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Heat-conducting catalysts for the reactions at medium temperatures

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Abstract

Highly active composite catalysts having good thermal technical and mechanical properties were developed for the reactions at middle temperatures. These composite catalysts consist of the catalytic active component, metal powder and loosening material. These composites have excellent heat-conductivity (above 10 W/(m K)) and strength. The catalyst loading to composite is as high as 1–1.2 g/cm^3. At that, catalysts retain their activities, while the effectiveness factors of the catalyst usage are even higher than for the traditional pellets in the tubular fixed bed reactor (e.g. 50% versus 35% for the water gas shift reaction). The scheme of catalyst layer design is proposed, having effective mass- and heat-exchange and low resistance to the reaction gas flow.

Keywords: Heat-conducting catalysts; WGSR; Selective methanation of CO

1. Introduction

Routine catalysts: metal oxides or metals supported on oxides have low thermal conductivity. Heat transport from the catalyst grain to the reactor wall occurs mostly through the reaction gas. Low heat transfer coefficient for the ‘‘gas–solid’’ interface determines the effective radial heat-conductivity of the fixed catalyst bed being as low as 0.3–0.5 W/(m K). For the catalytic processes with strong thermal effects (both, absorption or release of heat) the tubular fixed bed reactors are often used having the tube diameter as small as 20–30 mm. Even in the tube of such a diameter the radial temperature drop could achieve 20–30 K, and it is higher for larger tubes [1,2].

Meanwhile, many processes need very isothermal conditions to be efficient. It is especially important for the processes, which are operated close to the thermodynamic equilibrium or for those characterised by a sharp temperature sensitivity of the process selectivity [3]. Water gas shift reaction (exothermal) and methane steam reforming (endothermic) are the examples of such processes. Fig. 1 shows another example: the preferential CO methanation in the mixture of CO (1%), CO_2 (20%), H_2O (18%) and H_2 (61%) for the pure hydrogen production. The experimental points show the temperature dependence of the proportion of hydrogen consumed to hydrogenate CO with respect to the total amount of hydrogen consumed. The data show clearly that the selectivity of hydrogen consumption to CO hydrogenation is high at below 490 K. The reaction temperature increase leads to a dramatic drop of the selectivity due to the thermal activation of CO_2 hydrogenation process [4,5].

Radial temperature drop could be significantly diminished by the use of heat-conductive elements introduced into the reactor. Recently in Corning Inc. the method and process of preparation of metal monoliths with high heat-conductivity have been developed [6]. The study of such a monoliths produced from porous copper and aluminium in ref. [7] has shown that their thermal conductivity is about 10–20 W/(m K) providing the heat transfer of 1000 W/(m^2 K). It was shown that the characteristics of the monolith meet the demanding of heat transfer for highly exothermic reactions. In ref. [8] on an example of the metal monolith produced from copper, excellent radial distribution of heat owing to high heat-conductivity of structure is shown.

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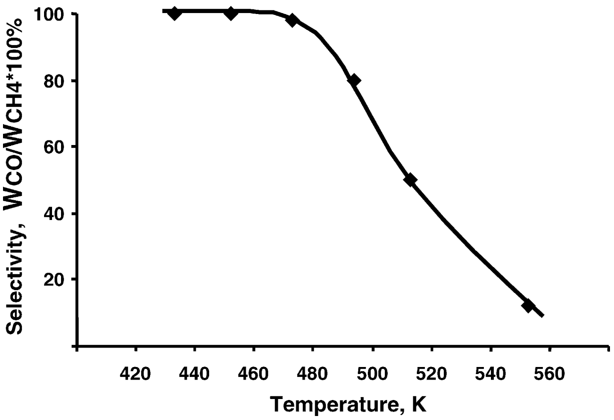

Fig. 1. Temperature dependence of the selectivity of preferential CO methanation in the reaction mixture of CO (1%), CO_2 (20%), H_2O (18%) and H_2 (61%) at 12000 h^{-1}, Ni-based catalyst.

Authors consider as a headache the heat transfer from a monolith to a wall of a reactor.

The most efficient the heat transfer could be, if these heat-conductive elements are the catalytic active particles, for example, metal- and catalyst-containing composites. There are quite a few composite materials, which have excellent heat-conductivity; however, are not suitable for catalytic activation, since their preparation needs sintering at high temperatures [9]. The high temperature sintering kills many of the supported catalysts causing sintering of the active metal particles. On the other hand, many works report the use of reactors with the catalyst introduced into metallic foams, over metallic plate, etc. [10,11]. These metallic supports have high heat-conductivity and direct metal–metal contact with heat-exchangers or with the reactor wall. The main problem is to fix the active component over the metallic surface and this problem is not yet solved, the catalyst can peel of the metallic support during the operation. That is why such reactors are not commonly used at present.

The topic of the present study is finding the ways to prepare the metal-oxide composite catalysts for the reactions at medium temperatures: water gas shift reaction, preferential CO methanation. For these processes, the suitable catalysts are usually prepared (i.e. calcined, activated) at medium (below 673 K) temperatures and are not very thermostable. One should not treat these catalysts at above 673–723 K.

2. Experimental

Catalytic active thermal conductive composite plates (TCP) were prepared on the base of the set of oxide Cu-, Co-, Ni-containing catalysts. Copper metal powder of a dendrite type structure was used as a metal component and copper hydroxocarbonate, as loosening component. Carefully mixed components were pressed and calcined at adjusted temperature in the inert gas flow.

The homogeneity of the components distribution on the surface of TCP was checked by optical microscope MBS-2. The front-mounted TCP surface images were obtained by digital camera Konica Minolta DiMAGE Z3. Total surface area of TCP was measured by BET method. The mechanical strength of TCP was determined by the measuring of the stress, destroying the plate. The estimation of thermal conductivity of TCP was performed by Wiedemann–Franz equation from experimental data on specific electroconductivity [12].

The efficiency of commercial Cu/Zn/Al catalyst in the composition of TCP was determined by the comparison of water gas shift reaction rate constants on TCP and on the small granules of 0.25–0.5 mm of the catalyst. The experiment was performed in an interval of temperatures 450–520 K in the gradientless reactor at 0.1 MPa far from the equilibrium gas mixture composition. The initial gas composition was $CO:CO_2:H_2 = 18:10:72$, steam:gas ratio = 0.4.

3. Results and discussion

The variations of the components ratio (oxide catalyst, copper metal, copper hydroxocarbonate) and fractional compositions have shown that the effective TCP may be obtained from the 0.1–0.2 mm granules with the stress of pressing of 1.7–3.0 tonnes/cm^2. Optimal calcination temperature was 623–723 K. TCPs, obtained at these conditions, possess of high thermal conductivity and high mechanical strength. The destruction of the plates occurred at the stress on the face plane 230 tonnes/cm^2.

The activity of the TCP in great extend depends on the portion of the surface of TCP formed by the catalyst's active mass. This characteristic depends on the homogeneity of the components distribution. Fig. 2 shows the typical optical microphotograph of the typical TCP surface, prepared from the commercial WGSR CuZnAl oxide catalyst. The observed light spots present the reinforcing metal particles, more dark spots—catalyst particles. Microphotograph shows the homogeneous distribution of the catalysts mass on the plate's surface. Specific surface area of TCP by BET method is about 100 m^2/g. It is to be referred to the surface of active catalytic mass, since specific surface value of copper metal skeleton is about 0.5 m^2/g.

For the plates of a hollow disc shape of 18 and 8 mm in diameter and 2 mm in height the 50–55% efficiency is determined, while for the traditional pellets of 4 mm × 5 mm the efficiency is not higher than 30–35%. At the same time the TCPs have high heat-conductivity about 10 ± 2 W/(m K) according to our estimations. Experimental temperature field on the TCP hollow disc, measured in the hydrogen oxidation reaction, corresponds to the thermal conductivity 10–15 W/(m K). In water gas shift reactor such conductivity will provide the temperature gradient not more than 1–2 K. These results are in agreement with the results of [7].

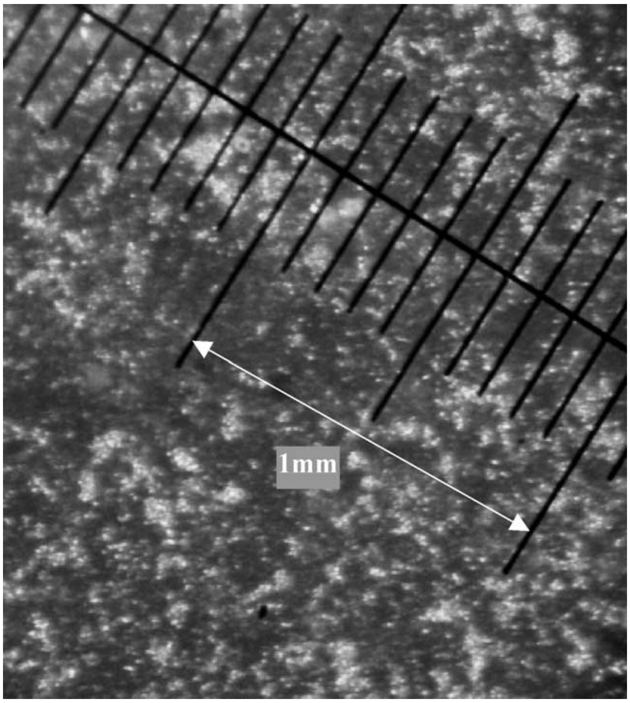

Fig. 2. Optical microphotograph of the front-mounted TCP's typical surface.

It is common knowledge that Cu/Zn/Al catalyst operates at 450–520 K [13,14]. In conventional multiple-shell reactors owing to the non-homogeneity of hydrodynamic resistance in catalyst bed and its low thermal conductivity the hot spots arise. As a result the size of copper metal crystals increases because of the agglomeration of dispersed particles, activity of the catalyst decreases significantly. The application of Cu/Zn/Al catalyst in the form of a TCP solves the problem of heat transfer in radial direction, no hot-spotting arising. In such a way the stability of catalyst operation is improved. Data on the study of thermal regimes in the model reaction of hydrogen oxidation will be published separately.

With respect to the application of designed composites, we consider different versions of the catalyst bed and reactor design in order to organise isothermal catalyst bed with low hydraulic resistance.

The effective application of TCPs may be realised in the reactor providing: (1) the direct contact between TCP and heat-exchange device (for example, between the reactor wall and heat-exchanger); (2) intensive mass transfer to each of the sides of TCP; (3) low resistance to the gas flow. It is achieved by the fixing of the plates of any shape on the perimeter of reactor and placing the plates on some fixed distance from each other so that to provide the full streamline of each plate from each of the sides.

Further, the variants of the catalytic reactor's design are considered, which provide the direct contact between TCP and cooling agent: (a) through walls of reactor and (b) through a wall of the tube in the centre of reactor. The schemes from Fig. 3 show the catalyst's bed design and distribution of reaction gas and cooling agent.

(a) The TCPs are fixed athwart to gas flow to two or three walls and have a gaps for passing of reaction gas along a layer serially at the left and to the right of a plate (Fig. 3a). The plates of 25 mm × 25 mm × 2.5 mm in size have the gap in between the plates of about 1–1.5 mm and the same side gap. This scheme provides the effective mass-exchange for each the side of the plate. The pressure drop in the catalyst bed, at passage of 1 m^3/h, is about 0.1–0.2 bar.

(b) The TCPs of rectangular or hollow disc shape are stringed on the tube. Cooling agent passes through the tube. The distance between the plates is about 1.0–1.5 mm and is fixed by the narrow rings. Plates are

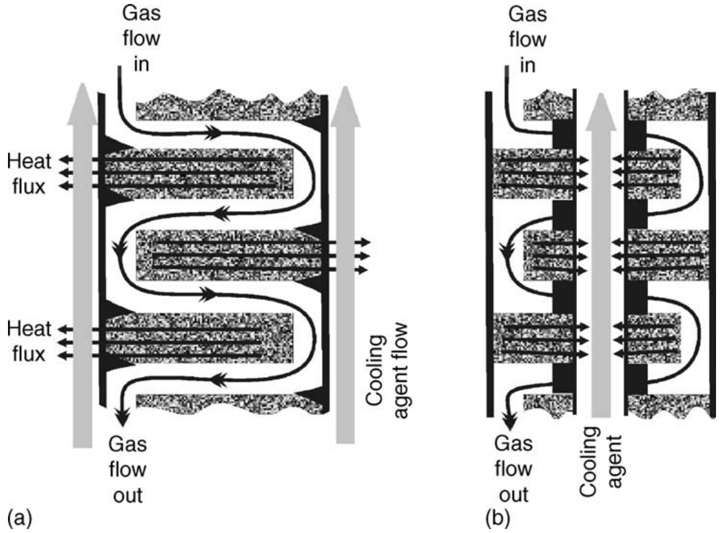

Fig. 3. The schemes of catalytic layer design and the distributions of the reaction gas and cooling agent with outer (a) and inner (b) heat-exchange.

placed on the tube with a gap of 1–2 mm between the sides of a reactor and a plate, serially on the right and at the left, while other sides of plates densely adjoin to walls of a reactor. The reaction gas mixture enters in a top of reactor on a surface of the first plate and moves downwards, flows round the top and bottom sides of plates. (Fig. 3b).

4. Conclusions

Highly active composite catalysts having good thermal technical and mechanical properties were developed for the reactions at middle temperatures. These composite catalysts consist of the catalytic active component, metal powder and loosening material. The scheme of catalyst layer design is proposed, having effective mass- and heat-exchange and low resistance to the reaction gas flow.

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