Application of Polyfunctional Catalysis in Synthesis of Motor Fuels from CO$_2$ as an Approach to the Problem of CO$_2$ Utilization

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Abstract

The development of civilization is inevitably connected with the increase of energy consumption. Nowadays the main part of energy is produced through incineration of organic fuel, the products of fuel combustion (CO$_2$) being discharged into atmosphere. However the ecological problems impelled the world community to intensify their activity in order to decrease CO$_2$ emission. There is a great number of known chemical reactions, both catalytic and non-catalytic, which bound CO$_2$ chemically into various products. Specifically, the processes of hydrogen reduction of CO$_2$ may proceed with the production of methanol, dimethyl ether (DME), methane, light hydrocarbons, or liquid motor fuels. Among these, the processes of motor fuel production on the bifunctional catalysts are most likely to be industrially applied in a large scale. The scientific and technological aspects of the processes of hydrogen reduction of carbon dioxide are considered with regard to CO$_2$ utilization. The influences of the catalysts composition, pressure, temperature, (H$_2$–CO$_2$)/(CO + CO$_2$) ratio, duration of the test run (up to 1000 h) on the activity and selectivity of the bifunctional catalysts in the synthesis of liquid motor fuels were studied. Depending on the composition of the liquid organic products, utilization of carbon in CO и CO$_2$ comprised 70 to 90 %.

INTRODUCTION

The life activity of the mankind and the processing of the natural resources entail a great amount of solid, liquid, and gaseous wastes, including carbon dioxide discharge. Among the sources of CO$_2$ emission are the metallurgical, chemical, oil-and-gas, and engineering industries, transport *etc*. The amount of the above wastes is measured by millions of tons per year. Using the fire method of solid and liquid wastes neutralization partially accomplishes the task of protecting the water basins and the ground areas but generates another problem, that of the increasing emission of gaseous carbon dioxide into the planet atmosphere. In the present review the catalytic methods of CO$_2$ conversion into commercial products such as methane, DME, aromatic hydrocarbons, liquid motor fuels *etc*. are considered.

THE ALTERNATIVE WAYS TO DECREASE THE CO$_2$ CONTENT IN THE EARTH ATMOSPHERE

The development of civilization is inevitably connected with the increase of energy consumption. Nowadays the main part of energy is produced through incineration of organic fuel – natural gas, coal, and black oil. The fuel combustion products, CO$_2$ and H$_2$O, together with deleterious admixtures (dust, chemical compounds) are therefore discharged into atmosphere. The waste gases of industry and transport are also intense atmosphere pollutants. However many research teams are concentrated on the preferential prevention of the emission of CO, NO, chlorinated and sulphur-bearing wastes. It is only in the last decade of the 20th century, under the menace of a global ecological catastrophe, that the world community intensified their activity in order to decrease CO$_2$ emission. In May 1992 in Rio

de Janeiro, 143 countries ratified an agreement on supervising upon the global warming and on decreasing CO_2 emission into atmosphere [1]. The consequent conferences held in 1994 and 1997 in Japan supported the Agreement with a special protocol which legitimated the international sanctions against increased rates of CO_2 emission into atmosphere.

There are several methods to reduce the growth of CO_2 content in atmosphere:

1. To retard deforestation and to plant vegetation highly effective in CO_2 absorption.

2. To reduce the world production of thermal energy and to increase the portion of alternative energy resources: atomic, solar, and hydroelectric energy.

3. To extract carbon dioxide from the exhaust gases and to dispose it in ocean depths and in geological cavities.

4. To convert CO_2 chemically into useful products.

In the present review the methods of carbon dioxide chemical conversion into commercial products are briefly discussed.

CO₂ AS A SOURCE OF A CHEAP RAW MATERIAL FOR THE CHEMICAL INDUSTRY

Regardless of the greenhouse effect problem, carbon dioxide can be viewed as a potential promising source of chemical raw material. The total amount of CO_2 emission into atmosphere is proportional to the quantity of the processed natural fuel, namely oil, coal, hydrocarbon gases, and comprises about 6 000 000 000 t per year [1]. An obstacle to a large-scale application of carbon dioxide as a raw material is its low concentration in atmosphere and in exhaust gases of power stations. The main industrial CO_2 consumers are productions of carbamide, soda ash, and salicylic acid. In all these cases, the main source of CO_2 is either the secondary industrial gases or solid carbonates, mainly limestone, rather than atmospheric CO_2. The problem of utilization of carbon dioxide discharged into atmosphere remains technologically unsolved so far. Natural gases and the waste gases of metallurgical works appear to have good prospects as sources of CO_2 as a raw material, due to high carbon dioxide content − 20−30 % vol.

Many large chemical plants producing nitrogen fertilizers have significant overstocks of commercial high-purity CO_2 under excessive pressure, the surpluses coming up to hundreds of thousands tons per year.

THE CHEMICAL PROCESSES BASED ON CO₂

Carbon dioxide can be involved into various reactions with other substances, for example [1]:

1) embedding CO_2 into the C−C, C−H, and C−N bonds with formation of carboxyl- and carbonyl-containing compounds;

2) reactions of carbon dioxide reduction.

The reactions of the first type proceed at low temperatures being catalysed by homogeneous complexes of transition metals; they don't contribute to solving the problem of CO_2 emission decrease nor of its large-scale utilization because in all these cases, to involve CO_2 into the reaction, a large amount of auxiliary chemical compounds is required, *e. g.* of ammonia, phenol *etc.*, the production of which would be accompanied by additional emission of CO_2.

The redox reactions using CO_2 as an oxidizer are more favourable to its large-scale industrial utilization. In this case, the reducing agents either occurring in the natural sources of raw material (hydrocarbons, carbon) or produced from them (hydrogen, alcohols, aldehydes) can be involved into the reaction. Thus, the main point is to choose the cheapest and most available reducing agent.

THE PROCESSES BASED ON THE REACTIONS OF CO₂ REDUCTION

Carbon dioxide reforming of natural gas

Carbon dioxide conversion of methane can be considered the most elaborated method of CO_2 reduction. The reaction between CH_4 and CO_2 is highly endothermic and at high temperatures (600−900 °C) proceeds towards synthesis gas formation:

$$CH_4 + CO_2 = 2CO + 2H_2,$$
$$\Delta H = 209.3 \text{ kJ/mol} \tag{1}$$
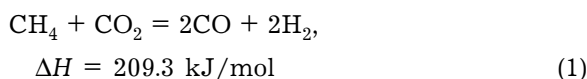
The reaction (1) is catalysed by Ni-catalysts [2−5]; other metals (Co, Fe, Pt, Pd, Rh, Ru, Ir), applied onto various carriers, can also be used as catalysts [6−15]. The most frequently-used catalysts for synthesis-gas production are the nickel ones, but they tend to be poisoned by carbon [16−18]. Iridium and ruthenium catalysts are active and poison-resistant but they are expensive. Being highly endothermic, the reaction (1) requires constant heat supply so as to keep the thermal balance in the reactor; this may be provided by partial incineration of the methane (natural gas) resulting in CO_2 formation. The product of the carbon dioxide reforming of methane is synthesis-gas of an H_2/CO mole ratio close to 1. However for most of the reactions based on synthesis-gas, the most favourable H_2/CO mole ratio, for stoichiometric reasons, should be 2. An excess of CO results in a decrease of its conversion and considerable CO_2 formation. Therefore, the efficiency of carbon dioxide conversion of methane as a method of CO_2 utilization into chemical products appears rather low.

Methods of hydrogen production

For carbon dioxide, hydrogen is an effective reducing agent. The main obstacle in using hydrogen in CO_2 conversion is the lack of sufficiently easy and cheap methods of hydrogen production in the industrial practice. Let us consider the most feasible methods of hydrogen production from the available natural resources.

The following processes can be used in the industrial production of hydrogen:

1) steam conversion of methane:
$CH_4 + H_2O = CO + 3H_2$,
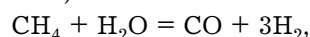
2) electrolysis of water: $2H_2O = 2H_2 + O_2$,

3) pyrolysis of methane: $CH_4 = C + 2H_2$.

All of these require high energy inputs, from 1 kW h/nm^3 H_2 (processes 1 and 3) to 3 kW h/nm^3 H_2 (process 2) [19−21]. Steam conversion of methane is considered to be the cheapest method used in the large-scale industrial hydrogen production. The difficulty of using process 1 for the purpose of CO_2 utilization is that it would be also necessary to utilize the concurrently formed CO without produc-

ing additional carbon dioxide. Electrolysis of water produces high-purity hydrogen but requires 3 times as much electric power, which is in fact equivalent to an additional emission of CO_2.
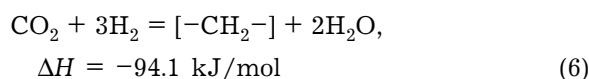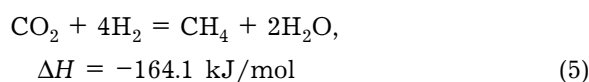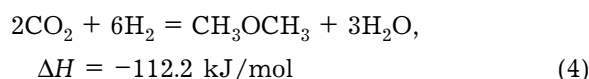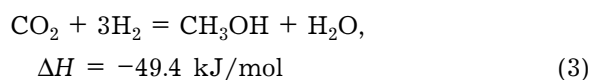
By its theoretical background, the process of methane pyrolysis seems to be most suitable for hydrogen production with the least possible energy consumption and therefore the least additional CO_2 formation. The only problem left now is that of accumulating and utilizing as a carbon by-product. Provided that the reduction of 1 nm^3 of CO_2 requires 3 nm^3 of H_2, which implies production 0.8 kg of carbon, utilization of hundreds of million cubic metres of CO_2 will produce hundreds of thousand tons of carbon. Many branches of industry make use of pure carbon but in far less quantities than those discharged into atmosphere. The problem could be solved by partial substitution of the coke used in industry for either carbon or carbon monoxide produced via the reaction:

$$C + CO_2 = 2CO \qquad (2)$$

which results in binding both carbon and CO_2.

The reaction of chemical binding of CO_2 by hydrogen

After having chosen the most expedient process of hydrogen production, the next problem will be to implement industrially, on a large scale, concentration of CO_2 and its hydrogen reduction into commercial chemical products. The products of hydrogen reduction of CO_2 may be methanol, dimethyl ether (DME), methane, light hydrocarbons, or liquid motor fuels. The reactions of obtaining these substances from CO_2 and H_2 are as follows:

$$CO_2 + 3H_2 = CH_3OH + H_2O,$$
$$\Delta H = -49.4 \text{ kJ/mol} \qquad (3)$$

$$2CO_2 + 6H_2 = CH_3OCH_3 + 3H_2O,$$
$$\Delta H = -112.2 \text{ kJ/mol} \qquad (4)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O,$$
$$\Delta H = -164.1 \text{ kJ/mol} \qquad (5)$$

$$CO_2 + 3H_2 = [-CH_2-] + 2H_2O,$$
$$\Delta H = -94.1 \text{ kJ/mol} \qquad (6)$$

All the reactions (3)−(6) are exothermic and besides, one to two water molecules accompany each one carbon atom in the desired product molecule (CH_3OH, CH_3OCH_3, CH_4, or motor fuel fragment [−CH_2−]), thus the major part of the expensive reagent, hydrogen, proves to be just spent for the production of water. On the other hand, the thermodynamic calculations show that generation of water, which is a high-stable compound, facilitates deep proceeding of CO_2-reducing reactions.

There are known reactions of CO_2 reduction without water formation, *e. g.*, the reaction of formic acid synthesis [22, 23]:

$$CO_2 + H_2 = HCOOH, \quad \Delta H = 16.7 \text{ kJ/mol} \quad (7)$$

but under standard conditions the reaction is thermodynamically unfavourable, therefore only minor yields of formic acid are observed.

The thermodynamical restrictions are avoided by the reaction of $CO_2 + H_2$ mixture conversion into methylformate *via* carboxylation of the intermediate methanol:

$$2CO_2 + 4H_2 = HCOOCH_3 + 2H_2O \quad (8)$$
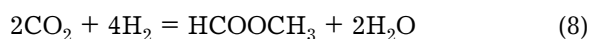
The reaction (8) proceeding with water formation was carried out over a bifunctional catalyst composed of a catalyst for methanol synthesis and a K−Fe/zeolite L catalyst [24].

CO₂ hydrogenation into methanol

Methanol is produced on a large scale, its world production and consumption approaching 30 million tons per year. Along with its conventional applications, primarily in formaldehyde production, application of methanol as an energy carrier has been recently developed, both directly in motor fuels and in synthesis of oxygen-containing additives for motor fuels. The fact that methanol can be produced from various carbon-containing raw material, for instance from CO_2, facilitates its wide application.

Since 1990, a technology has been under development in Japan aimed at production of methanol from CO_2 contained in the products of organic fuel combustion. The said technology consists of three stages [25, 26]:

1) membrane separation of CO_2 from the combustion products stream;

2) obtaining hydrogen from water *via* electrolysis;

3) synthesis of methanol from CO_2 and H_2.

The paper [27] reports on a novel technology of methanol synthesis developed by companies Lurgi and Sudchemie, making use of carbon dioxide extracted from air and surplus hydrogen generated at chemical and oil-and-gas plants.

A many-stage method and installation are proposed for methanol production from urban wastes and CO_2 generated through fuel combustion, *via* the processes of fermentation [28]. The technology for CO_2 extraction from waste gases consists of two stages:

1) conversion of CO_2 into carbonates through contacting the waste gases with granular metal oxides (MgO, CaO, ZnO) at temperature 350−375 °C;

2) decomposition of metal carbonates to oxides and CO_2 at temperature 500−540 °C.

Then the obtained CO_2 is mixed with hydrogen and fed to the reactor where methanol is produced at temperature 150−300 °C and pressure 20−50 atm.

Methanol synthesis from CO_2 and H_2 is known to be feasible under the same conditions and on the same catalysts as those used in synthesis from CO and H_2. Normally, synthesis-gas containing about 5 % vol. of CO_2 is used in industrial methanol production [29]. Zinc−chromium-oxide catalysts have been mainly used for a long time, providing a high productivity of the process at temperature 320−400 °C and pressure 300 atm. After the inventions of the ICI Company were published in the 60-ies, Cu−Zn-oxide catalysts came into wide use allowing to abate temperature to 220−280 °C and pressure to 50−80 atm.

The mechanism and kinetics of methanol synthesis from CO and H_2 were thoroughly researched, mainly over Cu−ZnO−Al_2O_3 and Cu−ZnO−SiO_2 catalysts [30−32]. The influence of various additives (Ag, Pt, Rh, Ru, Cr, Ga, Co, Mn, Mo, Ti, Zr) on the catalysts activity and selectivity towards methanol was studied in [33−35]. In [35], it is shown that adding Al_2O_3 and ZrO_2 results in an increase of the catalyst surface but doesn't affect the specific activity of Cu. However adding Ga_2O_3 does increase this specific activity by 40 % and adding

Gr_2O_3 − by 30 %. The studied palladium catalysts on various carriers proved to be more active in methanol synthesis than Cu/ZnO. For example, using the catalyst Pd/Ga_2O_3 at 250 °C, 50 atm and the ratio $H_2 : CO = 3$ resulted in the yield of methanol 2 times higher than that achieved over the Cu/ZnO catalyst [36]. To remove the excess heat, the liquid-phase methanol synthesis from CO_2 and H_2 might be used [37].

A study on the mechanism of methanol synthesis through carbon oxides hydrogenation showed that carbon dioxide was the key reagent in the synthesis [38−40]. In small quantities, CO_2 retains the high oxidizing ability of the reaction mixture therefore preventing deactivation of active sites Cu (I) [41] but a high concentration of CO_2 in the synthesis-gas would inhibit the process, on account of either the concurrent adsorption with CO [42] or water concentration increase [43], water being an inhibitor of the process. However it is shown that adding CO into $CO_2 + H_2$ mixture would increase the yield and selectivity towards methanol [44].

The technology of methanol synthesis *via* $CO_2 + H_2$ conversion has both advantages and disadvantages as compared with the conventional technology of synthesis-gas conversion into methanol. When $CO_2 + H_2$ conversion is carried out adiabatically, the comparatively high thermal capacity of CO_2 facilitates temperature control in the reactor. Besides, the conversion of $CO_2 + H_2$ mixture into $CH_3OH + H_2O$ is less exothermic than that of the mixture $CO + H_2$, which reduces the temperature grow along the catalyst bed and depresses the formation of dimethyl ether [45]. On the other hand, the CO_2 version requires 1.5 times more hydrogen and the produced crude alcohol contains about 35 % of water, against 2−8 % produced from $CO + H_2$, which hinders its distillation. To reduce the inhibiting effect of the water adsorbing on the catalyst, high space velocities of the gaseous flow in the reactor must be used [43], therefore increasing the power consumption for gas circulation.

Dimethyl ether synthesis from CO_2 and H_2

The conversion of synthesis-gas (or of $CO_2 + H_2$ mixture) may be increased owing to the reaction of methanol dehydration into dimethyl ether (DME):

$$CO\ (CO_2) + H_2 \rightleftarrows CH_3OH\ (+ H_2O) \qquad (9)$$
$$\Updownarrow$$
$$(CH_3)_2O + H_2O$$
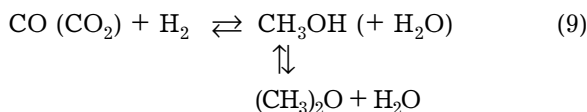
The reason is that equilibrium constant of the reaction of methanol dehydration into DME at 327 °C is 80 000 times higher than that of methanol synthesis. This helps to avoid the thermodynamical restrictions of methanol synthesis, directing the conversion of synthesis-gas (or of $CO_2 + H_2$ mixture) towards methanol and DME formation [46, 47]. Thus, it is reported in [48] that to achieve 70 % conversion of synthesis-gas in the process of methanol production over a Cu-containing catalyst, a pressure of about 100 atm is required, while the use of a bifunctional Cu-containing catalyst with a dehydrating component added (say, Al_2O_3) allows to carry out the similar synthesis-gas conversion (to DME) at as low pressure as 60 atm.

The conception of DME importance for energy production has changed fundamentally after the joint report of representatives of well-known companies (Amoco, AVL, Haldor Topsoe) at the International Congress-Exhibition held in Detroit in spring 1995, who reported on the properties of DME as an environmentally safe diesel fuel [49, 50]. The reaction of methanol dehydration to DME proceeds easily on the alumina catalysts at 300−350 °C [51]; therefore, in DME synthesis from CO, CO_2, and H_2, bifunctional catalysts based on Cu−Zn−Al(Cr) catalysts of methanol synthesis and γ-Al_2O_3 are mainly used. The authors of [52, 53] report on the results of DME synthesis over bifunctional catalysts containing various acid components − γ-Al_2O_3, amorphous aluminosilicate, zeolites of HY, HZSM-5 types and mordenite. Bifunctional catalysts composed of Cu−Zn−Al(Cr) catalyst of methanol synthesis and HZSM-5 zeolite show high productivity but lower selectivity than those with γ-Al_2O_3. Depending on the bifunctional catalyst composition and the process conditions, selectivity of DME synthesis from synthesis-gas is 92−98 % and the catalyst productivity towards DME is 10 000 kg/(m^3 of catalyst × day) and higher [54, 55]. $CO_2 + H_2$ conversion into DME was carried out over the mixture of Cu−ZnO−Al_2O_3 catalyst with

solid acid catalysts (zeolites, WO_3/SiO_2, silicalite) [56]. The catalyst containing Y-type zeolite showed the best results: at 240 °C selectivity towards DME was 55.1 % and towards methanol 13 %, their total yield being 17 %.

Combined synthesis of methanol and DME in the same reactor is very attractive for CO_2 utilization, allowing high productivity to methanol (5.6 t/t of methanol cat. per hour) and DME – up to 1.65 t/t of sum. cat. per hour [57].

Production of high-calorific gas, higher alcohols and light olefins via CO_2 hydrogenation

Thermodynamically, the most advantageous of the above reactions of $CO_2 + H_2$ mixture conversion are the reactions of hydrocarbon synthesis, including the reaction of methane formation (5). This reaction is widely used in industry to remove CO_2 from the process gases [58]. It proceeds at temperatures above 200 °C over various catalysts, the most active among them being ruthenium and nickel on carriers [59–64]. We cannot consider CO_2 hydrogenation to methane as its utilization, because the production of hydrogen required for the reaction would cause emission of more CO_2 than would be utilized by hydrogenation [57].

Many publications are devoted to the process of CO_2 hydrogenation over Ni, Fe, Co, Rh, Ru-catalysts into $C_1–C_4$ hydrocarbons [65–70], aliphatic alcohols and hydrocarbons [71], $C_2–C_{20}$ olefins [72–76]. In [65], the mixture of 80 % H_2 and 20 % CO_2 was converted over catalysts Co/SiO_2, Ru/SiO_2, Ni/SiO_2 and Fe/SiO_2 at temperatures 180–280 °C and pressures 1–11 atm. The main products of the mixture conversion were CH_4 (12.9–99.8 % mol.) and CO (10.7–83.2 % mol.), the conversion of CO_2 being 6–11 %. Over the rhodium catalysts, a high selectivity of CH_4 (35–37 % mol.) and CO formation (16–42 % mol.) was also observed [71]. In this investigation, the mixture $CO_2 : H_2$ = 1 : 2 was converted into alcohols, mainly into methanol (19–40 % mol.), under 260 °C and 50 atm. A high selectivity toward light olefins formation was reported in [72], the catalyst composition [40 % ($Fe_5C_2/2$ % K) + 60 % amorphous carbon] being used here. This investigation showed that reducing the molar ratio

H_2/CO_2 from 7.0 to 1.7 increased the content of olefins in $C_2–C_4$ hydrocarbons from 80 to 99 %, decreased the selectivity towards CH_4 from 16.5 to 4.2 %, and decreased the conversion of CO_2 from 37 to 13 %.

In publications [74, 77, 78], the stability of Fe-containing catalysts in CO_2 hydrogenation and possibility of regeneration of their activity were studied in detail. Fe–Cu–K–Al catalysts showed a high stability in $CO_2 : H_2 = 1 : 3$ mixture long-run conversion under 10 atm and 300 °C [74]. During over 1500 h the CO_2 conversion degree remained 40–41 %. The composition of the hydrocarbons produced also remained practically constant throughout the period. After in operation during 1536 h the catalyst began to lose gradually its activity. After 2005 h of operation, the CO_2 conversion degree diminished to 36.8 %. The consequent redox treatment of the catalyst didn't succeed in restoring its initial activity.

It is shown in [74] that deterioration of Fe–Cu–K–Al catalysts activity results from increase of the crystals of the active component, Fe, which depresses the promoting effect of Cu and K. In contrast to Fe–Cu–K–Al catalysts, $Fe–K/Al_2O_3$ catalysts show lower activity and stability but completely restore their catalytic characteristics after redox treatment [77]. The reason is that their deactivation results from carbon depositing on the catalysts surface, which is removed by oxygen oxidation.

Liquid motor fuels synthesis from CO_2 and H_2 over bifunctional catalysts

After the unique acid and structural properties of crystalline aluminosilicates (particularly, of synthetic high-siliceous zeolites) had been discovered, the bifunctional catalytic systems were developed composed of a component active in synthesis of hydrocarbons and/or oxygen-containing products (particularly, methanol) from synthesis-gas and of a high-siliceous zeolite catalysing the reactions of dehydration, oligomerization, isomerization, and aromatization of the intermediates [79–82]. The bifunctional catalysts of hydrocarbons synthesis were used in hydrogenation of CO [83–99], CO_2 [100–118], and CO + CO_2 [98, 99, 119–125].

In [98, 99], transformations of $CO + CO_2 + H_2$ mixtures are studied in the presence of the Co−MgO−ZSM-5 catalyst under atmospheric pressure in the temperature range 150−250 °C. It is shown that the gaseous hydrocarbons synthesis can involve CO, CO_2 and hydrogen while the liquid hydrocarbons can be produced only through CO and H_2 interaction. Introducing CO_2 into the mixture CO/H_2 (1/2) considerably decreases the yield of hydrocarbons. It would also change the composition of the liquid hydrocarbons produced, namely, increase the content of *iso*-paraffins and decrease the chain length of the hydrocarbons. The depressing effect of CO_2 on synthesis of hydrocarbons from CO and H_2 is also noted in [45]; the effect is especially noticeable when its concentration in synthesis-gas exceeds 20 % vol.

Under certain conditions, a strong dilution of $CO_2 + H_2$ mixture facilitates formation of light paraffins and olefins over bifunctional catalysts [103, 114]. Thus, ethylene was produced from $CO_2/H_2/Ar = 3/6/91$ mixture over $Fe_3(CO)_{12}$/ZSM-5 catalyst at temperature 260 °C and pressure 1 atm with selectivity 91.7 % mol. The degree of CO_2 conversion was 18.5 % [103]. The conversion of gaseous mixture of 50 % vol. $CO + CO_2 + H_2$ and 50 % vol. N_2, carried out at 210 °C and 1 atm over the bifunctional catalyst 32 % Co−3 % MgO−ZSM-5, resulted in liquid hydrocarbons synthesis with selectivity 60 % [119]. Elevating the pressure up to 10 atm increased the concentration of *n*-paraffins in the reaction products from 69 to 87 % [121].

Considerable variations in the selectivity of $CO_2 + H_2$ conversion over bifunctional catalysts 17 % Fe/HY (LiY, NaY, KY, RbY) were reported in [55]. Hydrogenation of CO_2 ($H_2/CO_2 = 3$) was carried out under flow conditions at 10 atm and 300 °C. The subsequent substitution of the acid carrier of the catalyst, HY, for each member of the series: LiY, NaY, KY, RbY gradually decreases methane content in the produced hydrocarbons from 72.56 to 9.54 % and increases selectivity towards the C_{5+} hydrocarbons from 1.49 to 54.39 %.

In many investigations, bifunctional catalysts composed of a metal-oxide catalyst of methanol synthesis and an acid component, for instance, mechanical mixtures of Cu-contain-ing catalysts of methanol synthesis and HZSM-5 [102, 107], HY [100, 101], dealuminated HY [104], SAPO-5, 44 [107] or ferrosilicate [118] were used in the process of CO_2 hydrogenation. The pressure range of the process was 14−50 atm and the temperature range was 220−400 °C. The main products of the synthesis were found to be $C_1–C_3$ paraffins [102, 118], $C_2–C_5$ paraffins [104] or propane-butane fraction [107]. Aromatic hydrocarbons either were absent in the reaction products or comprised less than 1 % of the total hydrocarbons. To intensify the synthesis of hydrocarbons, small quantities of ethylene were added to the synthesis-gas [107], which increased the yield of $C_3–C_4$ hydrocarbons and especially of C_5 hydrocarbons. In order to obtain C_{5+} hydrocarbons, the attempts were made to use bifunctional catalysts including Cu, Zn, Cr oxides and HY zeolites at a high temperature (400 °C) and pressure 50 atm but the maximal achieved selectivity towards C_{5+} hydrocarbons wouldn't exceed 25 % mol. [100]. The main results of CO_2 and CO hydrogenation over various Cu, Zn, Cr, Pd, Zr / H^+ bifunctional catalysts are shown in Table 1.

Via substituting Cu, Zn, Cr oxides for a mixture of Cs−Cu−Zn chromates the authors [116, 117] considerably increased (up to 49 % mol.) the selectivity towards C_{5+} hydrocarbons. It was reported that, while the maximal methanol yield over Cu−Zn chromates was achieved at 300 °C, the maximal yield of hydrocarbons over Cu−Zn chromate/HY catalysts was, none the less, achieved at the temperature 400 °C. The authors concluded that for obtaining the gasoline fraction hydrocarbons from CO_2 and H_2, a relatively high temperature (over 300 °C) was required as well as an active metal-oxide component with a lower hydrogenating activity and a highly-active coking-resistant zeolite.

We have performed syntheses of the gasoline fraction hydrocarbons with a high aromatics content (from 20 to 80 % mass) both from $CO_2 + H_2$ mixtures and from synthesis-gas with various percentage of CO_2 additives [126]. The syntheses were carried out in the presence of Zn−Cr/HZSM-5 catalysts at temperatures 340−420 °C and pressures 40−80 atm; gas circulation was applied after the condensed

TABLE 1

$CO + H_2$ and $CO_2 + H_2$ conversion to hydrocarbons on Cu, Zn, Cr, Pd, Zr / H^+ bifunctional catalysts

Parameter	Cu–Cr–Zn/ Al₂O₃ [102]	Cu–Cr–Zn/ H-ZSM-5 [102]	Cu–Cr–Zn/ Al₂O₃ [102]	Cu–Cr–Zn/ H-ZSM-5 [102]	Cu–Cr–Zn/ H-ZSM-5 [102]	Cu–Cr–Zn– Pd–Na/ H-ZSM-5 [102]	Zn–Cr/ Amorph. SiO₂–Al₂O₃ [116]	Pd/SiO₂ + H–Y [117]	Cu–Zn–Zr/ H-Fe silicate [118]
H_2/CO	2	2	–	–	–	–	2	2	–
H_2/CO_2	–	–	2.7	2.7	2.7	2.7	–	–	3
Pressure, atm	20	20	20	20	50	50	11	20	28
Temperature, °C	290	290	320	320	320	320	390	357	400
Hydrocarbons distribution, % mass:									
Aliphatics:									
C_1	44.4	2.3	85.3	67.9	61.4	28.2	24.0	5.3	64.0
C_2	24.0	15.2	11.1	25.5	35.3	31.9	20.4	23.1	30.8
C_3	17.3	32.6	3.2	4.9	2.5	17.4	17.3	34.9	5.2
C_4	13.4	25.4	0.3	1.3	0.4	10.3	22.8	25.8	0
C_{5+}	0.9	24.0	0	0.4	0.4	12.2	13.0	10.9	0
Aromatics	0	0.3	0	0	0	0	2.5	0	0

products were separated. The constant removal of water and liquid hydrocarbons from the gaseous mixture after the reactor and recycling the non-condensed products back to the reactor facilitate deep conversion of low-active carbon dioxide to monoxide through the following equilibrium reaction of the water gas:

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (10)$$

The use of gas circulation and of bifunctional catalysts composed of a metal-oxide component with a low hydrogenating activity (Zn and Cr oxides) and a HZSM-5 zeolite selective towards gasoline fraction formation resulted in the production of liquid hydrocarbons consisting mainly of the aromatics and isomerised C_5–C_{10} paraffins. The mean selectivity towards the gasoline fraction comprised about 74 % mass. Under circulation conditions, the degree of CO_2 conversion exceeded 87 % while the methane content in the hydrocarbon products was 2 to 7 % [126].

Tables 2 and 3 show the influence of the reaction pressure (from 40 to 80 atm) and temperature (320−400 °C) on productivity and selectivity of Zn−Cr/HZSM-5 catalysts towards C_{5+} hydrocarbons in the reaction of CO_2 hydrogenation. It can be seen that in the studied range, productivity and selectivity towards C_{5+} hydrocarbons grow as the reaction pressure and temperature increase. Comparing the processes of conversion of gaseous mixtures $CO_2 + H_2$, $CO + H_2$ and $CO + CO_2 + H_2$ of various composition (see Tables 2−4 and Fig. 1) we can conclude that replacing CO by CO_2 in the initial gas decreases the activity of bifunctional Zn−

TABLE 2

Dependence of C_{5+} productivity (g/l cat./h) upon pressure and temperature in CO_2 hydrogenation ($H_2/CO_2 = 3$) on Zn−Cr/ZSM-5 catalyst

Temperature, °C	Pressure, atm		
	40	60	80
320	Not determined		11
340	11	14	18
360	12	24	41
380	15	38	47
400	24	56	67

TABLE 3

Dependence of selectivity upon pressure and temperature in CO_2 hydrogenation ($H_2/CO_2 = 3$) on Zn−Cr/ZSM-5 catalyst

Characteristic	$CO_2 + H_2$				$CO + H_2$
	340 °C	340 °C	400 °C	400 °C	400 °C
	40 atm	80 atm	40 atm	80 atm	80 atm
HC distribution, % mass:					
C_1	2.2	4.2	6.9	4.5	4.1
C_2	1.6	3.3	3.0	2.1	3.4
C_3	28.6	13.7	10.0	13.9	5.3
i-C_4	6.8	2.7	7.5	3.1	9.0
n-C_4	0.5	0.7	1.3	0.8	2.0
C_{5+}	60.4	75.4	71.3	75.6	76.2
C_{5+} distribution, % mass:					
Aromatics	62.8	65.6	41.0	44.6	28.1
n-C_{5+}	0.1	0.2	0.2	0.9	3.3
Other C_{5+}	37.1	34.2	58.8	54.5	68.6

TABLE 4

$CO + CO_2$ hydrogenation on Zn−Cr/ZSM-5 catalyst as depending on CO/CO_2 ratio, $P = 80$ atm, $T = 400$ °C, $H_2/CO = 2.8-2.9$

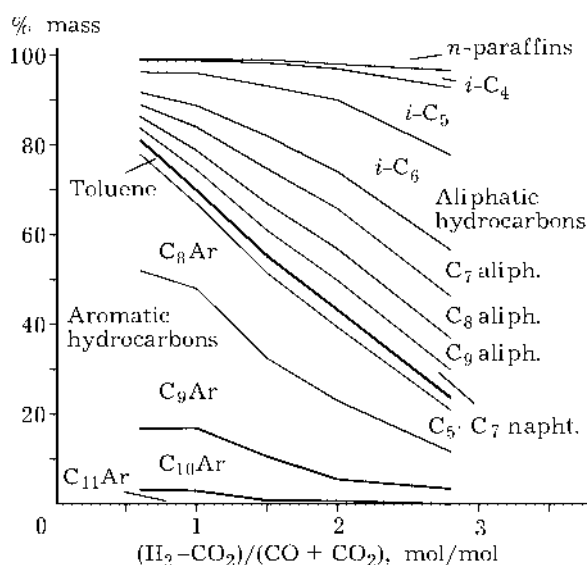| Parameter	CO/CO_2 molar ratio			
	98.9	3.7	1.6	0.7
	1200*	1000*	600*	300*
Conversion, %:				
CO	96	90	78	28
CO_2	90	81	80	52
Productivity, g/l cat./h	167	125	67	15
Mol. mass of liquid HC	91	100	104	111

*GHSV, h^{-1}.

Fig. 1. Influence of syngas composition on the C_{5+} hydrocarbons distribution.

Cr/HZSM-5 catalyst in hydrocarbons synthesis but facilitates formation of the liquid gasoline-fraction hydrocarbons with a high aromatics content and low n-paraffins content (less than 1 % mass). The produced gasoline fractions have a high octane number (above 93 RON) and contain practically no benzene (less than 0.5 % mass) [126].

CONCLUSION

The present review considers the chemical aspects of various methods of CO_2 utilization into commercial products (carbon, methanol, DME, aromatic hydrocarbons, liquid motor fuels *etc.*) and industrial feedstock (carbon oxide, synthesis-gas, olefins, synthetic natural gas *etc.*). A thorough analysis is made of the re-

search works devoted to bifunctional catalysis application in conversion of CO_2-containing gases into hydrocarbons, including liquid motor fuels. The examined facts allow to conclude that the processes of CO_2 conversion into liquid hydrocarbons (aromatic hydrocarbons, motor fuels) can be considered as a promising way of carbon dioxide utilization. For a more profound analysis of the problem of environmental protection against CO_2-containing gases, a comparative feasibility study should be carried out for various techniques of CO_2 conversion into the above commercial products.

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