The catalysts were prepared by homogeneous codeposition in the presence of urea, a complex procedure using citric acid, codeposition with aqueous NH_3 solution, *etc*. The promoters of the Cu–Mn-catalyst included Fe, Al, Zr, Ce, Zn and Cr. The Cu–Mn–Fe catalyst with a 1 : 1 : 1 component ratio showed high activity at low temperatures (175–300 °C), *viz*., the degree of conversion of CO at 200 °C was 87% (Fig. 16).

The activities of two groups of catalysts in the WGS reaction were determined.[151] The catalysts represented com-

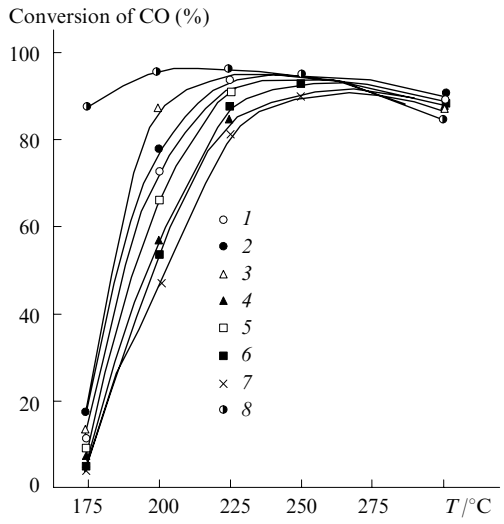


Figure 16. Conversion of CO on Cu–Mn–B catalysts (B = Al, Fe, Zr, Ce, Zn, Cr).[150]
Reaction conditions: gas mixture composition (vol.%): H_2 — 37.5, CO — 5.0, H_2O — 25.0, CO_2 — 12.5%; volume rate of the reaction mixture 6400 h^{-1}. Catalyst: Cu–Mn (*1*), Cu–Mn–Al (*2*), Cu–Mn–Fe (*3*), Cu–Mn–Zr (*4*), Cu–Mn–Ce (*5*), Cu–Mn–Zn (*6*), Cu–Mn–Cr (*7*) and $Cu/ZnO-Al_2O_3$ (*8*).

pounds of one out of twenty transition metals supported on the spinel $MgAl_2O_4$ or on a mixed oxide $Ce_{0.75}Zr_{0.25}O_2$.

The following activity series were established:
for the samples supported on $MgAl_2O_4$

$$Cu > Pt > Rh > Pd > Re > Ni > Au > Ru \sim Co \approx \approx Ag > Ir\ (\sim Fe);$$

for the samples supported on $Ce_{0.75}Zr_{0.25}O_2$

$$Pt > Re > Rh \sim Pd > Ru > Ni > Ir \approx Co > Cu > > Ag\ (> Fe) > Au.$$

Tests were carried out using a gas mixture containing 16 vol.% CO and 16 vol.% H_2O in argon at a gas rate of 60 Nml min^{-1} at 270 °C. It was concluded that the catalytic properties in the WGS reaction are affected by several parameters. The choice of the catalytically active metal is determined by the support. In the case of spinel $MgAl_2O_4$, it is desired to use metals and alloys that are more reactive towards oxygen rather than copper. The mixed oxide support $Ce_{0.75}Zr_{0.25}O_2$ requires such metals and alloys that form stronger bonds with CO than the Pt—CO bond.

A series of Co–V oxide-based catalysts of the WGS reaction was prepared.[152] Yet another catalyst represents cobalt supported on perovskite-type transition metal oxides or mixed oxides.[153] The first results obtained suggest high stability of these catalysts in the high-temperature reduction and re-oxidation. The catalysts are recommended for use in fuel processors for transportation vehicles.

Catalysts of the WGS reaction described in a patent[154] and representing molybdenum or tungsten carbide, boride or nitride doped with such metals as Fe, Ni, Co and Cu are stable to poisoning with sulfur compounds. Tests of the catalyst Mo_2C in the temperature interval 220–295 °C at atmospheric pressure showed that the reaction rate is somewhat higher than that attained on the commercially available Cu–Zn–Al catalyst.[155] High activity of the Mo/Al_2O_3 catalyst in the WGS reaction in the temperature range 350–400 °C was reported.[156] The activity and stability of the molybdenum-containing carbide catalyst is somewhat higher than the corresponding characteristics of the commercially available low-temperature Cu–Zn catalyst.[157] Co–Mo-oxides with different cobalt/molybdenum ratio supported on activated carbon at different temperatures were reported.[158] The catalysts were tested in the WGS reaction at 180 °C in a gas flow containing CO (10.5 vol.%) and H_2O (21 vol.%) in helium. After 5-min operation, the sample $Co_{0.5}Mo_{0.5}$/C-873 is more active than the commercially available Cu–Zn catalyst; however, after 5-h operation the activity of the former catalyst decreases.

Thus, there is a number of noble metal-based catalysts and oxide catalysts containing transition elements, which provide an alternative to the industrially used Fe–Cr-containing catalysts. Such catalysts are active in the temperature range 150–500 °C, but they contain noble metals (or noble metal oxides), which makes them of limited use in industry. At the same time, the activities of the alternative catalysts of LT WGS reaction are higher than those of the known Cu–Zn catalysts only at temperatures above 250 °C. Also, the operating lifetime of these catalysts casts some doubt.

The search for copper-based catalysts that are more efficient than modern industrial catalysts is in progress; some good results were obtained. To improve the stability at high temperatures, catalysts containing not only copper and zinc oxides and alumina, but also zirconia, chromium oxide and other metal oxides were studied.

It should be noted that copper-containing catalysts may be promising for the design of more compact single-stage WGS reaction.

III. Single-stage designs of the water–gas shift reaction

The reactors for a conventional WGS reaction are large because large volumes of catalysts are used. The reaction is conducted in two stages. The reaction conditions are as follows: temperature range 350–500 °C and the volume rates of the reaction mixture from 1000 to 3000 h^{-1} for the first stage (HT WGS reaction) and the temperature range 180–250 °C and the volume rates from 2000 to 5000 h^{-1} for the second stage (LT WGS reaction).[3] The temperature dependence of the degree of conversion of CO for this design of the WGS reaction is presented in Fig. 17.[4]

To improve the mass and dimensional characteristics, single-stage arrangements of the WGS reaction are developed. There is a particular need for compact reactors in connection with production of hydrogen for fuel cell applications. A conventional two-stage arrangement of the WGS reaction in the 50-kW fuel processor requires about 60 litres of catalysts of the HT and LT stages for CO conversion from (30–34) vol.% to about 1.2 vol.% and about 40 litres for CO conversion from (10–13) vol.% to nearly 0.4 vol.%.[159]

Clearly, it is appropriate to conduct the reaction at high temperatures. At the same time, low final concentrations of CO (< 1 vol.% – 1.5 vol.%) can be attained at temperatures below 270–300 °C.[3] Therefore, the reaction should proceed in the catalyst bed with a specified and optimized, as applied to the reaction conditions, temperature distribution along the bed.

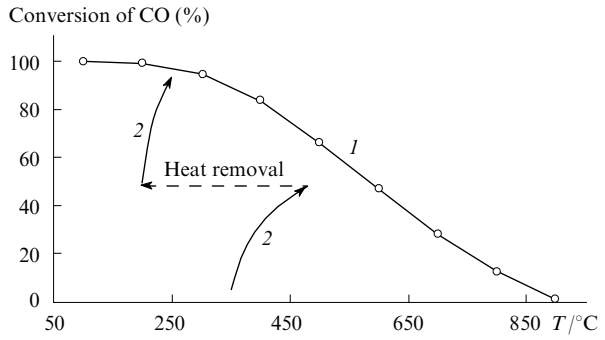


Figure 17. Conversion of CO plotted *vs*. temperature for conventional design of industrial WGS reaction.[4]
Equilibrium degree of conversion (*1*) for the gas mixture containing CO (6.3 vol.%), CO_2 (4.7 vol.%), H_2 (4 vol.%) and H_2O (45 vol.%); typical temperature profile conventional two-stage WGS reaction (*2*).

It was proposed to conduct a single-stage WGS reaction with continuous heat removal, *i.e*., by specifying a particular temperature profile along the catalyst bed in, *e.g*., a tubular reactor with the counter-flow motion of coolant.[4] In this case, the temperature dependence of the CO concentration at the outlet will pass lower than the curve corresponding to the thermodynamic equilibrium (see Fig. 1).

A leading concept ammonia (LCA) technology including a single-stage WGS reaction was developed by Imperial Chemical Industries (UK) and described in a monograph.[160] The first setup including a single-stage reactor for the WGS reaction started operation in 1988. The converter represents a water-cooled isothermal tubular reactor for the LT WGS reaction.[161]

It was proposed to optimize the mass and dimensional characteristics of a fuel processor for a power plant based on a proton-exchange membrane fuel cell.[162] The results of comparative calculations of the volumes of the known commercially available and original catalysts (both containing noble metals and noble metal-free) used in conventional two-stage adiabatic reactors are presented in Table 11.

The dimensions of the reactor for the WGS reaction can be reduced using the single-stage arrangement with the temperature profile decreasing along the catalyst bed. Approximation of experimental data obtained in carrying out the WGS reaction in three successive isothermal reactors (three-stage process) allowed one to calculate the temperature profile of the single-stage reactor (Fig. 18).

The ANL catalysts developed at the Argonne National Laboratory (USA) were proposed for the use in the single-stage reactor. Such catalysts can operate in a wide temperature range, are noble metal-free and not pyrophoric, but their activities are lower than those of industrial copper–zinc catalysts.

Theoretical models for the design of a catalyst bed with controlled temperature profile in a tubular reactor for a single-stage WGS reaction were reported.[4] Numerical evaluation of the temperature regimes providing a maximum conversion of gas containing 34 vol.%–30 vol.% and 15 vol.%–10 vol.% of CO suggested that the efficiency of conversion of natural gas in the WGS stage in production of fuel gas for fuel cell applications and in hydrogen production for, *e.g*., the synthesis of ammonia can be significantly improved using the Fe–Cr–Cu (see Ref. 6) and Cu–Zn–Zr oxide catalysts[85] in the reactors with controlled temperature profile. The Cu–Zn–Zr oxide catalyst[85] was loaded in a tubular reactor for the WGS reaction as compact stage in the design of a fuel processor for a 5-kW power plant. Based on the results obtained, a comparative table of the volumes of the catalysts of the WGS reaction in the design of a fuel processor for a 50-kW power plant (Table 12) was reported.[4] Table 12 also includes the volumes of the catalysts in the form of thermal conductive

Table 11. Characteristics two-stage adiabatic reactor conversion CO until a concentratin of 1 vol.% (on dry gas).[162, 163]

Catalyst	T/°C		CO concentration (%)		Catalyst volume / litre	
	inlet	outlet	inlet	outlet		
Fe–Cr (HT WGS reaction)	400	455	11.4	4.3	5.5	19.2
Cu–Zn (LT WGS reaction)	200	227	4.3	1.0	13.7	
ANL-1 (HT WGS reaction)	400	455	11.4	4.3	0.8	13.5
ANL-1 (LT WGS reaction)	300	327	4.3	1.0	12.7	
ANL-2 (HT WGS reaction)	400	457	11.4	4.3	2.8	21.2
ANL-2 (LT WGS reaction)	300	327	4.3	1.0	18.4	

Note. Composition of gas mixture to be converted: CO (10 vol.%), CO_2 (10 vol.%) and H_2O (13 vol.%) in nitrogen. The reactor volume was calculated using the experimentally measured reaction rate and activation energy for the ANL-1 and ANL-2 catalysts and the published kinetic data for commercially available catalysts.

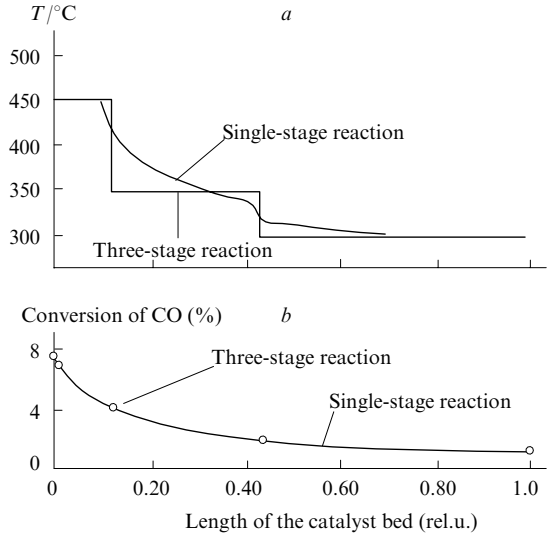


Figure 18. Changes in temperature (*a*) and CO concentration (*b*) along the catalyst bed for the single-stage WGS reaction with the decreasing temperature profile and for the three-stage isothermal reactor for WGS reaction (according to Ref. 162).

Table 12. Comparison of the volumes of the catalysts of the WGS reaction as a stage of a fuel processor for a 50 kW-power plant.[4]

Catalyst	CO (%) (outlet)	Catalyst volume /litres	Ref.
Two-stage arrangement			
HT and LT WGS reactions	~1	19.2	163
Single-stage arrangement			
Pt-containing	~1	13.5	162
Cu–Zn–Zr oxide catalyst			
5 × 5 mm pellets	~1	12.0	85
HCCP array	0.75 (calculated)	9.0	164
	~0.73 (reached)	10.5	164

plates (TCP) whose characteristics were calculated elsewhere.[164]

As can be seen, the use of a particular catalyst in reactors with controlled temperature profile may significantly improve the efficiency of conversion of natural gas in the WGS stage.

1. The WGS reaction designs for fuel processors

Heat transfer across the catalyst bed and from the surface of the catalyst to the reactor wall occurs by reaction gas. Low coefficient of heat transfer from the solid to gas determines a low thermal conductivity of the catalyst bed. In industrial reactors, the thermal conductivity of the fixed granular bed in the radial direction is low; this leads to large temperature gradients in this direction. To improve the heat removal conditions, tubular reactors are used, but the temperature gradient across the tube section in the WGS reaction may reach 20–30 °C even at a tube diameter of about 30 mm.[165,166] Usually, the WGS reaction in fuel processors for fuel cell power plants is implemented using two reactors (one for the HT and one for the LT stage) and an intermediate heat exchanger.

A multistage fuel processor for a 50-kW fuel cell power plant was considered.[167] It was proposed to carry out the WGS reaction in two successively arranged reactors loaded with industrial catalysts of the HT and LT stages, respectively. The efficiency of industrial catalysts in the form of pellets is at most 50%. The authors of Ref. 167 showed that only the reactor for the LT WGS reaction requires nearly 50 litres of catalyst.

In the text below we will discuss various versions of a compact design of the WGS reaction using metallic plates and various ceramic and metallic monoliths.

In yet another fuel processor[168] the WGS reaction proceeds in two zones, *viz*., the high-temperature zone (on the Fe–Cr-catalyst) and the low-temperature zone (on the Cu–Zn-catalyst). Both zones represent multichannel single-stage reactors made of a heat-conducting material.

A compact reactor for the WGS reaction was proposed in a patent.[169] It was shown that a conventional 200-kW power plant requires 199 litres of catalysts of the HT and LT WGS reactions, whereas for the compact reactor the catalyst volume was reduced by a factor of 2.4 to 84 litres. This compact reactor represent an array of heat-exchange plates on which the catalysts of the HT and LT WGS reactions are immobilized by moist application on different sides of channels arranged normal to one another. The dimensions of the compact reactor should decrease upon an increase in pressure.

The next studies are devoted to the catalysts used for production of hydrogen for fuel cells, in the form of granules or supported on ceramic monoliths or on various metallic items. The active mass is in some way coated on a ceramic monolith or metallic item. For instance, possible supports include ceramic monoliths, metallic honeycombs, metallic foams, plates and heat-exchange plates for the catalysts based on combinations of noble metals (Pt, Pd, Rh, Ru, Ir) with the readily reducible and re-oxidizable oxides of such metals, as Ce, Zr, Ti, V, Mn, Fe, as well as Al_2O_3, SiO_2, TiO_2, rare-earth element oxides or zeolites.[95,96]

It was proposed[109] to deposit the catalyst Pt/CeO_2 on a honeycomb ceramic monolith. A high coverage of the support (400 g litre^{-1}) was attained and the equilibrium conversion was obtained at ~290 °C (initial CO content 10 vol.% volume rate of the reaction mixture 20 000 h^{-1}). The use of the monolithic catalyst allowed one to considerably decrease the reactor volume.

Good results were obtained using the known commercially available catalysts of the HT and LT WGS reactions supported on ceramic monoliths (93 channels per cm^2).[170]

The Nissan Motor Corporation (Japan) recommends to carry out the LT WGS reaction on a platinum/zirconium catalyst supported on monolithic ZrO_2.[91]

A study aimed at optimizing the operation of a reactor for the WGS reaction on $Pt/CeO_2–Al_2O_3$ monoliths was reported.[171] The compositions and conditions for the synthesis of catalysts in the form of ceramic monoliths and large metallic items, *e.g*., based on metal foams, were determined. Tests of a high-temperature Ru/ZrO_2 catalyst (65–100 mesh powder) and the same catalyst supported on a foam-like nickel monolith (5–25 mm long, three pores per mm) were performed using a reactor characterized by millisecond contact times between the reaction mixture and catalyst.[93] Based on the results obtained, it was assumed that the block catalysts and reactors providing millisecond contact times can be promising for the WGS reaction in processors for fuel cells.

Thus, using catalysts supported on ceramic monoliths or various metallic forms, one can considerably reduce the mass and dimensional characteristics of conventional CO converters. However, such catalysts have significant drawbacks, *viz*., the active component may fall and be removed by the reaction flow; the activities of the original catalysts are no higher than those of the known catalysts.

2. The use of thermal-conducting catalysts based on composite materials

Efficient heat removal is usually achieved with tubular reactors having tube diameters to 20–30 mm. However, even in this case an exothermic WGS reaction characterized by a typical power density of 0.2–0.4 W cm^{-3} is accompanied by temperature gradients of 20–30 °C in the radial direction of the catalyst bed; the larger the tube diameter the larger the temperature gradient.[165,166]

Conventional catalysts used in the reactors mentioned above represent oxides or oxide-supported metals and exhibit low thermal conductivity. Heat transfer from the catalyst pellet to the reactor wall occurs through the reaction gas. The thermal conductivity of a gas–solid system is much lower than that of a metal; this predetermines heating of the catalyst bed. It follows that the problem of intense heat removal in the case under consideration can be solved by preparing a catalyst with high

thermal conductivity. The transverse dimension, *e.g.*, the diameter, of the thermal-conducting component of the catalyst should be comparable with the diameter of the reactor. It is also desired to provide a direct contact with the reactor wall through which heat is removed.

The available composite materials with known thermal-engineering and mechanical properties [172, 173] do not show high catalytic properties in most reactions, because they are obtained by high-temperature sintering of oxide and metallic components. Catalysts in the form of metallic plates or metal foams coated with oxide catalysts [174, 175] for which direct contact with reactor walls can be implemented with ease are also difficult to use because of the problem of immobilization of the active component on the metal.

Experimental data and the results of simulations showed that even at high thermal loads a nearly isothermal operating regime of the reactor can be achieved using specific materials (honeycomb supports) showing high thermal conductivity in the radial direction.[176] In this case, the limiting heat resistance is the high 'near-wall' heat resistance in the space between the surface of the monolith and the internal surface of the reactor wall, which depends on both the dimensions of the monolith and the thermal conductivity of the gas involved in the reaction.

Reactions proceeding at 250–400 °C are usually catalyzed by catalysts prepared at low temperatures. At high temperatures, the catalytic properties (activity and selectivity) of such catalysts significantly deteriorate. The heat treatment temperature of these catalysts cannot be higher than, *e.g.*, 400–450 °C.

An efficient thermal-conducting composite catalyst for production of hydrocarbons and oxygen-containing organic compounds from the synthesis gas was developed.[177] The catalyst exhibits new properties necessary to efficiently conduct the Fischer–Tropsch process and shows a high thermal conductivity [at least 1 W (m K)$^{-1}$] and high mechanical strength. A method of preparation of a composite permeable thermal-conducting working substance of the catalyst, comprised of three components, *viz.*, an oxide catalyst, metal particles (thermal-conducting agent) and a cellulating agent was elaborated.

Using this form of the catalyst, one can attain a two- or threefold increase in the efficiency of the Fischer–Tropsch process compared to that obtained with conventional catalysts and technologies.[178]

Thermal-conducting catalysts for the three-phase production of hydrocarbons enable significant improvement of the mass and dimensional characteristics of the reactor and the heat distribution in the radial direction of the catalyst bed.[178] However, these catalysts are difficult to prepare and their use in the two-phase WGS reaction is inappropriate. A composite catalyst of the WGS reaction described in a patent [179] shows high thermal conductivity but poor gas permeability. The procedure for preparation of such catalysts is much simpler and the results obtained on an experimental 5-kW power plant [164] demonstrate high efficiency of composite catalysts in the WGS reaction.

IV. Conclusion

Based on the aforesaid, there are three groups of highly active and thermally stable (in a wide temperature range) catalysts of the WGS reaction:

— cerium-promoted iron and Fe–Cr oxide compounds with a rather high activity; high activity is also demonstrated by Au- and Ag-doped samples; lanthanide oxides also act as good promoters; finally, Fe–Cr–Cu oxide compounds with the ferrihydrite structure are promising catalysts;

— transition metal-promoted Cu–Zn oxide compounds (Al, Cr or Zr are the best promoters); and

— noble metal-containing compositions providing an alternative to the traditionally used catalysts of the HT and LT WGS reactions.

A special position is occupied by catalysts in the form of gold-doped transition metal oxides. There is a large number of catalysts containing ceria promoted by either noble metals or transition metals and lanthanides. It should be noted that the use of cerium compounds as promoters often leads to contradictory results.

Although there is a large array of data on the search for highly active and stable catalysts of the WGS reaction, it is difficult to compare the results obtained in different studies on the catalytic activity because not only the reaction conditions, but also the sample preparation procedures and characteristics of the activity of catalysts are different. Such a comparison is only possible for some particular compositions of catalysts reported in a few studies.

By and large, the development of catalysts of the single-stage WGS reaction, which are active and stable in a wide temperature range, seems not to be unsolvable.

In addition to the development of catalysts, carrying out a single-stage WGS reaction requires optimization of the temperature profile of the catalyst bed by using specific forms of the catalyst to improve its thermal conductivity. Using catalysts that are highly active in a wide temperature range and show a sufficiently high thermal conductivity offers prospects for the design of compact reactors for the WGS reaction as a stage of the fuel processor. Recently, this has been particularly topical in connection with the development of environmentally safe methods for energy production.

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