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HETEROGENEOUS CATALYTIC HYDROGENATION OF CARBON DIOXIDE INTO HYDROCARBONS: ACHIEVEMENTS AND PROSPECTS

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Abstract: *The works published over the past 10 years on the catalytic hydrogenation of carbon dioxide into methane and C_{2+} hydrocarbons are considered. The choice of catalysts based on their elemental and phase composition, structural-porous characteristics, grain-size and acidic properties, the reaction mechanism and problems and prospects for the industrial application of heterogeneous catalytic conversion of CO_2 to hydrocarbons are discussed.*

Keywords: *carbon dioxide, hydrogenation, heterogeneous catalysts, methane, C_{2+} hydrocarbons*
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Introduction

Today, there is no doubt that the upward trend in CO_2 emissions into the atmosphere since the beginning of industrialization is a key factor in changing the planet's climate over the past two centuries [1,2]. Solutions aimed at mitigating the above problem are based on: a) full and / or partial replacement of carbon fuels with renewable energy sources, b) technologies for capturing and storing carbon dioxide, and c) chemical conversion of CO_2 into valuable chemicals and fuels [3,4] . The latter approach has attracted a lot of interest in recent decades. Carbon dioxide is a cheap, safe and renewable source of carbon for the production of organic compounds. At the moment, the use of CO_2 as a chemical raw material is limited to the synthesis of urea and its derivatives, salicylic acid and carbonates [5]. This is due to the thermodynamic stability of the carbon dioxide molecule and the high endothermicity of its involvement in chemical reactions. Among the methods of processing carbon dioxide CO_2, catalytic hydrogenation is one of the most promising [6,7]. The most studied are the photo- [8,9], electro- [10,11] and thermocatalytic (the latter is often called simply catalytic) [12,13] variants of CO_2 hydrogenation. There are known works in which ionic liquids and supercritical CO_2 are used [14-16]. For hydrogenation of CO_2, both homogeneous and heterogeneous catalysts are used [17–22]. Homogeneous catalysts exhibit high activity and selectivity in this process, but their recovery and regeneration are problematic. Heterogeneous catalysts are stable, easily regenerated, and are preferred for large-scale production [23, 24].

Hydrogenation of CO_2 produces methane, C_{2+} hydrocarbons, their mixtures, mainly gasolines, as well as methanol, dimethyl ether and a number of other oxygen-containing substances used in the chemical, petrochemical, pharmaceutical, medical, electronic and other industries [25, 26]. This review considers the works published mainly over the past 10 years on the catalytic hydrogenation of carbon dioxide to methane and C_{2+} hydrocarbons.

Methanation of carbon dioxide

Methanation of carbon dioxide ($CO_2 + 4H_2 = CH_4 + 2H_2O$), i.e. the Sabatier reaction is a highly exothermic reaction with the release of ~ 164 kJ of heat per mole of CO_2. When the ratio CO_2 / H_2 = 1/1, carbon dioxide is reduced to carbon monoxide ($CO_2 + H_2 = CO + H_2O$). The reaction proceeds with heat absorption (ΔH_{298} = 41.5 kJ / mol). The main side reaction proceeding in this system and affecting the yield and composition of the resulting products is the Bell-Budard reaction ($2CO = CO_2 + C$; ΔH_{298} = - 172.3 kJ / mol). It increases with increasing temperature and is the reason for the decrease in catalytic activity due to the deposition of carbon on the catalyst surface. The reduction of CO_2, in which carbon has the highest oxidation state (+4), occurs with significant kinetic limitations, which require the selection of effective catalysts to achieve acceptable rates and selectivity of the process [27, 28]. In [29-31], thermodynamic analysis was performed to predict the maximum theoretical yield and selectivity of the expected products. H_2, CO_2, CO, C, CH_4, and H_2O were considered as the main reaction products.

Mainly mono- and bimetallic systems containing Group VIII metals (Fe, Co, Ni, Rh, Pd, Pt) have been studied as catalysts for CO_2 hydrogenation [32–34]. Nickel and ruthenium deposited on various oxides (SiO_2, TiO_2, Al_2O_3, ZrO_2, CeO_2, etc.) turned out to be the most active catalysts for CO_2 methanation. Ni-based catalysts are widely used for industrial purposes due to their low cost. However, the nickel catalyst is deactivated even at sufficiently low temperatures, mainly due to the sintering of Ni particles and the formation of carbon deposits [35, 36]. To increase the stability of nickel catalysts, they are modified, the other metals are introduced into them, and the support is changed. γ-Al_2O_3 [37,38], SiO_2 [39-41], TiO_2 [42], CeO_2 [43,44], ZrO_2 [45,46], hydrotalcite [47], various zeolites and carbon materials, including carbon nanotubes, etc. [48-50]. Note that acidity, structural and porous characteristics (surface area, pore volume, and their size distribution) of the support play an important role in determining the properties of catalysts for CO_2 methanation [51, 52]. The use of zeolites in the hydrogenation of carbon dioxide to methane shows that zeolite-based catalysts are more active and selective than commercial materials. The information available in the literature shows that, taking into account the well-known properties of zeolites and the possibility of fine modulation of their properties, it is possible to achieve good results in controlling their catalytic properties in the reaction of hydrogenation of CO_2 into hydrocarbons by directionally changing its structural and dimensional properties of metal, metal-oxide particles, introduced into the zeolite. The possible correlations between the structural features, acidity and catalytic properties of zeolites are presented and discussed [53]. Effects of crystal phase of supports and metal–support interaction on tuning product distribution are shown in CO_2 hydrogenation on unpromoted and Zr, K, Cs-promoted Co/TiO_2 Catalysts [54]. In [55], nickel nanoparticles were deposited on yttrium-stabilized zirconium oxide (YSZ) obtained by electroplating. The catalytic conversion of carbon dioxide to CH_4 was studied on five Ni/YSZ samples with the same nickel loading (10 wt%), but with different sizes of Ni particles. The results showed that the catalytic activity and selectivity for CH_4 depend on the size and morphology of the Ni particles. In [56] CO_2 methanation over sponge Ni was investigated. When CO_2 methanation was carried out using sponge Ni without any pretreatment, the sponge Ni exhibited a CO_2 conversion of 83% at 250 ^{o}C under a high space velocity (0.11 mol(CO2) g(cat)(-1) h(-1)). It was suggested that the sponge Ni is a promising new catalyst for CO_2 methanation because it showed the high activity even under the high GHSV, and it is possible to design a small plug flow reactor compared to a conventional reactor, resulting in a low manufacturing cost for the reactor. The high activity can be derived from the great number of crystal defects of fcc-Ni in the sponge Ni. On the other hand, with high-temperature pretreatment, the sponge Ni lost its activity in CO_2 methanation as well as the surface defect sites. The activity loss is explained by the disappearance of the surface defect sites by the high-temperature pretreatment. Ni-CeO_2/SBA-15-V catalyst was prepared by the impregnation method with vacuum thermal treatment and used for CO_2 methanation reaction. Compared with Ni-CeO_2/SBA-15-air catalyst with thermal treatment in air, the reduced Ni-CeO_2/SBA-15-V catalyst with vacuum thermal treatment exhibited higher Ni dispersion and smaller Ni particle size. In CO_2 methanation reaction, the Ni-CeO_2/SBA-15-V catalyst was more active and selective than the Ni-CeO_2/SBA-15-air catalyst. It was suggested that the good activity and selectivity of Ni-CeO_2/SBA-15-V catalyst should be due to highly dispersed Ni in contact with small CeO_2 particles [57]. The works indicated below [58-79] describe nickel-containing mono-, bi- and more-component catalysts for CO_2 methanation with different bases and contents of metal components. In [58] mixed oxides of the NiO-CeO_2 composition with a Ni content in the range of 5-35 wt% were synthesized using SBA-15 as a matrix and tested in the methanation of CO_2. They were found to be highly catalytic in this reaction. It was revealed [59] that a Ni-Co / ZrO_2-CeO_2 catalyst prepared by impregnation and coprecipitation methods can achieve 100% CO_2 conversion at a temperature of ~ 573 K and ≥95% CO_2 conversion at 673 K, 99% selectivity with respect to CH_4. The activity of CO_2 methanation on nickel-containing catalysts based on CeO_2 and ZrO_2 in order to optimize the nickel content, its charge state and distribution in the catalyst structure, and the CeO_2/ZrO_2 mass ratio to improve the activity and stability of the catalyst in [60] are discussed. The effect of the support on the reducibility, morphology, and dispersion of the active metal during the methanation of CO and CO_2 over Ni, Co / ZrO_2 (SiO_2, Al_2O_3) - CeO_2 in a catalytic fixed-bed reactor was studied. It has been shown that the binary ZrO_2-CeO_2 oxide support promotes the formation of oxygen vacancies, which leads to an increase in the adsorption capacity of CO_2 and, hence, to a higher catalytic activity. A catalyst based on ZrO_2-CeO_2 can achieve 100% CO conversion at 573 K and ≥95% CO_2 conversion at 673 K is considered in [61]. In [62, 63], a high activity of a Ni-containing catalyst with a base of tetragonal ZrO_2 and W- doped Ni-Mg mixed oxide catalyst accordingly for the methanation of CO_2 is reported. It was shown in [64] that nickel nanoparticles deposited on t-ZrO_2 have better adsorption of CO_2 than those deposited on m-ZrO_2. Zhou et al. [65] prepared Ni-containing catalysts for CO_2 methanation based on γ-Al_2O_3 and studied the effect of CeO_2 introduced as an activator on the size, dispersion of nickel particles, their interaction with the substrate, and catalytic properties. CO_2 hydrogenation reactions were carried out in a fixed bed reactor at atmospheric pressure. It was found that the introduction of CeO_2 into this catalyst leads to a decrease in the particle size of Ni and, as a result of its interaction with Al_2O_3, the amount of CO_2 adsorbed on active sites and the conversion of CO_2 increased significantly. The productivity of the process has also increased. It was also shown that the samples obtained by various preparation methods differed markedly in structure and catalytic properties. The recent research progresses of constructing highly efficient Ni based catalysts toward CO_2 methanation in the review. Specifically, the strategies on how to enhance the catalytic performances of the Ni based catalysts have been studied, which include various influencing factors, such as catalytic supports, catalytic auxiliaries and dopants, the fabrication methods, reaction conditions, etc. Finally, the future development trend of the Ni based catalysts is also prospected, which will be helpful to the design and fabrication of the Ni catalysts with high efficiency toward CO_2 methanation process. Comparative studies of iron, nickel-containing mono and bimetallic catalysts have been carried out, which showed that bimetallic nickel-iron catalysts are more active than monometallic nickel. Research shows that the nature of the second metal has a significant impact on the catalytic activity of the nickel catalyst. Thus, in comparison with Co and Cu, Fe noticeably enhances the catalytic activity of Ni/ZrO_2 even at low temperatures [66-69]. The Co-modified Ni / SiO_2 catalysts by co-impregnation with further coprecipitation in the methanation of CO_2 is prepared and it was found that these catalysts with an increased amount of Co show a high conversion of CO_2 in the temperature range 523-623 K [70]. Modification of the Ni/Al_2O_3-based catalyst with ruthenium and iron made it possible to obtain promising catalysts for CO_2 methanation [71]. In [72] nanosized zirconium dioxide used as a carrier for nickel catalysts is reported. The results revealed the dependence of their activity in CO_2 methanation on a specific surface area and pore volume of the support.

Figure 1 shows the EMR spectra: a) recorded at room temperature, sample 5% Fe-15% Ni / Al oxide catalyst, reduced in a current of H_2 for 1 hour at: 1- 573, 2 - 673, 3 - 773K; b) 5% Fe, 15% Ni /Al oxide sample: 3- calcined in air at 773K for 4 hours and recorded at room temperature, 1.2- recorded at 553K after holding it at this temperature in a current of CO_2/H_2 with a ratio of 1/3 (1) and 1/4 (2) for one hour.

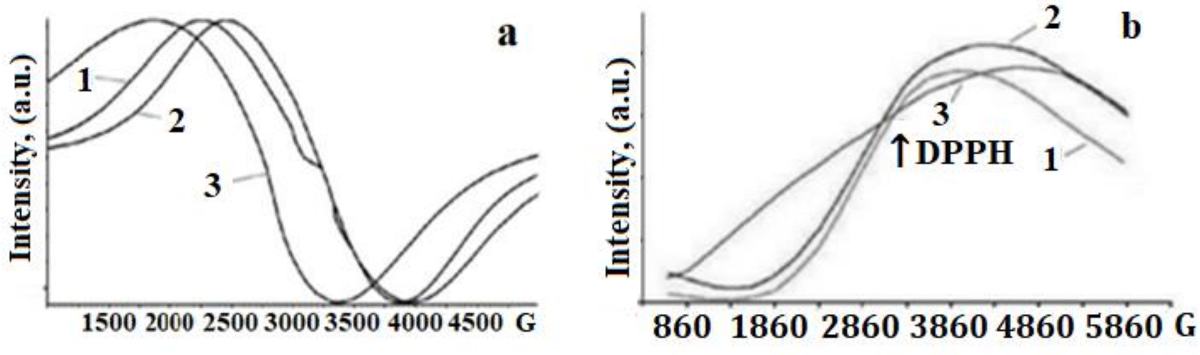


Fig. 1. EMR spectra: a) recorded at room temperature, a sample of 5% Fe-15% Ni/Al-oxide catalyst, reduced in a current of H_2 for 1 hour at: 1- 573, 2 - 673, 3 - 773K; b) 5% Fe, 15% Ni / Al oxide sample: 3- calcined in air at 773K for 4 hours and recorded at room temperature, 1.2- recorded at 553K after holding it at this temperature in a current of CO_2/H_2 with a ratio of 1/3 (1) and 1/4 (2) for one hour.

The EMR spectra shown in Fig. 1, are characteristic to superpara / ferromagnetic particles of Fe, Ni - containing catalysts with an oxide base [73, 74]. As seen from Fig. 1, a (curves 1, 2, 3) and b (curve 3), the magnetic characteristics of samples with the same iron and nickel content, first of all, significantly depends on the conditions of their preliminary heat treatment. Secondly, the conditions of the CO_2 hydrogenation reaction noticeably affect the magnetic characteristics of these samples.

In figure 2 shows the EMR spectra of the oxide catalyst 5% Fe, 15% Zr / Al (a) and 35% Fe, 15% Zr / Al (b) under the different reaction conditions.

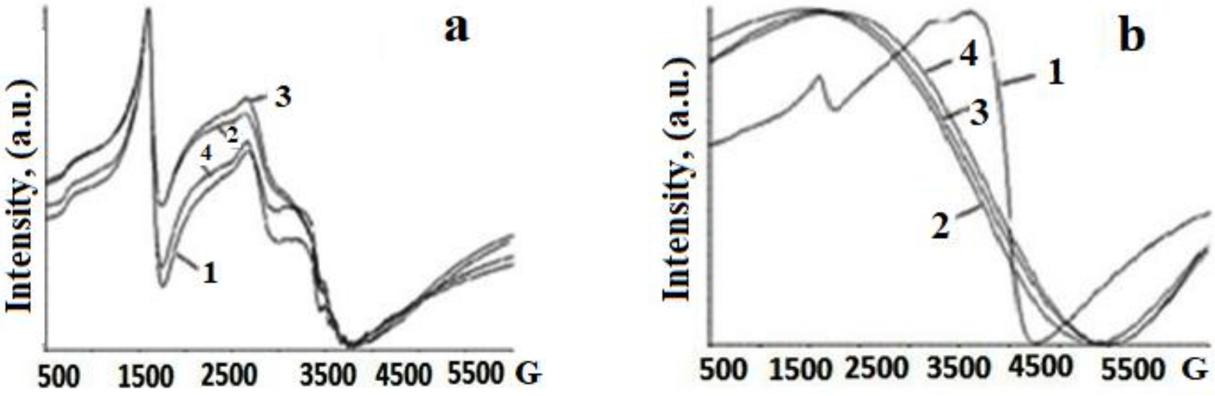
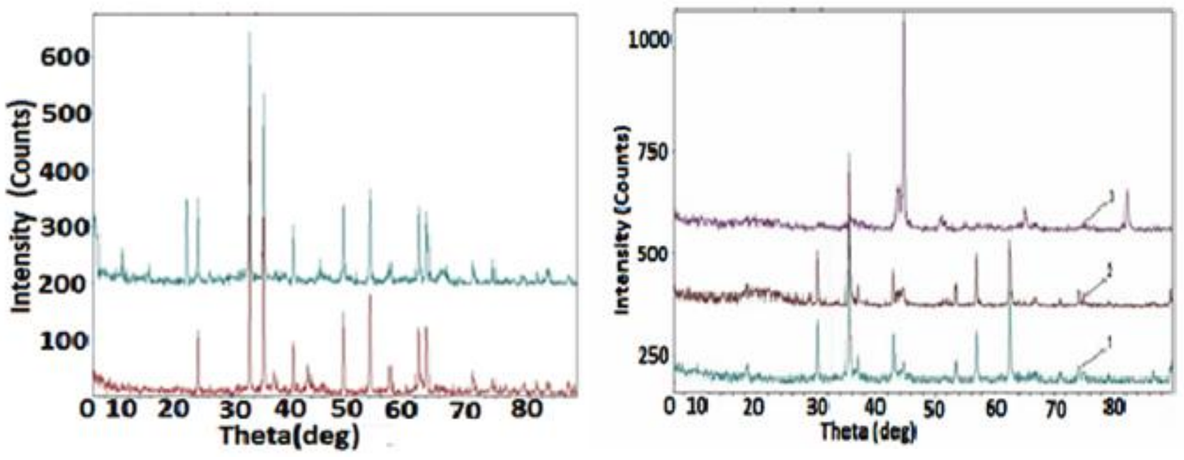


Fig. 2. The EMR spectra of: a) the initial (1) and reduced at 573 (2), 673 (3), and 773 K (4) samples of 5% Fe, 15% Zr/Al and b) 35% Fe, 15% Zr/Al: 1 - calcined in a stream of air for 2 h at 773 K; 2, 3, 4 - reduced in a current of H_2 at 573, 673 and 773 K, respectively.

The EMR spectrum of a sample of an oxide catalyst 5% Fe, 15% Zr / Al, oxidized at 773 K in an air flow, is a superposition of at least three signals - a wide one with an average g-factor of 2.3 and a width of ΔH ~ 140 mT, rather narrow with a g-factor of 4.21, and a shoulder with g ~ 7.2. Upon restoration, the shape and intensity of this signal noticeably change, splitting into two signals with g-factors of ~ 2.0 and 2.9. For the initial sample of the 35% Fe, 15% Zr / Al oxide catalyst oxidized at 773 K in a flow of air, an EMR spectrum is observed, which consists of a superposition of three signals. The components of this spectrum with g ~ 4.21 are hardly noticeable, the shoulder with g ~7.2 is practically not manifested. This spectrum is mainly due to magnetic particles with a g-factor of 2.0 and a width of ΔH 110 mT. Upon restoration, the EMR spectrum of this sample completely changes and is observed in all cases (Fig. 2, b) a wide, slightly asymmetric isotropic signal with average values of the g-factor 2.25-2.42 and width ΔH ~ 290-310 mT depending on the reduction temperature in hydrogen. It can be assumed that the EPR signal observed for samples oxidized at 773 K in air with a g -factor of 2.0 and a width of ΔH ~ 110 mT is due to Fe_2O_3 nanoparticles, while an EMR signal with average g-factors of 2.25-2.42 and ΔH ~290-310 mT width belongs to ferromagnetic particles Fe_3O_4. Its appearance is most likely associated with the reduction of a part of Fe^{3+} iron ions in the original oxide structures of iron to Fe^{2+} and the formation of oxide structures with a mixed oxidation state of iron such as magnetite Fe_3O_4, which, clustering, form magnetically concentrated phases. Note that the intensity of the signal with a g- factor equal to 4.21 and the shoulder with g ~ 7.2 practically does not change when the catalyst is treated in a flow of hydrogen at 573, 673, 773 K, as well as with an increase in the iron content in the samples. This gives grounds to believe that signals with g = 4.21 and 7.20 can be attributed to isolated Fe^{3+} ions in crystal fields of rhombic and axial symmetry, respectively, while resonance with g ~2.0 is due to Fe^{3+} ions associated with exchange interactions in the magnetically concentrated phase [74]. Thus, the experimental data allow us to conclude that the catalysts before and after the methanation reaction contain superpara / ferromagnetic particles, most likely nickel, iron oxides FeO_x, possibly also $Ni_xFe_{1-x}O_y$. The shape (width, intensity, position in a magnetic field) of the EMR spectra depends on the composition of the samples, the content of iron, nickel (zirconium) in them.



a) b)

Fig. 3. X-ray diffraction patterns recorded at room temperature: a) Fe, Ni / Al and Fe, Zr / Al - oxide catalysts calcined at a temperature of 773 K in a stream of air; b) catalyst Fe, Ni / Al reduced by hydrogen for 2 hours at: 1 - 573, 2 - 673, 3 - 773 K.

The magnetic state, phase composition of these catalytic compositions, the dispersion of the active components in them is determined by the conditions of their preliminary heat treatment. However, for some compositions, for example, Ni, Ni-Fe, Ni-Co and a number of similar oxide systems, the reaction conditions may change and be different. The magnetic properties of these systems can vary from ferromagnetic to superparamagnetic due, most likely, to a change in the particle size, their size distribution in the catalyst structure during its heat treatment in different media and reaction conditions.

The X-ray diffraction patterns of the Fe, Ni / Al_2O_3 oxide catalyst reduced with hydrogen are shown in figure 3.

The given XRD patterns indicate the presence and absence, respectively, of a metallic phase in hydrogen-reduced Fe, Ni / Al and Fe, Zr / Al - oxide catalysts. Thus, it can be argued that while the magnetism of the former is due to particles of Fe, Ni, and Fe(Ni), $Fe(Al)_2O_4$, the latter is exclusively due to oxide structures [73-75]. It is not possible to say about any connection between the magnetic and catalytic properties of the studied systems in the hydrogenation of CO_2 into hydrocarbons. At the same time, both the magnetic and catalytic properties of these systems unambiguously depend on the composition and structural-dimensional, porous characteristics, and what should be especially emphasized, the acid-base properties of the catalysts. The relationship between the magnetic and catalytic properties in this case is not obvious, although it can be easily traced between the catalytic and acid-base properties of catalysts [76-79].

Highly dispersed ruthenium nanoparticles were synthesized by sputtering on a TiO_2 support [80]. The prepared Ru / TiO_2 sample catalyzed the methanation reaction at 300K at a rate of 0.04 μmol $min^{-1} \cdot g^{-1}$. At 433K, 100% yield was observed, i.e. much higher than for a wet impregnated catalyst. The introduction of yttrium into catalysts based on Ru not only increases the active surface area and dispersion of ruthenium, but also promotes catalytic activity and prevents catalyst deactivation [80]. In [81] Ru/γ-Al_2O_3 was used to determine the kinetic parameters of methanation. The activation energy was 82.6 kJ $\cdot$ mol^{-1} at 50% dispersion of ruthenium. The order of reaction with respect to hydrogen decreased with an increase in the H / Ru ratio, which may be associated with a change in the heat of hydrogen adsorption and an increase in the number of coordination centers. Highly active and stable CO_2 methanation catalyst that was prepared from a Ru-impregnated zirconium-based metal organic framework (MOF) is described in [82]. MOF doped with Ru is converted under the reaction conditions into an active catalyst that provides 96% CO_2 conversion and 99% CH_4 selectivity. The final catalyst consisted of a mixture of Ru nanoparticles supported on monoclinic and tetragonal ZrO_2 nanoparticles. The mechanism of CO_2 methanation over Rh/γ-Al_2O_3 catalyst is analyzed in [83]. In [84] the state-of-the-art activation methods and also highlighting similarities in different modes of CO_2 activation and correlations to product selectivity to evaluate coherent views on CO_2 transformation over catalytic surfaces. CO_2 is a thermodynamically stable molecule with the standard formation enthalpy of -393.5 kJ mol^{-1}. However, CO_2 can be transformed with notable reactivity depending on the chemical environment. Among them catalysis offers specific sites to activate CO_2 for its chemical transformation. There are several activation methods over catalyst surface reported to date and each method generally leads characteristic reactivity of CO_2 and products due to the unique form of activated CO_2 during transformation. This article describes the main strategies to activate and convert carbon dioxide into valuable chemicals over catalytic surfaces. Coherent elements such as common intermediates are identified in the different strategies and concisely discussed based on the reactivity of CO_2 with the aim to understand the decisive factors for selective and efficient CO_2 conversion.

Hydrogenation of carbon dioxide to C_{2+} hydrocarbons.

Analysis of the literature data showed that to date, noticeable activity in the hydrogenation of carbon dioxide to C_{2+} hydrocarbons has been established mainly for iron-containing catalysts with an oxide base [85-87]. In [88-90], bimetallic Fe - M (M = Co, Ni, Cu, Pd) catalysts based on Al_2O_3, as well as the corresponding monometallic catalysts in the reaction of CO_2 hydrogenation to C_{2+} hydrocarbons, were investigated. It was found that the formation of

C_{2+} hydrocarbons is characteristic of iron-containing catalysts, while the Co and Ni catalysts selectively gave higher CH_4 yields than other catalysts. The combination of Fe and Cu or Pd led to a significant increase in the formation of C_{2+} hydrocarbons during the hydrogenation of CO_2. The Fe-Ni bimetallic catalyst is also capable of catalyzing the hydrogenation of CO_2 to C_{2+} hydrocarbons, but at a low Ni / (Ni + Fe) atomic ratio. The introduction of a small amount of K into the Fe-Co catalyst stimulates and noticeably enhances the formation of C_2 -C_4 olefins, while olefins prevail among C_{2+} hydrocarbons with an atomic K / Fe ratio of 1. Studies have shown that for the synthesis of C_2-C_4 olefins, the Fe-Cu catalyst / K is more preferable than Fe / K, Co / K and Fe-Mn / K [91-93].

When using a zeolite catalyst, C_{2+} hydrocarbons of a certain composition were obtained by hydrogenation of carbon dioxide with the use of zeolite and mixed zeolite-oxide systems as catalysts. The dependence of the activity of these catalysts in the hydrogenation of CO_2 to methanol and hydrocarbons on the amount of acid sites was studied [94-96]. The C_5-C_{11} gasoline fraction was obtained with high selectivity on the In_2O_3 / HZSM-5 catalyst. The activity of catalysts based on SAPO-5 and SAPO-44 in the hydrogenation of CO_2 to C_{2+} hydrocarbons was established. The synthesis of light alkenes by hydrogenation of carbon dioxide over the bifunctional catalyst In_2O_3 / ZrO_2-SAPO-34 was studied. It is assumed that methanol is formed on the oxygen vacancies of In_2O_3, which is converted into light olefins on the SAPO-34 zeolite. Hydrogenation of CO_2 at atmospheric pressure was studied on various catalytic model systems based on Pd, Rh, and Ni deposited on SiO_2, Al_2O_3, and CeO_2 oxides and aluminosilicates ZSM-5 and MCM-41 at various specific ratios of reagents and temperatures from 423 to 723 ^{0}C. The carrier material and the reaction conditions play an important role in the hydrogenation process. Research results indicate that a metal oxide such as cerium can interact with CO and promote the hydrogenation reaction by directly forming surface carbonates and formates. K / Fe-Al-O oxides obtained by coprecipitation in the presence of the surfactant CTAB have shown a significant effect on the performance of catalysts in the hydrogenation of CO_2 to hydrocarbons. It was studied the production of light olefins over a Cu / Zn / Zr and SAPO-34 catalyst. The distribution of products was strongly influenced by the ratio of metals, the acidity of the zeolite, and the method of catalyst preparation. The promotion of SAPO-34 with zinc reduced the acidity and led to a sharp limitation of the secondary reactions of the formed olefins. On the ZnO / ZrO_2 and ZSM-5 catalysts, aromatic compounds can be obtained with selectivity up to 70%, while the selectivity for methane is only 1% [97-101].

The thermodynamics of CO_2 hydrogenation into hydrocarbons, the effect of temperature, pressure, and composition of the feedstock on equilibrium conversion were studied in [102]. An increase in temperature above 550 K negatively affects the equilibrium conversion of CO_2 and H_2. The temperature is above 750 K and the pressure is about 30 atm. favorable for the synthesis of heavier hydrocarbons. Analysis of the literature data showed that iron-containing oxide-based catalysts are active in the hydrogenation of carbon dioxide to obtain C_{2+} hydrocarbons. The activity of these catalysts increases markedly when they are promoted with alkali metals. A disadvantage of iron-containing catalysts is their deactivation due to particle sintering at elevated temperatures and surface carbonization. Cobalt-based catalysts are less active in the synthesis of hydrocarbons from CO_2 and hydrogen; on their surface, the reaction of direct methanation, the Sabatier reaction, proceeds [103, 104].

Mechanism of CO_2 hydrogenation to hydrocarbons

Analysis of the currently available data on CO_2 hydrogenation suggests that, depending on the operating conditions and the catalyst used, the reaction of CO_2 hydrogenation to hydrocarbons proceeds by methanation of CO_2 or the formation of C_{2+} hydrocarbons. It is assumed that the conversion of a mixture of CO_2 and H_2, for example, into methane, depending on the nature of the active component, can occur either directly or in two stages through the stage of carbon monoxide formation [105, 106]. Some studies suggest that monoxide is not involved in CO_2 methanation; the mechanism of monoxide hydrogenation is of a different nature [107, 108]. It was shown in [109] that the 3% Ru / Al_2O_3 catalyst is active in the conversion of CO_2 into methane at atmospheric pressure. At 673 K and above, thermodynamic equilibrium is fully achieved; at 623 K, the yield of CH_4 is above 85%. IR studies show that hydrogen-reduced ruthenium catalysts are capable of oxidizing CO to CO_2 at 173–243 K and the formation of methane from both CO and CO_2 occurs when both surface carbonyl and surface formate structures are observed. CO_2 is hydrogenated to methane at 523-573K, even when no CO is observed in the gas phase.

The mechanism of the formation of C_{2+} hydrocarbons during hydrogenation of CO_2 is described through the intermediate formation of methanol and without the stage of methanol formation [110, 111]. Hydrogenation of CO_2 through intermediate methanol occurs in the presence of mainly copper-zinc catalysts with the formation of light alkanes as the main products with hydrogenation of alkenes [112, 113]. According to the second mechanism, CO_2 hydrogenation proceeds in two stages: the stage of the reverse reaction of the conversion of water gas (OCWG) and the Fischer-Tropsch synthesis (FT). Note that, in general, the catalyst components for the synthesis of hydrocarbons from CO_2 are the same as for the synthesis of FT. The review [114] presents the progress achieved in recent years in the synthesis of catalysts for the hydrogenation of CO_2. In C_{2+} hydrocarbons, the study of the mechanism of this reaction by combining experimental data and calculations based on the density functional theory (DFT), the factors influencing the performance of the catalysts are indicated, the mechanism of the formation of the C-C bond through various routes is given.

Industrial application prospects

CO_2 is currently an important carbon resource for disposal and CO_2 hydrogenation is a promising process, especially for methanation. However, CO_2 is chemically stable and CO_2 methanation is from a thermodynamic point of view an unfavorable process. The most effective catalysts for this reaction are systems based on noble metals such as Ru, Rh, and Pd, which catalyze the formation of methane under relatively mild conditions. However, their high cost limits their practical application. Therefore, researchers are paying more and more attention to catalysts based on 3d - transition metals, mainly Fe, CO, Ni. A strategy is required to obtain highly efficient catalysts with low temperature methanation and resistance to carbon formation. In addition, it is necessary to understand the detailed mechanism of the functioning of catalysts for methanation of CO_2 and to study its dependence on the composition and structure of the catalyst using both theoretical calculations and experimental approaches to develop new effective catalytic systems. It can be assumed that catalysts with a larger surface area and a higher dispersion of the metal component will have higher activity and selectivity and longer stability during CO_2 hydrogenation. However, for catalysts, for example, based on nickel, the problem of carbonization is fundamental. As for the technical and economic viability of the CO_2 hydrogenation technology, it is important to note the following. Although the capital investment in CO_2 hydrogenation technology is similar to the capital investment in conventional syngas technology, the operating costs are unfavorable primarily due to the high hydrogen requirements and the use of significant amounts of electricity. In addition, the cost of CO_2 capture also needs to be considered when determining the economic viability of this technology.

Conclusion

In this review, an attempt is made to summarize the works published, mainly over the past 10 years, on the catalytic hydrogenation of CO_2 to hydrocarbons. These studies, first of all, showed that unmodified carriers do not exhibit catalytic activity in the hydrogenation of CO_2, which indicates the key role of the metals of the 8th group of the Periodic Table. Nickel, iron, ruthenium catalysts, and especially ruthenium catalysts promoted with potassium, exhibit high catalytic activity. The highest activity was observed for carriers that strongly interact with nickel particles, which also indicates a significant role of the properties of the carrier in the activity under hydrogenation conditions. The differences in catalytic activity were likely the result of differences in dispersion and particle size of active metals, as well as interactions between support particles and active metals. These results can be considered primary and, of course, studies of the effect of particle size and their distribution on the activity of catalysts for this reaction will most likely continue. Experiments that discriminate between the size effects of metal particles, such as Ni and substrate, can provide valuable insights for the development of efficient catalysts for CO_2 hydrogenation.

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ГЕТЕРОГЕННОЕ КАТАЛИТИЧЕСКОЕ ГИДРИРОВАНИЕ ДИОКСИДА УГЛЕРОДА В УГЛЕВОДОРОДЫ: ДОСТИЖЕНИЯ И ПЕРСПЕКТИВЫ

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Рассмотрены опубликованные за последние 10 лет работы по каталитическому гидрированию диоксида углерода в метан и углеводороды C_{2+}. Обсуждаются выбор катализаторов по элементному и фазовому составу, структурно-пористым характеристикам, гранулометрическим и кислотным свойствам, механизму реакции, а также проблемы и перспективы промышленного применения гетерогенно-каталитической конверсии CO_2 в углеводороды.

Ключевые слова: *диоксид углерода, гидрирование, гетерогенные катализаторы, метан, углеводороды C_{2+}.*

KARBON DİOKSİDİN KARBOHİDROGENLƏRƏ HETEROGEN KATALİTİK HİDROGENLƏŞMƏSİ: NAİLİYYƏTLƏR VƏ PERSPEKTİVLƏR

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Son 10 ildə karbon dioksidin metan və C_{2+} karbohidrogenlərə katalitik hidrogenləşməsinə aid nəşr olunmuş əsərlərin təhlili verilir. Element, faza tərkibi, quruluş-məsamə xüsusiyyətləri, ölçü və turş xassələri, reaksiya mexanizmi baxımından katalizatorların seçimi, həmçinin CO_2-nin karbohidrogenlərə heterogen katalitik çevrilməsi prosesinin sənayedə tətbiqinin problem və perspektivləri müzakirə olunur.

Açar sözlər*: karbon dioksid, hidrogenləşmə, heterogen katalizator, metan, C_{2+} karbohidrogenlər*