Absorption and Catalytic Conversion of Hydrocarbons: Reactors, Adsorbents and Catalysts

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Abstract

We consider the absorption and catalytic conversion of a single-stage method of obtaining high yield of pure hydrogen. This process involves simultaneous catalytic conversion of hydrocarbons into hydrogen and sorption removal of by-product − carbon dioxide. Different aspects of absorption and catalytic conversion are analyzed, including its technical implementation in flow reactors with fluidized and fixed bed, as well as high-temperature CO_2 absorbents and catalysts necessary for the process. It is shown that the preferred scheme for production of hydrogen from methane is that with two or more fixed bed reactors, loaded with a mixture of a conventional nickel containing catalysts of steam conversion and a high temperature reversible absorbent. The analysis of the perspective high-regenerated absorbent of CO_2: individual and deposited oxides of alkaline-earth metals, mixed lithium salts, promoted hydrotalcite. It is shown that the absorbents based on CaO have sufficient stationary dynamic capacity, stable under conditions of absorption and catalytic conversion, and optimal thermodynamic properties.

Key words. hydrogen, methane, absorption and catalytic conversion, the fuel processor reactor, catalyst, adsorbent

Contents

INTRODUCTION

Absorption and catalytic conversion (ACC) is the process of producing hydrogen from hydrocarbon fuels, which combines two stages: the catalytic steam conversion of hydrocarbons and the sorption purification of resulting gas from one of the reaction products − CO_2 [1]. Besides the main effect (purification of products from CO_2), according to Le Chatelier principle, the removal of the reaction product leads to a more complete conversion of hydrocarbons and CO and increases the yield of hydrogen. Absorption and catalytic conversion of methane is known since 1867 [2]. Further interest in this method revived periodically, and the last peak of interest falls on the current decade, due to the rapid development of hydrogen energy and the need for independent compact supply source of hydrogen [3, 4].

This review describes various aspects of ACC, including its technical implementation in flow reactors with fluidized and fixed bed. Based on the characteristics of the process implementation, the requirements for high-temperature absorbents of CO_2 and catalysts, as well as perspective conforming materials are defined.

PRINCIPLES OF ABSORPTION AND CATALYTIC CONVERSION OF HYDROCARBONS

Currently, more than 90 % of the hydrogen used in the industry, are obtained by the conversion of hydrocarbons, among them methane holds a unique position. Steam catalytic conversion of methane is carried out at high temperatures, and its result can be described by a sequence of two reactions, the first one is actually steam methane reforming (SMR) to form CO and hydrogen:

$$CH_4(g) + H_2O(g) \Leftrightarrow CO(g) + 3H_2(g)$$

$$\Delta H^o_{298} = 206 \, kJ/mol \qquad (1)$$
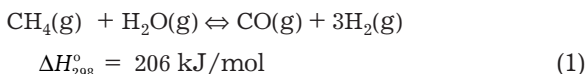
The products of subsequent reaction of steam conversion of CO (HSC) are hydrogen and carbon dioxide:

$$CO(g) + H_2O(g) \Leftrightarrow CO_2(g) + H_2(g)$$

$$\Delta H^o_{298} = -41 \, kJ/mol \qquad (2)$$
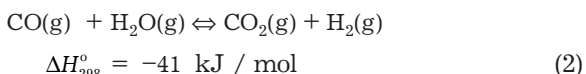
Reaction (1) is strongly endothermic. Efficient conversion of methane is possible only at temperatures of 700 °C and above. On the other hand, the equilibrium constant of reaction (2) is close to unity, resulting in almost equal amounts of CO and CO_2 in the products of hydrocarbon steam conversion [5].

Removing CO_2 from the gas phase during the process (for example, the binding by a solid absorbent) should lead to a shift in the equilibrium of reactions (1) and (2) toward the formation of products, including hydrogen. The reaction of CO_2 removing can be written as

$$CO_2(g) + S(s) \rightarrow S \cdot CO_2(s) \qquad (3)$$
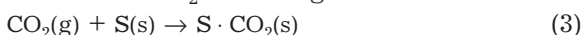
and the gross equation of hydrocarbon steam conversion in the presence of the absorbent is a

$$CH_4(g) + 2H_2O(g) + S(s) \rightarrow 4H_2(g) + S \cdot CO_2(s) \quad (4)$$
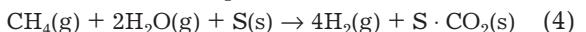
Comparative analysis of ACC and the classical steam reforming provides a complete picture of the benefits of the process using a sorbent. Calcium oxide is selected as an absorbent of carbon dioxide; it reversibly absorbs CO_2 in the temperature range 650–850 °C [6–8], the typical SMR reaction [9]:

$$CaO + CO_2 \rightarrow CaCO_3 \qquad (5)$$

For simplicity the possibility of formation of calcium hydroxide is not considered, this affects the equilibrium composition of products at temperatures below 600 °C. Examples of similar estimates of ACC, including those taking into account the formation of $Ca(OH)_2$ can be found in [1, 10–14]. Using the reference thermodynamic data [15] the equilibrium composition of the mixture for the catalytic steam reforming without and with the absorbent was calculated (Fig. 1). In the first case hydrogen containing gas can be obtained, its hydrogen content does not exceed 80 vol. % and the content of CO, CO_2 and CH_4 varies from one to several tens of percents (in terms of dry gas). In the presence of CO_2 sorbent in a reaction volume the degree of conversion of methane to hydrogen increases at temperatures below 700 °C, this is associated with a shift of equilibrium of reactions (1) and (2) caused by removal of CO_2 from the reaction mixture. Under equilibrium conditions ACC allows to produce reformate with the content of CO and CO_2 less than 100 ppm, which cannot be achieved by steam conversion without the absorbent. Thus, ACC is no need for reactors of high- and low-temperature steam conversion of CO, which cover 40 % of conventional plants.
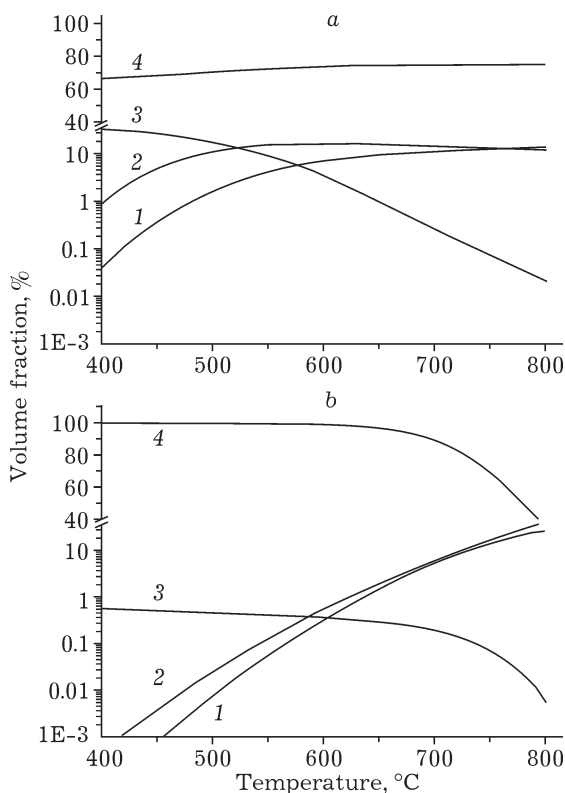

Fig. 1. Equilibrium of the reaction products of methane steam reforming without removal of CO_2 (*a*) and with the sorption of CO_2 (*b*) (steam/methane = 4): *1* – CO, *2* – CO_2, *3* – CH_4, *4* – He.

The absorption of carbon dioxide leads to saturation of the absorbent, so it is necessary to perform its periodic regeneration via refining the reaction volume by a gas which does not contain CO_2 or increasing the temperature of the reactor, or a combination of these methods.

REACTORS

Studies of absorption and catalytic schemes of steam reforming of hydrocarbons in Russia began in the middle of 20th century [16, 17]. The largest contribution to the development of ACC in fluid bed reactors have the works Brun-Tsekhovoy et al. [16]. Figure 2 shows a diagram of the absorption and catalytic reforming in the fluid bed reactor with catalyst and adsorbent [18]. Fuel is continuously fed into a reformer (*1*) with a catalyst, while sorbent is continuously circulated between a reformer (*1*) and regenerator (*2*). The separation of catalyst and adsorbent at the outlet of the reformer can be carried out due to the different granularity of the sorbent and catalyst particles. In this way the authors of [19] were able to get the hydrogen purity of 96 vol. %. Specificity of the processes in a fluidized bed puts special demands on the strength of the catalysts and sorbents of CO_2, because they are exposed to heavy
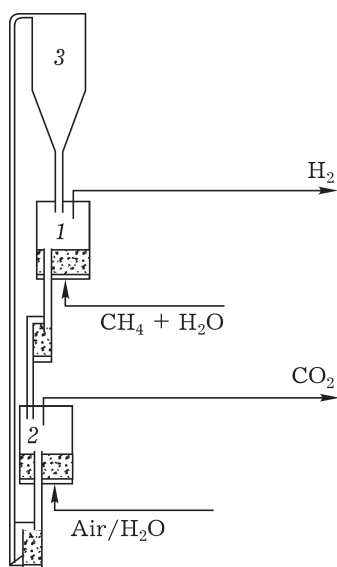

Fig. 2. Scheme of the absorption and catalytic conversion in reactor with a fluidized bed of catalyst and adsorbent [16]. Design. see text

attrition [20]. In [21, 22] it was shown that natural calcined dolomite with appropriate pretreatment have sufficient mechanical strength. On the other hand, the presence of the ballast MgO reduces CO_2 sorption capacity of the dolomite, so the frequent regeneration and more intensive circulation of the absorbent between the reformer and regenerator should be provided.

The advantages of the above schemes include the continuity of the process and the possibility of scaling. On the other hand, the circuit with circulating absorbent does not allow for conversion and regeneration stages in the presence of significant pressure drop. In this regard in recent years considerable attention is also paid to ACC reactors with a fixed bed and absorbent [23]. To ensure the continuity of the process of hydrogen production at least two reactors are required, one of them is involved in the production of hydrogen and the other one − in regeneration of the sorbent [24, 25]. For a fixed-bed reactor requirements for mechanical strength of the sorbent and catalyst are not so critical. This opens up the possibility of using new types of high carbon dioxide sorbents and expands the available range of temperatures and pressures of the process [1].

Generally sorbent regeneration and conversion of methane is carried out at different temperatures and in different reaction media [14]. The temperature of air which is used at the stage of regeneration is 100−150 °C higher than that at the stage of SMR [26]. During the regeneration of the sorbent the oxidation of catalyst can take place and for its recovering the temperature of the reaction medium should exceed 700 °C as described in [27−30]. To solve this problem the authors of [3] suggested to make use of a gradient temperature distribution in the absorption and catalytic reactor, which can be obtained during the regeneration of the sorbent in the moving heat wave front [31].

The effectiveness of ACC depends on the stability of the catalyst (especially for the process in fixed bed, where the catalyst undergoes a change of atmosphere from reducing to oxidizing) and the stability of the sorption properties of the absorbent of CO_2. The catalysts and chemisorbents of CO_2 used in ACC are considered below. The ways to preserve the cata-

lysts activity, as well as favourable conditions for the chemisorbent regeneration stage are identified.

CATALYSTS FOR ACC

Unlike traditional stationary catalytic conversion of hydrocarbons, the temperature and atmosphere over the catalyst change during the process of ACC in a fixed bed. We can expect in ACC the catalytic activity of the same materials as in traditional steam reforming, but their resistance to non-stationary operation mode and changes of work conditions should be taken into consideration.

The metals of VIII group of the periodic system exhibit high activity in the reaction of steam reforming of hydrocarbons. In descending order of activity they form the following series: Rh, Ru > Ni, Pd, Pt > Re > Co [2].

The most active element rhodium is also highly resistant to carbonization [2]. However, the high price of this metal interferes with its industrial application. In ACC, the rhodium catalyst also shows high and stable activity from cycle to cycle in contrast to the platinum catalyst, for example; the activity of the latter decreases monotonically in the cycles (Fig. 3). In [32] the stability of the rhodium catalyst is explained by redispersion of the active component in the oxidation-reduction reactions. The applied platinum catalyst undergoes considerable sintering (Fig. 4) during ACC and loses activity. Despite the high activity in the reaction of steam
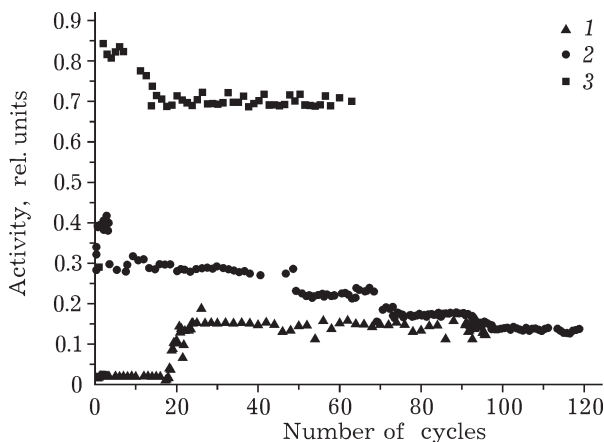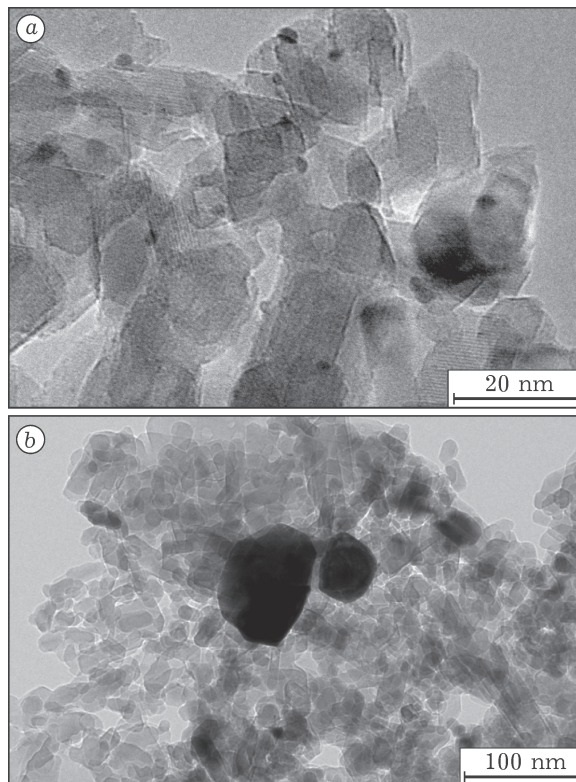
Fig. 4. Enlargement of platinum particles in ACC of methane: a − before the process; b − 10 h later [34].

reforming of hydrocarbons, ruthenium cannot be used as a catalyst in ACC reactor with a fixed bed due to formation of volatile oxide RuO_4 and entrainment of the active ingredient during the air regeneration [33].

Considering the ratio of catalytic activity and cost it is preferable to use catalysts based on nickel. Despite the sintering of nickel catalysts during the conversion phase, the subsequent oxidation (at the stage of regeneration of the absorbent) and recovery (before starting a new cycle) obviously lead to redispersion of nickel particles. Possible redispersion in RedOx cycles is associated with a significantly lower molar volume of Ni in comparison with NiO [32]. It should be noted that redispersion related with the cyclic changes of atmosphere during ACC allows to develop the catalytic properties of the initially inactive materials such as solid Nichrome. After 100 cycles the initially smooth surface of the Nichrome wire is covered with particles of nickel stabilized by chromium oxide (Fig. 5). The specific catalytic activity of the mass of the "catalyst" is comparable to the activity of 1 % Pt/Al_2O_3 (see Fig. 3).

Fig. 3. Changes in the catalytic activity of Nichrome wire (*1*), platinum (*2*) and rhodium (*3*) catalysts of steam reforming of methane in ACC cycles [34].

Recovery of the active ingredient after the regeneration stage can be carried out by hydrogen either directly by hydrocarbon-steam mixture. While the recovery of hydrogen is easy, direct reduction of NiO by steam/methane mixture occurs only at temperatures above 700 °C and above, with the threshold temperature above which recovery process is possible, increases with the proportion of vapour in the mixture [34].

It is important to note that ACC increases the stability of the catalyst to carbonization and sulphur poisoning compared to conventional catalytic conversion [2, 35]. Purging the catalyst bed with air, which is regular during ACC, is a main way to remove deposits of carbon and sulphur from the catalyst surface [36, 37].

Thus, the catalysts based on nickel are the most promising for use in ACC. Although large-scale use of precious metals (rhodium, plati-

num) would be inappropriate because of their cost, a small amount of precious metal in the frontal layer can significantly facilitates recovery of nickel catalyst by the reaction steam/ methane mixture [34].

ABSORBENTS OF CO$_2$ FOR ACC

There are five basic requirements for high-temperature CO$_2$ absorbents during ACC: 1) high capacity; 2) high CO$_2$ selectivity, 3) the stability of the material for long-term tests, and 4) rapid sorption/desorption rate; 5) sufficient mechanical strength [38].

Oxides of alkaline earth metal during the interaction with carbon dioxide form carbonates. This property can be used to obtain high-regenerated CO$_2$ sorbents. The estimates of the equilibrium pressure of CO$_2$ over the carbonates of magnesium, calcium and barium at different temperatures are given in Fig. 6 [15].

Under CO$_2$ partial equilibrium pressure of 0.1 atm carbonates of magnesium, calcium and barium decompose at temperatures above 220, 760 and 1100 °C, respectively. Thus, under conditions of steam reforming of hydrocarbons efficient absorption of CO$_2$ is possible for the oxides of calcium and barium. Since regeneration of BaO requires very high temperatures that can be achieved only with expensive construction materials, most of the papers are devoted to research of CaO based materials.

Reaction of chemisorption of CO$_2$ by calcium oxide rarely comes to the end within a reasonable time, because CO$_2$ should diffuse through the surface layer of the product − calcium carbonate [39, 40]. Along with the temperature fall the depth of the reaction over a fixed period of time (dynamic capacity) rapidly decreases. A typical temperature above which absorber has a significant CO$_2$ dynamic capacity for CaO is about 550 °C [41], and it determines the operating temperature range at the stage of conversion from 550 to 750 °C.

Efficiency of chemisorbents largely depends on the conditions of their regeneration. Regeneration of calcium oxide is often carried out in air at temperatures of 800−850 °C [1, 4, 25]. Thus, the temperature difference between the stages of the sorption and regeneration may
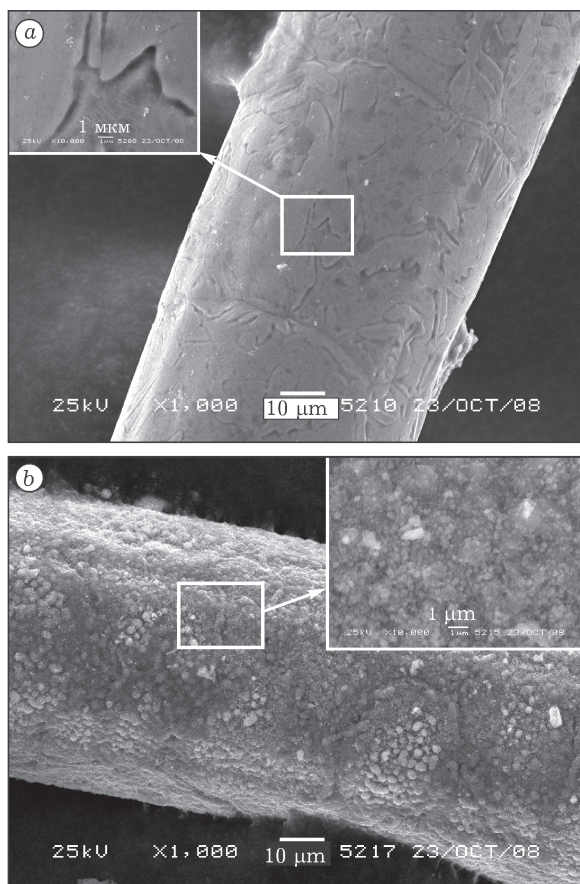

Fig. 5. SEM micrographs of nichrome wire: a − initial, b − after cyclic steam reforming at 800 °C [34].
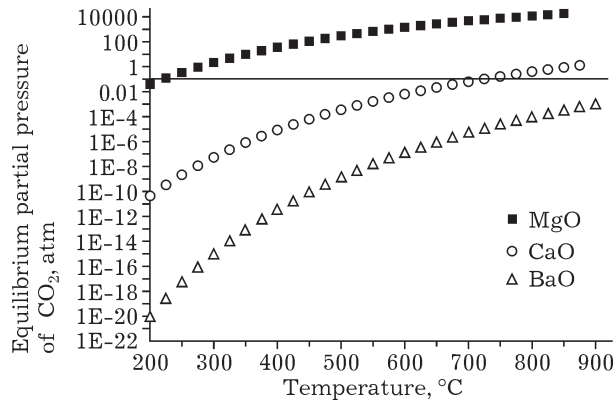
Fig. 6. Equilibrium partial pressure of CO$_2$ over various oxides of alkaline earth elements.

be several hundred degrees. Minimizing the cost of heat input for the absorber heating during regeneration requires the use of materials with high dynamic capacity.

The main problem with the use of CaO as the absorber is associated with rapid decrease in its dynamic capacity. For example, the capacity of CaO obtained by thermal decomposition of calcium carbonate in the first absorption of CO$_2$ is 90 % of the stoichiometric value, while it is typically less than 12 % after a few tens of cycles of CO$_2$ absorption and regeneration [42, 43]. For the processes in a fluidized bed some part of the absorbent can be removed with its replacement by fresh material [18, 44], but as for fixed bed reactors great attention should be paid to the stability of the sorptive capacity of the sorbent.
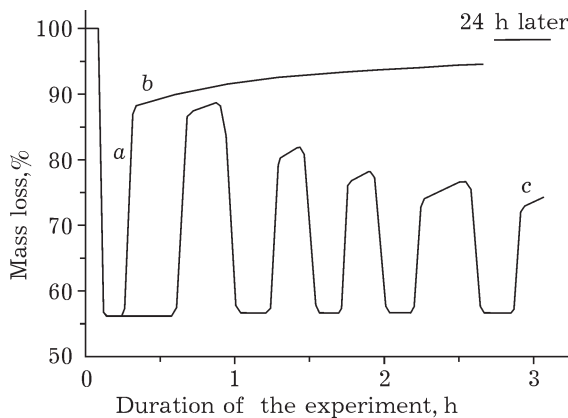
Ii is shown in [7] that oxide appearing after the first CaCO$_3$ decomposition does not completely react during re-carbonation reaction even after 1 day of the experiment. Two areas − the fast and slow − can be clearly seen at the curve of sorption of carbon dioxide by calcium oxide (Fig. 7, the area with increase in mass). Fast reaction on the porous grains of CaO occurs in the diffusion-controlled mode, when the rate of reaction is determined by the diffusion of reactants in the pores of the absorbent. This part of the curve is related with transformation of the surface layer of calcium oxide (see Fig. 7, *a*). After the formation of a dense layer of calcium carbonate the rate of carbon dioxide absorption is limited by CO$_2$ diffusion through the surface layer of carbonate. In this mode CO$_2$ carbonation proceeds very slowly and even after 24 h of reaction with CO$_2$ the process is not completed (see Fig. 7, *b*). The Pilling-Bedworth ratio (ratio of molar volumes of solid product and reactant) for the reaction of CaO carbonization is much higher than unity and is 36.9/16.5 = 2.23 [45]; it confirms the assumption about formation of gas-tight layer on the surface of the reacting CaO [7]. From cycle to cycle the capacity of the absorber decreases (see Fig. 7, *c*), and for longer cycles (Fig. 8, curve *1*) the rate of capacitance fall is much less than that for short cycles (curves *2*, *3*) It should be noted that attempts to increase the capacity of chemisorbent after a large number of cycles using a prolonged stage of sorption

Fig. 7. Change in mass on the CaO based chemisorbent: *a* − kinetic sorption area, *b* − the diffusion area of the sorption, *c* − conducting loops with a small contribution of the diffusion component. Temperature 886 °C, pressure of CO$_2$ at the stage of the sorption 1 atm [7].
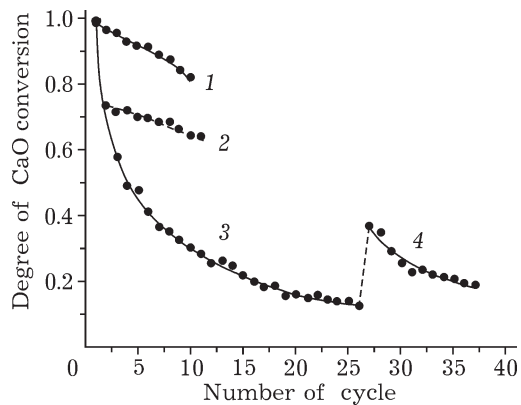

Fig. 8. Relationship between the degree of conversion of CaO in the reaction of CO$_2$ removal and the number of cycle: *1* − cycles of 24 h; *2*, *4* − one cycle of 24 h, followed by short cycles; *3* − short cycles. Temperature 886 °C, the pressure of CO$_2$ during the sorption 1 atm [7].

lead to a slight increase in the capacity of calcium oxide for several cycles, and after that its value returns to its initial value (see Fig. 8, curve *4*). According to the author [7] a quick binding of CO_2 by the whole volume of calcium oxide requires the radius of CaO particle be approximately equal to the thickness of a layer of $CaCO_3$ formed after the rapid phase of sorption. According to estimates given in the same paper the thickness of this layer is about 22 nm. However as it was shown in [46] nanometre particles of calcium oxide react rapidly and completely only in the first cycle, and then also lose their sorption capacity. The blocking of internal pores of the surface layer of calcium carbonate is indicated as one of the reasons for the fall of the sorption capacity [7]. Another more common cause of the calcium oxide capacity fall – is its sintering, in which there is enlargement of the primary particles of the source chemisorbent (Fig. 9) [47, 48]. An
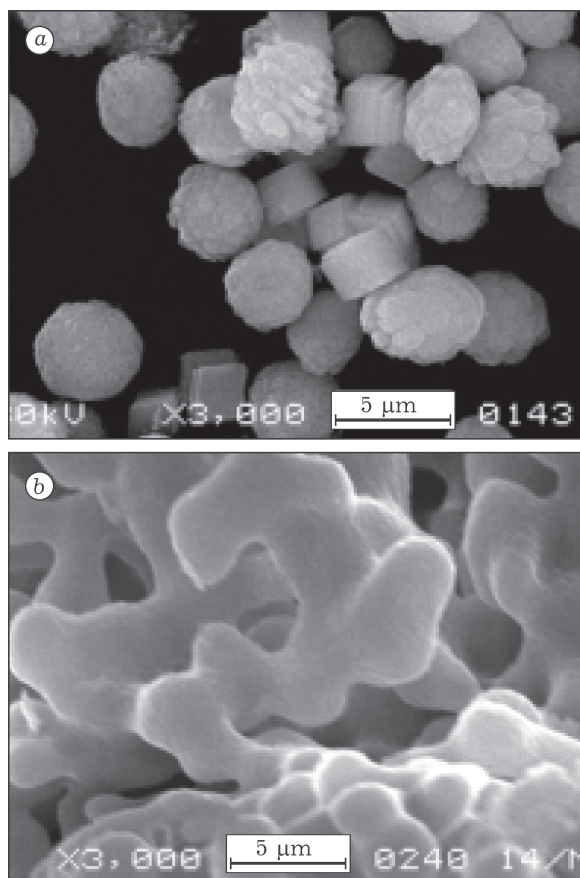

Fig. 9. Comparison of fresh calcium oxide (*a*) and that after 100 cycles of adsorption of CO_2/regeneration (*b*). The division on the scale corresponds to 5 μm [50].
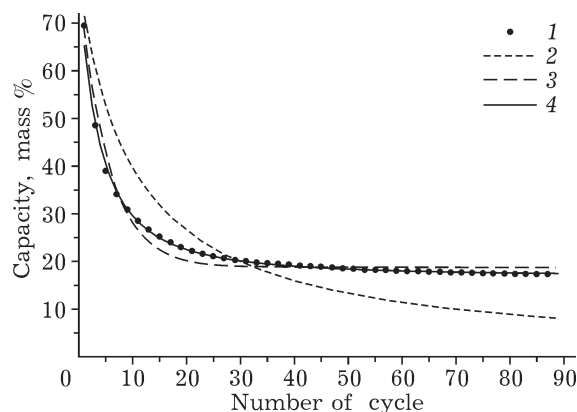

Fig. 10. Approximation of the CaO capacity reduction in various models of sintering [34, 47, 48]: *1* – experimental points, *2* – model of Wang, Anthony (2005), *3* – model of Abanades, Alvarez (2003), *4* – model of Lysikov, Okunev (2007).

empirical equation describing the dependence of capacity on the number of cycles is proposed in [6] (Fig. 10):

$$x_N = f^{N+1} + b \qquad (6)$$

where x_N is capacity of CaO in the cycle N; f is an empirical parameter responsible for the sintering rate of CaO and b is the residual capacity of the absorber, which is observed after a rather large number of cycles. This equation describes well the behaviour of the sorption properties only within the first ten cycles (correlation coefficient 0.97). For longer experiments, the correlation coefficient is much the worse. The authors of [49] modified eq. (6) basing themselves on the analysis of pore structure of CaO. It was proposed to divide the pores of CaO into two groups: those with a large pore size resistant to sintering and small pore size which turn into larger ones according to this point of view eq. (6) looks like following:

$$x_N = x_{N,m} + x_{N,w} \qquad (7)$$

where $x_{N,m}$ and $x_{N,w}$ are contribution to the capacity of CaO from the small and large pores in the N cycle, respectively. The authors [50] succeeded to obtain the following dependence of the capacitance of the number of cycles (see Fig. 10) given that the small pores disappear completely at the stage of sorption gradually moving to larger pores:

$$x_N = (f_m^N(1 - f_w) + f_w)x_{0,m} \qquad (8)$$

where f_m and f_w are coefficients corresponding to the loss of small pores and the formation of large pores at their expense, respectively;

$x_{0,m}$ is initial capacity of calcium oxide. This formula describes the fall in capacity of CaO significantly more effectively than the earlier one (correlation coefficient 0.99). However, as in the previous case, the approximation of the results of long-term experiments results in the significantly reduced accuracy of the description of CaO capacity. It should be noted that the proposed formula does not take into account the actual mechanism of sintering of CaO and are withdrawn on the basis of an empirical approach.

A more accurate expression for reducing of the sorbent capacity is obtained based on the conception of reduction of CaO reacting surface as result of sintering and shrinkage in the cyclic tests [43]. Pseudomorphic porous CaO particle with a size of the primary crystals of about 10 nm appears during decomposition of the small particle of calcium carbonate [51]. Simultaneously, a small shrinkage take place; as result the pseudomorphosis volume is somewhat less than that of the original non-porous particle of $CaCO_3$. Subsequent reaction with CO_2 leads to filling of voids, but the available pore volume is not sufficient for accumulation of stoichiometric amounts of CO_2. For this reason, after the fast stage of the reaction unreacted CaO remains, which can be accessed only in the diffusion through the solid. Repeat of the process leads to a complete sintering of small particles, the boundaries between these particles smear out and a connected skeleton of CaO appears as result. Interestingly, after the formation of the calcium oxide skeleton capacitance remains almost unchanged. The process is well described by a typical power function of sintering [52], adjusted for the residual capacity of p_4 (a value which is reached after the end of sintering) (see Fig. 10) [43]:

$$x_N = \frac{p_1}{(p_2 + N)^{p_3}} + p_4 \qquad (9)$$

where p_1 is the sintering rate constant; p_2 is the parameter depending on the intrinsic characteristics of the sorbent (porous, sintered *etc*); p_3 is the parameter that depends only on the mode of sintering ($p_3 \approx 1$ for CaO [43]). In the case where the capacity is expressed by the degree of conversion of calcium oxide, all the system parameters are dimensionless.

In addition, the authors of [43] proposed a method of forming a given morphology of the sorbent with high and stable capacity based on CaO. They showed that the calcination of powdered calcium carbonate at 1150 °C and above can enable to receive absorbents with a capacity of up to 25 mass %, stable for several thousand cycles.

Another approach to reduce the sintering is to use a textural promoter, reducing the speed of this process. Thermal treatment of the mixture 80−90 mass % of CaO with SiO_2 gives a durable material suitable for use in a fluidized bed [53]. During the thermal treatment of mixed oxides and the subsequent sorption of CO_2 a stable phase of the interaction of $Ca_5(SiO_4)_2CO_3$ composition is produced [54]. The absorption of carbon dioxide takes place with the participation of uncombined calcium oxide, while the carrier determines the mechanical strength of chemisorbent. According to [55] chemisorbent promoted with SiO_2 withstand pressures up to 320 atm. Capacity of the system reaches up to 50 mass % based on uncombined calcium oxide and 40 mass % based on total mass of chemisorbent. However, the use of materials containing SiO_2 in steam reforming of hydrocarbons is undesirable because at temperatures above 500 °C a volatile silicon hydroxide forms, which leads to the destruction of material and dusting [2].

Alumina may be used as another additive. Calcium oxide deposited on Al_2O_3 is very strong because its composition is similar to cement [56]. Unfortunately, because of the reaction of CaO with Al_2O_3 the material capacity is rather reduced in comparison with pure CaO [57]. Number of phase interaction of CaO and Al_2O_3 increases from cycle to cycle leading to a symbatical fall of absorbent capacity. Thus, for 75 mass % $CaO/Ca_{12}Al_{14}O_{33}$ there is a fall of capacity of more than two times for 56 sorption−regeneration cycles [58]. In addition, the regeneration of such chemisorbent does not permit overheating above 1000 °C because of the rapid reaction of CaO with a carrier [56].

In general, the use of promoters should be approached with caution if the absorber is exposed to temperatures above 800 °C, since the stability of mixed oxides to sintering is lower than the resistance of initial CaO. The exception is the heat-resistant magnesium oxide,

which does not form phases of interaction with CaO. A significant number of works is devoted to obtaining high temperature CO_2 chemisorbent be means of the calcination of dolomite, which are mixed calcium carbonate and magnesium ($CaCO_3 \cdot MgCO_3$) [59]. The decomposition of dolomite during the calcination occurs in steps: first the magnesium carbonate decomposes, which forms chemically inert and stable phase of periclase at high temperatures [22], and then calcium carbonate. In this way, chemisorbent on the basis of CaO deposited on MgO. Due to the frame of the periclase, which has high mechanical strength and abrasion resistance, such absorbent can be used in fluidized bed reactors [60]. CO_2 capacity of calcined dolomite is slightly lower than that of pure CaO because of significant amount of ballast MgO [13].
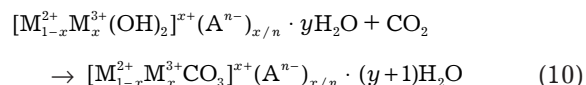
Despite the presence of an inert carrier the sintering of the active component is also observed in the CaO/MgO system [13]. One way to increase capacity is to regenerate the absorbent with steam at high pressure, which enable to convert calcium carbonate not into the oxide, but more easily carbonized hydroxide [21]. Carbonation reaction of calcium hydroxide takes place with virtually no change in the molar volume of the absorber (the Pilling−Bedworth ratio for this reaction is equal to 1.12), so a higher dynamic capacity of the absorbent can be achieved.

In addition to materials in which CaO acts as the active component there are other systems based on double oxides or hydroxides. For example, hydrotalcite promoted with potassium carbonate has a stable capacity in ACC [61]. Hydrotalcites usually have a chemical composition described by the formula

$$[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$$
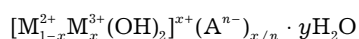
where M^{2+} and M^{3+} are cations of bivalent (usually Mg, Ca, Ni, Mn, Cu or Zn) and trivalent (Al, Cr) metals, respectively; A^{n-} are anions of $CO_3^{2-}, NO_3^-, SO_4^{2-}, Cl^-$; n is the anion charge, y is the degree of hydration of hydrotalcite, the value of x varies in the range from 0.1 to 0.35 [62, 63]. The compounds of this type have a layered structure. The first layer consists of cations Mg^{2+} and Al^{3+}, surrounded by tetrahedrons of the OH^- groups, and the intermediate layer is a hydrate of opposite charged anions, such as CO_3^{2-} [64]. The inter-

action with carbon dioxide at the first stage is caused by incorporation of sorbate into the anionic layer, and then by substituting OH^- groups on the CO_3^{2-}. Typically, the sorption in these systems is described by [38]

$$[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O + CO_2$$

$$\rightarrow [M^{2+}_{1-x}M^{3+}_x CO_3]^{x+}(A^{n-})_{x/n} \cdot (y+1)H_2O \qquad (10)$$

For hydrotalcite, the relationship between the capacity and the ratio of bi- and trivalent cations takes place, with the highest dynamic capacity achieved at a ratio of 1 : 1 [65]. On the other hand, the temperature and removal of CO_2 also affects the sorption properties of hydrotalcite. As it is shown in [66], the temperatures being up to 200 °C there is physical adsorption on the surface of the absorbent, and if it is 300 °C or above there is chemisorption, which can be described by Langmuir adsorption equation [61]. This observation is made on the basis of dependence of the sorption properties of hydrotalcite on temperature: with increasing temperature up to 200 °C hydrotalcite capacity gradually decreases and then begins to increase (Fig. 11) [65]. When cycling hydrotalcite in the temperature range 300−450 °C [67] their dynamic capacity decreases rapidly and reaches values of about 0.45 mol CO_2/kg$_{sorb}$ (~2 mass %) (Fig. 12) [61]. When using regeneration with water vapour a capacity of hydrotalcite decreases faster than in case of the re-
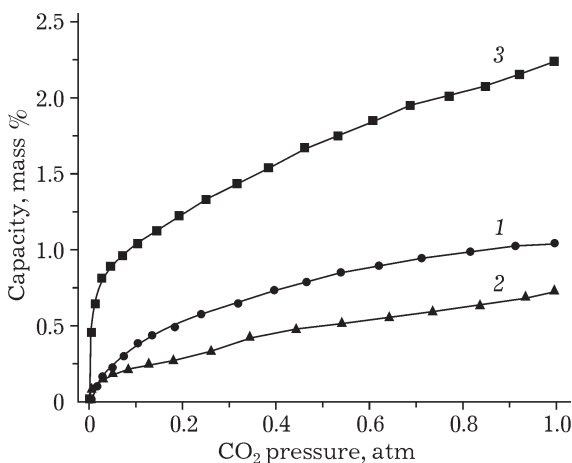

Fig. 11. Dependence of the absorption capacity of hydrotalcite $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2}$ from the pressure of CO_2 and sorption temperature [61], °C: 20 (1), 200 (2), 300 (3).
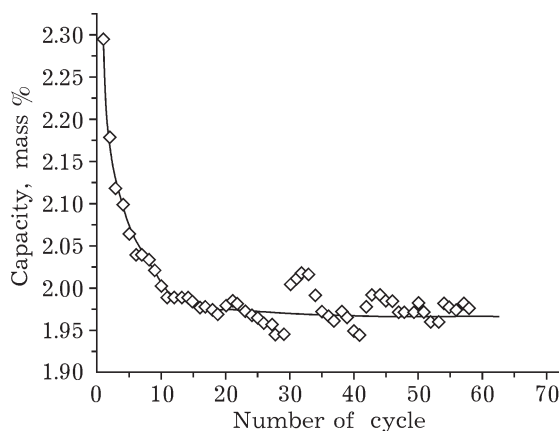
Fig. 12. Dependence of the capacitance $Mg_{1-x}Al_x(OH)_{2+x} \cdot yH_2O$ promoted K_2CO_3, depending on the number of cycle of CO_2 sorption/regeneration by pure nitrogen. The temperature of the experiment is 400 °C, the duration of one cycle is 2 h [61].

generation by dry nitrogen or by air [68]. In this context for the regeneration of chemisorbent in ACC usually carried out at temperatures of ~600 °C, it is worthwhile to use the air.

Because of oxidation of nickel catalyst during the regeneration of the absorbent, when hydrotalcite is used it is necessary to introduce an additional step of reducing the catalyst with hydrogen, since the direct reduction of NiO by reaction medium under these conditions is difficult. The use of catalysts based on precious metals, which do not require the intermediate reconstruction may be an alternative.

Thermal regeneration of hydrotalcite is disadvantageous because of their low capacity. In [61, 69, 70] the possibility of regeneration of hydrotalcite in the pressure swing adsorption mode. However, the low temperature-effective range of hydrotalcite has a negative effect on the kinetics of reaction (1), and defines a low degree of v conversion. In [69] the maximum hydrogen content was only 88−94 vol. %. Theoretical predictions of the possibility of hydrogen purity of 99.99 vol. % with the use of hydrotalcite as an absorbent of CO_2 [71] have not yet found experimental confirmation.

Another type of sorption systems are binary oxides such as zirconates [72], titanates and silicates of lithium, as well as double oxides of lithium and iron, nickel, *etc.* [73]. For example, lithium zirconate reacts with carbon dioxide in a reversible substitution reaction [74, 75]:
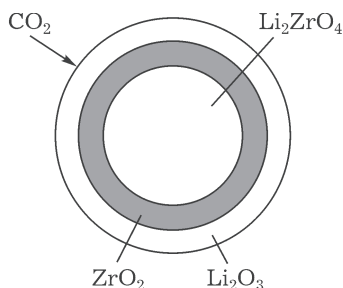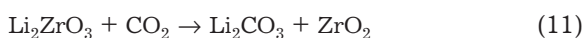

Fig. 13. Distribution of products and reactants in a grain of lithium zirconate after interaction with CO_2 [78].

$$Li_2ZrO_3 + CO_2 \rightarrow Li_2CO_3 + ZrO_2 \qquad (11)$$

However, nonpromoted lithium zirconate has a very low rate of CO_2 absorption [76], which is associated with steric hindrances in the course of the reaction (Fig. 13). During the interaction with carbon dioxide a layer of lithium carbonate forms on the grain surface, and a layer of zirconium oxide is beyond [75]. At the same time unreacted Li_2ZrO_4 remains in the grain core, which makes it inaccessible to CO_2 because of the weak diffusion of reactants through a layer of solid products [77].

In some studies a positive effect of the addition of potassium carbonate on the rate of adsorption of CO_2 by lithium zirconates is noted [76, 78]. According to the authors, this is due to the formation of the mixed melt of carbonates of lithium and potassium, which dissolves the reaction products [79], and it significantly improves the rate of diffusion of CO_2 to the unreacted core of the absorbent. Thus, the capacity of the systems based on zirconate of alkali metals up to 20 mass % can be provided for more than 50 cycles of adsorption/regeneration at 650 °C [74].

Silicate of lithium seems to have the highest capacity, their interaction with carbon dioxide proceeds in the reaction:

$$Li_4SiO_4 + CO_2 \rightarrow Li_2SiO_3 + Li_2CO_3 \qquad (12)$$

An extended temperature range (from room temperature up to 700 °C) and high specific capacitance, which can reach 30 mass % at a CO_2 pressure of 1 atm could be noted as advantages of silicates as well. According to the authors [73], this is due to a lower molecular weight of silicon compounds compared with the compounds of zirconium and other elements. The rate of CO_2 absorption can be increased by the addition
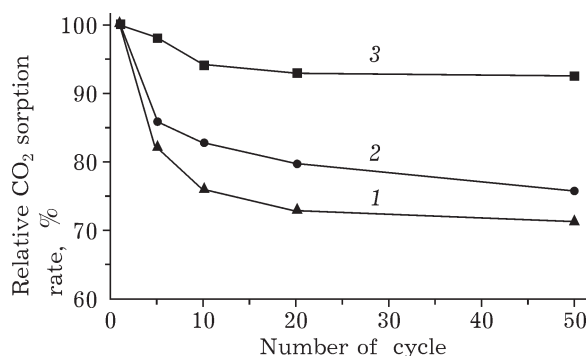
Fig. 14. Effect of potassium carbonate additives to the change in the rate of CO_2 absorption on Li_4SiO_4 in the cyclic tests (sorption conditions: 600 °C, pressure of CO_2 1 atm; regeneration conditions: 800 °C, air blowing at a pressure of 1 atm [1]): 1 − no K_2CO_3 additives, 2, 3 − mass fraction of K_2CO_3 is 2 and 5 %, respectively.

Fig. 15. Equilibrium partial pressure of CO_2 in the gas phase above the absorbents of different types depending on the temperature [1].

of potassium carbonate. Thus, the rate of sorption of CO_2 in the cycles for the systems potassium carbonate doped, decreased more slowly than for the pure samples (Fig. 14) [1].

Unfortunately, at low partial pressure of CO_2 these absorbents rapidly lose their sorption properties [80]. As it is shown in [73], the concentration of CO_2 necessary for the discharge of carbon dioxide from the air being 500 ppm, the capacity of lithium zirconate is only 1 mass % within two weeks of sorption. As the authors of the work explain, this is due to the order of reaction with respect to CO_2 which is close to 2.

On the other hand, a comparative analysis of the equilibrium pressures of CO_2 above different absorbent shows that the pressure of carbon dioxide on pure calcium oxide at the same temperatures is much lower than for the various alkali metal compounds discussed in this section (Fig. 15) [81]. Thus, the use of the precisely CaO based materials potentially allows better removal of carbon dioxide.

The additional problems with the use of absorbents containing alkali metals in ACC appear as result of catalyst poisoning. Melting of pure lithium carbonate takes place at a temperature of 730 °C [45]. The addition of carbonates of other alkali or alkaline-earth metals leads to the decrease of the temperature. As shown in [82], using the absorbent promoted by lithium carbonate, the hydrogen content can exceed 96 % in the first cycle. However, multicycle tests for lithium containing
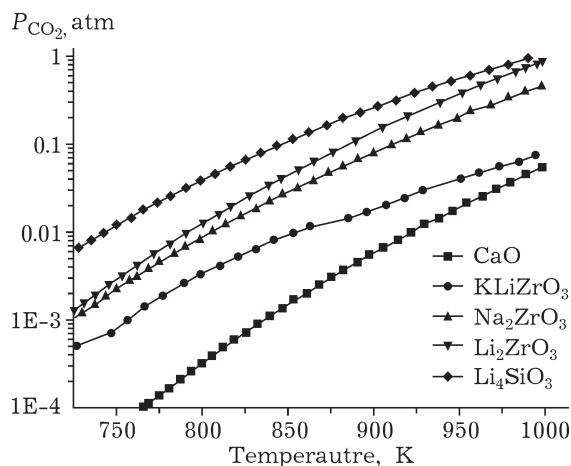
absorbents are not described in the literature. Apparently, at high temperature lithium carbonate transfer to the catalyst and poisoning of its active centres take place.

Such effect was not observed for the CaO based sorbents [1]. Moreover, the implementation of ACC in the laboratory and pilot reactors with the use of calcium oxide has demonstrated the stability of the catalyst and absorbent for hundreds of cycles [4, 83]. In this case the hydrogen content was more than 96 vol. % and the percentage of CO did not exceed 100 ppm. Thus, the prospect to implement ACC process on pure or deposited CaO is currently the most practicable one.

CONCLUSIONS

Absorption and catalytic conversion is of interest as an alternative few-stage way to produce hydrogen be means of steam reforming, especially in the case of low-tonnage production. For small hydrogen generators the scheme with two or more fixed bed reactors, loaded with a mixture of steam reforming catalyst and high temperature regenerable absorbent of CO_2 is preferred. Despite the frequency of ACC process in which materials are subjected to cyclic exposure of reducing and oxidizing atmospheres, the traditional nickel containing catalysts for the conversion are very effective and can be used, taking into account the characteristics of their operation. A periodic purge by

oxidant (air or water vapour) can process in ACC the fuel with high sulphur content or with the low of the vapour/gas ratio, which cannot be converted by conventional catalytic method.

The choice of absorbents of CO_2 has a significant influence on the purity of the resulting hydrogen. The absorbents on the basis of CaO, double alkali metal oxides and promoted hydrotalcite were the most actively investigated in the reaction of ACC. Low temperature of CO_2 adsorption by hydrotalcite does not allow to produce hydrogen with high purity, and their low dynamic capacity makes use of thermal regeneration is economically unjustified.

Oxides of alkali metals have a high and stable capacity, but poor kinetics of absorption of CO_2. The introduction of additional components (such as potassium carbonate) may improve the kinetics of absorption, but the question of the stability of the catalysts for steam reforming in the presence of molten carbonates of alkali metals requires further investigation. The best results are achieved in ACC by using calcium oxide. The conversion of methane by one stage can produce hydrogen purity higher than 96 vol. % with low CO content. The stability of the absorber and catalyst is confirmed by hundreds of cycles of tests in laboratory and pilot reactors. The main problem of the CaO based absorbents is sintered and the associated fall in the dynamic capacity. This problem is solved both by preliminary heat treatment of powder precursors of CaO, and through texture promotion of CaO by thermostable compounds (aluminates and silicates of calcium, magnesium oxide). Apparently, the process of ACC on the basis of CaO containing absorbents is the closest prospects for commercialization.

REFERENCES

1 Harrison D., *Ind. Eng. Chem. Res.*, 47 (2008) 6486.
2 Rostrup-Nielsen J. R. Catalytic Steam Reforming (Catalysis − Science and Technology). Berlin: Akad.-Verlag, 1984, Vol. 5, P. 280.
3 Song C., *Catal. Today*, 77 (2002) 17.
4 Lysikov A. I., Trukhan S. N., Okunev A. G., *Int. J. Hydrogen Energy*, 33 (2008) 3061.
5 Melnikov E. Ya. (Ed.), Spravochnik Azotchika, 2nd Ed., Khimiya, Moscow, 1987.
6 Abanades J. C., *Chem. Eng. J.*, 90 (2002) 303.
7 Barker R. J., *Appl. Chem. Biotechnol.*, 23 (1973) 733.

8 Bhatia S. K., Perlmutter D. D., *AIChE J.*, 26 (1980) 379.
9 Baade W. F., Parekh U. N., Raman V. S., Hoboken, Wiley-Intersci., New York, 2005, p. 759.
10 Balasubramanian B., Lopez Ortiz A., Kaytakoglu S., Harrison D. P., *Chem. Eng. Sci.*, 54 (1999) 3543.
11 Ortiz A. L. and Harrison D. P., *Ind. Eng. Chem. Res.*, 40 (2001) 5102.
12 Silaban A. and Harrison D. P., *Chem. Eng. Commun.*, 137 (1995) 177.
13 Silaban A., Narcida M. and Harrison D. P., *Chem. Eng. Commun.*, 146, 1 (1996) 149.
14 Yi K. B. and Harrison D. P., *Ind. Eng. Chem. Res.*, 44 (2005) 1665.
15 Ravdel A. A., Ponomareva A. M., Kratkiy Spravochnik Fiziko-Khimicheskikh Velichin, 8th Ed., Khimiya, Leningrad, 1983, p. 72.
16 Inventor's Certification No. 465897 USSR, 1974.
17 Inventor's Certification No. 1066634 USSR, 1981.
18 Inventor's Certification No. 747415 USSR, 1973.
19 Inventor's Certification No. 111894 USSR, 1958.
20 Inventor's Certification No. 778753 USSR, 1978.
21 Inventor's Certification No. 565697 USSR, 1975.
22 Inventor's Certification No. 796616 USSR, 1980.
23 Lukyanov B. N., Lysikov A. I., Okunev A. G., *Chem. Sust. Dev.*, 18, 2 (2010) 115.
URL: http://www.sibran.ru/English/csde.htm
24 RU Pat. No. 2271333, 2004.
25 Lee K. B., Beaver M. G., Caram H. S., Sircar S., *Ind. Eng. Chem. Res.*, 46, 14 (2007) 5003.
26 Manovic V. and Anthony E. J., *Environ. Sci. Technol.*, 41 (2007) 1420.
27 Lysikov A. I., Trukhan S. N. and Okunev A. G., 2nd World Congress of Young Scientists on Hydrogen Energy Systems (Proceedings), Turin, Italy, 2007.
28 Lysikov A. I., Okunev A. G., Trukhan S. N., II Mezhdunar. Simp. po Vodorodnoy Energetike (Thesises), Moscow, 2007.
29 Lysikov A. I., Trukhan S. N., Okunev A. G., Vseros. Konf. Laureatov Blagotvor. Nauch. Fonda im. K. I. Zamaraeva (Thesises), Novosibirsk, 2007, p. 31.
30 RU Pat. No. 2301772, 2007.
31 Zagoruiko A. N. and Okunev A. G., *React. Kinet. Catal. Lett.*, 91, 2 (2007) 315.
32 Lysikov A. I., Okunev A. G., III Mezhdunar. Simp. po Vodorodnoy Energetike (Thesises), Moscow, 2009.
33 Khimiya − Bolshoy Entsiklopedicheskiy Slovar' (Handbook), 2nd Ed., Bolshaya Nauchnaya Entsiklopediya, Moscow, 1998.
34 Lysikov A. I., Issledovaniye Poglotiteley i Katalizatorov dlya Absorbtsionno-Kalaliticheskoy Konversii Metana v Nepodvizhnom Sloye (Candidate's Dissertation in Chemistry), Novosibirsk, 2009.
35 Oudar J. and Wise H. (Eds.), Deactivation and Poisoning of Catalysts, Marcel Dekker Inc., New York, 1985, p. 99.
36 Figueiredo J .L., Trimm D. L., *J. Catal.*, 40, 2 (1975) 154.
37 Baker R. T. K. and Sherwood R. D., *J. Catal.*, 70, 1 (1981) 198.
38 Yong Z., Mata V. and Rodrigues A. E., *Sep. Purif. Technol.*, 26, 2−3 (2002) 195.
39 Bhatia S. K. and Perlmutter D. D., *AIChE J.*, 29, 1 (1983) 79.
40 Gupta H. and Fan L. S., *Ind. Eng. Chem. Res.*, 41, 16 (2002) 4035.

41 Linares-Solano A., Almela-Alarcon M. and Salinas-Martinez de Lecea C., *J. Catal.*, 125 (1990) 401.

42 Grasa G. S. and Abanades J. C., *Ind. Eng. Chem. Res.*, 45, 26 (2006) 8846.

43 Lysikov A. I., Salanov A. N. and Okunev A. G., *Ind. Eng. Chem. Res.*, 36, 13 (2007) 4633.

44 Abanades J. C., Anthony E. J., Wang J. S., Oakey J. E., *Environ. Sci. Technol.*, 39, 8 (2005) 2861.

45 Rabinovich V. A., Khavin Z. Ya., Kratkiy Khimicheskiy Spravochnik (Handbook), 2nd Ed., Khimiya, Leningrad, 1978, p. 42.

46 Barker R. J, *J. Appl. Chem. Biotechol.*, 24 (1974) 221.

47 Alvarez D. and Abanades J. C., *Ind. Eng. Chem. Res.*, 44, 15 (2005) 5608.

48 Wang J. S. and Anthony E. J., *Ind. Eng. Chem. Res.*, 44, 3 (2005) 627.

49 Abanades J. C. and Alvarez D., *Energy Fuels*, 17, 2 (2003) 308.

50 Abanades J. C., Anthony E. J., Lu D. Y., Salvador C., Alvarez D., *AIChE J.*, 50, 7 (2004) 1614.

51 Beruto D. T., Searcy A. W. and Kim M. G., *Thermochim. Acta*, 424, 1−2 (2004) 99.

52 Geguzin Ya. E., Fizika Spekaniya, Nauka, Moscow, 1967, pp. 55−91.

53 US Pat. No. 4330430, 1982.

54 US Pat. No. 4284528, 1981.

55 US Pat. No. 4231760, 1980.

56 Li Z. S., Cai N. S. and Yang J. B., *Ind. Eng. Chem. Res.*, 45, 26 (2006) 8788.

57 Li Z.S., Cai N. S., Huang Y. Y., Han H. J., *Energy Fuels*, 19, 4 (2005) 1447.

58 Li Z. S., Cai N. S. and Huang Y. Y., *Ind. Eng. Chem. Res.*, 45, 6 (2006) 1911.

59 Kurdyumov S. S., Brun-Tsekhovoy A. R., Rozental A. L., *Neftekhim.*, 36, 2 (1996) 142.

60 Johnsen K., Ryu H. J., Grace J. R., Lim C. J., *Chem. Eng. Sci.*, 61, 4 (2006) 1195.

61 Hufton J. R., Mayorga S. and Sircar S., *AIChE J.*, 45, 2 (1999) 248.

62 Basilea F., Fornasaria G., Gazzanob M., Vaccaria A., *Appl. Clay Sci.*, 16, 3−4 (2000) 185.

63 Mastalir A., Patzko A., Frank B., Schomacker R., Ressler T., Schlogl R., *Catal. Commun.*, 8, 11 (2007) 1684.

64 Reijers H. T. J., Valster-Schiermeier S. E. A., Cobden P. D., Brink R. W. van den, *Ind. Eng. Chem. Res.*, 45, 8 (2006) 2522.

65 Yong Z., Mata V. and Rodrigues A. E., *Ind. Eng. Chem. Res.*, 40, 1 (2001) 204.

66 Sircar S., Anand M., Carvill B. T., Hufton J., Mayorga S., Miller B., Proc. US DOE Hydrogen Program Rev., 1995, p. 815.

67 Anand M., Hufton J., Mayorga S., Nataraj S., Sircar S., Gaffney T., Proc. US DOE Hydrogen Program Rev., 1996, p. 537.

68 Hufton J. R., Weigel S. J., Waldron W. F., Rao M. B., Nataraj S., Sircar S., DOE-Air Products Co-operative Agreement. # DEFC36-95G010059, Final Report, 2000.

69 Waldron W. E., Hufton J. R. and Sircar S., *AIChE J.*, 47, 6 (2001) 1477.

70 Ding Y. and Alpay E., *Chem. Eng. Sci.*, 55, 18 (2000) 3929.

71 Lee K. B., *Ind. Eng. Chem. Res.*, 46, 14 (2007) 5003.

72 Ohashi T. and Nakagawa K., Mater. Res. Soc. Symp. Proc., 47 (1999) 249.

73 Kato Y., Yamada M., Kanie T., Yoshizawa Y., *Nucl. Eng. Des.*, 210, 1−3 (2001) 1.

74 Nakagawa K. and Ohashi T., *J. Electrochem. Soc.*, 145, 4 (1998) 1344.

75 Nakagawa K. and Ohashi T., *Electrochem.*, 67, 6 (1999) 618.

76 Ida J., Xiong R. T. and Lin Y. S., *Separ. Purif. Technol.*, 36, 1 (2004) 41.

77 Xiong R. T., Ida J. and Lin Y. S., *Chem. Eng. Sci.*, 58, 19 (2003) 4377.

78 Ida J. and Lin Y. S., *Environ. Sci. Technol.*, 37 (2003) 1999.

79 Thompson A., *Chemistry in Britain*, 20, 11 (1984) 1029.

80 Yi K. B. and Eriksen D. O., *Separ. Sci. Technol.*, 41, 2 (2006) 283.

81 Ochoa-Fernбndeza E., Haugena G., Zhaoa T., Rшnninga M., Aartunb I., Bшrresenb B., Rytterb E., Rшnnekleivb M., Chen D., *Green Chem.*, 9 (2007) 654.

82 Yi K. B., Meyer J. and Eriksen D., Nordic Hydrogen Seminar, Oslo, 2006.

83 Li Z. S., Cai N. S. and Yang J. B., *Ind. Eng. Chem. Res.*, 45, 26 (2006) 8788.