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Compact reactor for water gas shift reaction over thermal-conducting catalysts

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Abstract

Thermal conductive catalyst plates (TCP) for compact WGSR reactors were prepared and studied. High thermal conductivity of 2.5–5 W (m K)$^{-1}$ can be achieved, while the effective catalytic activity of TCP is even higher than that of the commercial size catalyst grains. TCP can be efficiently used for temperature sensitive exothermic reactions in compact apparatuses with controlled temperature profile. Using the TCP reactor WGSR of the fuel gas containing 12% of CO down to 1% of residual CO can be performed in one stage at GSHV of above 6000 h^{-1}. The TCP shape and the way of arrangement are important for the reactor performance and should be in the focus of our future studies.
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Keywords: WGSR; Compact reactor; Thermal-conducting catalysts; CO removal

1. Introduction

Decreasing the size of the reactors for the synthesis gas conditioning (water gas shift reaction, WGSR, and fine CO removal) makes an appeal to the researches due to the need in compact generators of pure hydrogen for fuel cell applications. For this purpose, a rather small scale reactor with optimal productivity related to a reactor volume is needed. In this case, the tubular bed reactors having the optimal temperature profile along the catalyst bed axis may be fruitful. Such an approach to optimizing the WGSR reactor was reported in Refs. [1,2]. For effective reactor heat abstraction, tubular reactors with the tube diameter 50–60 mm are used. Since the effective heat conductivity coefficient of a catalyst bed in the direction transverse to the gas flow does not exceed 0.5–1 W (m K)$^{-1}$, the radial temperature difference in the tubular catalyst bed for WGSR reaches 20–30 °C [3,4].

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 for the preparation of the metal monoliths with high heat conductivity have been developed [5]. The study [6] showed that thermal conductivity of such a monoliths produced from porous copper and aluminium is about 10–20 W(m K)$^{-1}$ and it provides the heat transfer of 1000 W(m^2 K)$^{-1}$. In Ref. [7], excellent radial distribution of heat owing to high heat conductivity of structure is shown when using the metal monolith produced from copper. Authors considered as a headache the heat transfer from a monolith to a wall of a reactor. Their recent results showed that heat transfer coefficient at the wall-to-monolith gap is very high and exceeds 400 W(m^2 K)$^{-1}$ at appropriate wall-monolith clearance [8].

The most efficient heat transfer could be achieved, provided 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 (see e.g. [10,11]). These metallic supports have high heat conductivity and direct metal–metal contact with heat exchangers or with the

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reactor wall. The main problem is to fix the active component over the metallic surface. This problem is not yet solved and the catalyst can peel of the metallic support during the operation.

In our present paper, we report on the possibility of efficient solution of the problem of intense radial heat abstraction and axial temperature profile control in the water gas shift reaction (WGSR) catalyst bed by: (1) using of a composite catalyst with high thermal conductivity of the catalyst body and (2) efficient arrangement of the thermal conductive composite catalyst bodies in the reactor.

2. Experimental

2.1. Thermal-conductive catalyst plates (TCP) preparation

The reported catalyst for water–gas shift reaction is a composite with high catalytic activity and thermal conductivity no less than 1 W (m K)$^{-1}$, which consists of particles of a catalytically active oxide component and heat conducting metal particles acting simultaneously also as reinforcing component. Such composites were prepared by a sequence of operations commonly used in powder metallurgy that includes: (1) preparation of a mixture of powders of a catalytically active oxide component, a metal and a porophore component; (2) mixture densification (pressing); (3) sintering at elevated temperatures. In present research, the powder of Cu-Zn-Zr WGSR catalyst containing 40 at.% of Cu and prepared according to the invention [12] was mixed with electrolytic metallic Cu powder of 20–50 μm in size having dendrite structure and malachite (as porophore), then pressed at 170–220 MPa (i.e. 1.7–2.2 tonnes cm^{-2}) to the 2.4–2.6 mm plates, which after all were sintered at 450 °C in flowing argon.

2.2. Thermal conductivity measurements

The effective thermal conductivity of TCP composites was measured using the TCP cylindrical plates of a greater thickness, which were prepared by the above-described procedure. A sample of TCP was placed between two identical metallic cylinders with known heat conductivity having the same diameter and polished basal surfaces. Two E-type thermocouples were sealed to each contacting surface of cylinders at the half-radius position. Thermal flux was organized by thermostating of the metallic cylinders outer surfaces at two different temperatures. Accuracy of thermal conductivity measurements was approx. 15%.

2.3. Catalytic studies

Three series of catalytic studies were performed.

Catalytic studies of catalyst fine fraction (0.25–0.5 mm), traditional-shape catalyst pellets (5 mm × 5 mm) and unarranged TCP plates were performed in the gradientless reactor with circulated gas flow at CO content in dry feed gas 12 vol.%, steam:gas ratio 0.6, atmospheric pressure. Measurements were performed at different temperatures in the range from 250 to 350 °C, the first rate kinetic constants were calculated. Performance of TCP plates was estimated as the effectiveness factor of catalytic substance usage, i.e. as the ratio of the experimental specific activity of TCP plate to that of the same catalytic substance as fine grains.

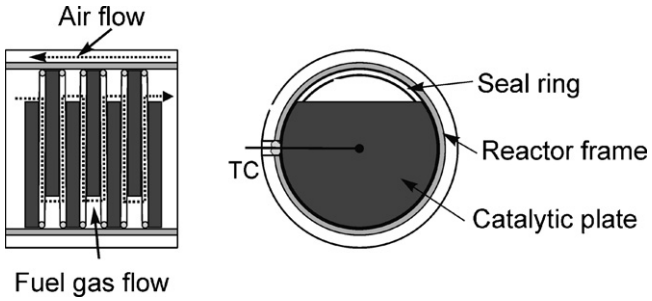

Fig. 1. Scheme of the segment TCP plates arrangement in the reactor TCP-2.

Additionally, two series of catalytic tests were performed using TCP plates arranged to the specially designed and manufactured TCP reactors. Reactor TCP-1 was designed to study catalytic performance of a square TCP plate, arranged in a set of 5 square plates made of inert metal (stainless steel) at realistic linear gas velocities. The size of the TCP plate and the inert plates was 20 mm × 20 mm, their thickness was 2.1 mm. This reactor was studied using the gas flow circulation with the gas flow rate of 0.4 $m^3_{STP}\,h^{-1}$.

Reactor TCP-2 was designed to study TCPs, having the base with the shape of circle segment. Fig. 1 illustrates the geometry of TCP and the way of their arrangement in the reactor volume. Reactor construction provided good thermal contact between TCP boundaries and the reactor wall. The temperature profile of the reactor was controlled by a countercurrent air flow in the external cooler. Temperature profile could be optimized by changing three parameters: inlet temperature of reaction mixture, inlet temperature of cooling air and air flow rate. The presence of massive metallic parts at the inlet and outlet of the reactor had certain impact to the temperature profile shape. The experimental temperature profile was collected by thermocouples, placed through the perforation in the cooling jacket and reactor wall into the reaction zone (see Fig. 1). TCs were placed in the gaps between TCP plates at approx. the center of the reactor tube. The clearance between the thermocouple jacket and perforation wall was sealed by silicon mastic. Five thermocouples were placed at different axial positions. The sixth thermocouple was placed at the outlet of the reactor.

Reactor contained 160 TCPs with diameter of 25 mm, thickness of 2.1 mm, chink between the TCPs of 1.2 mm. TCP were prepared by pressing at 170 MPa and sintering at 400 °C. Total amount of Cu-Zn-Zr catalyst in the reactor volume was 180 g. The reactor has length of 530 mm and total volume of 260 cm^3. The volume of voids is approx. 45%. The catalytic tests of TCP-2 were performed using the fuel gas produced by steam reforming of methane at the feed rate of methane 0.25 $m^3_{STP}\,h^{-1}$. The fuel gas flow was approx. 1.1 $m^3_{STP}\,h^{-1}$. Steam:(fuel gas) ratio was varied from 0.35 to 0.65. The optimal temperature profile described below was achieved at the inlet temperature of the reaction mixture, $T_{\text{inlet rm}}$, = 380 °C, inlet temperature of cooling air, $T_{\text{inlet air}}$ = 250 °C, flow rate of cooling air, $V_{\text{air}} = 2.2\,m^3_{STP}\,h^{-1}$. It is noteworthy that no additional

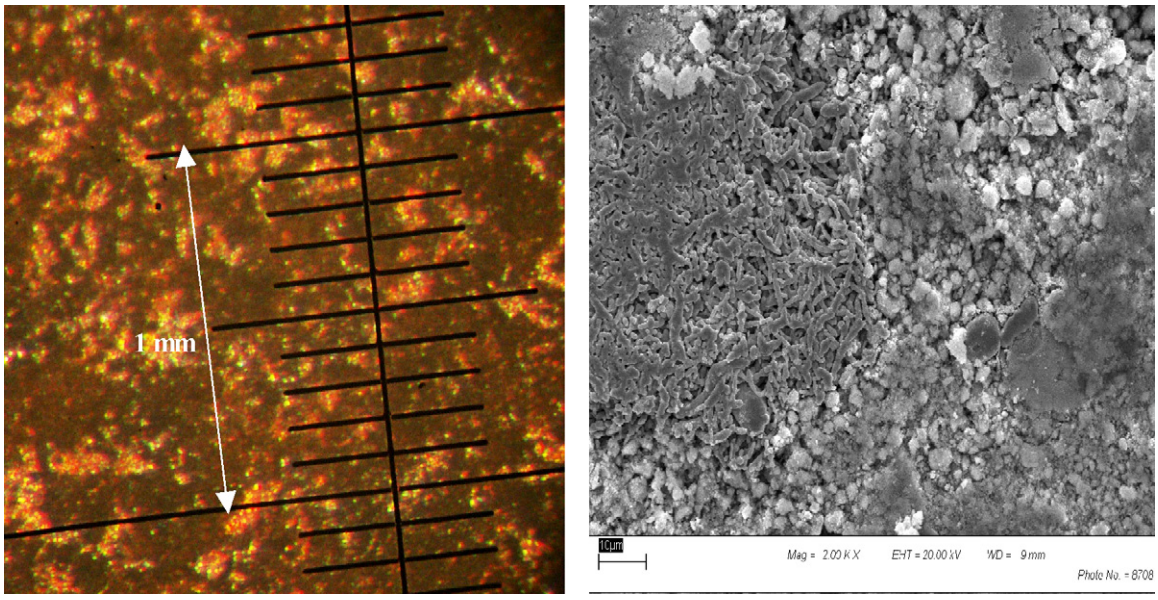

Fig. 2. Optical (left) and scanning electron (right) micrographs of a typical heat conducting catalyst plates. Scale bar at the right graph is 10 μm.

heating of the reactor or the outer surface of cooling jacket was applied after the steady-state had been achieved.

3. Results and discussion

3.1. Homogeneity of components distribution in the TCP

Fig. 2 shows the optical and scanning electron microscope images of a typical thermal-conducting catalyst plate (TCP). One can see that metallic copper and active component particles are evenly distributed through the TCP catalyst. This allows formation of a connected cluster of metallic copper in a plate providing high mechanical strength and heat-conductivity.

3.2. Thermal conductivity of TCP

The thermal conductivity of the TCP obviously correlates to the metallic copper content. Increase in thermal conductivity is due to electronic contribution of the metallic copper framework to the heat transfer processes. According to the percolation theory [13], conductivity appears in the three-dimensional mixture of conductor and dielectric particles, when the fraction of conducting particles exceeds the critical value x_c (percolation threshold). This threshold is $x_c = 0.31$ for cubic packing of spherical particles [13,14], while for free packing of balls having the same size it is as low as 0.15–0.16. This value does not significantly change if the conducting balls have the size different from dielectric (the value of 0.17 is reported in Ref. [13]). Fig. 3 shows that an improvement in the studied composites thermal conductivity can be obtained by introducing above 10–12 vol.% of metallic copper. Thus, for the composites under the study, the threshold value of copper content is as low as 0.11, which should be due to dendritic shape of the copper particles. The detailed study of the effect of TCP composition on its thermal and electric conductivity is published elsewhere [15]. It is noteworthy, however, that higher metallic

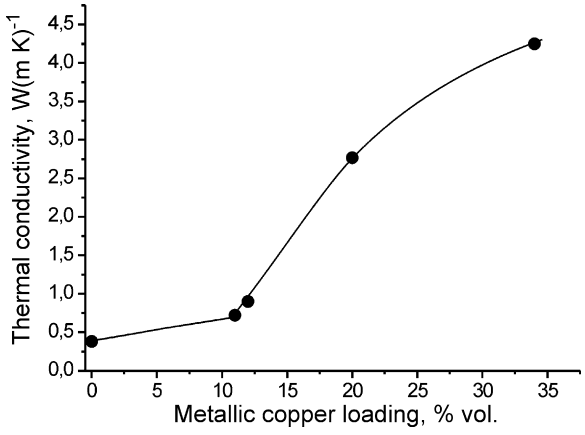

Fig. 3. The experimental correlation between the metallic copper loading and thermal conductivity of TCP. The plates were pressed at 170 MPa and sintered at 410 °C.

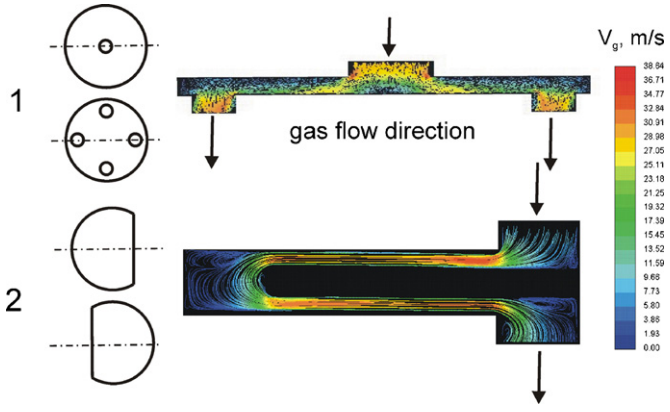

Fig. 4. Gas velocity fields for two different schemes for thermal conducting plates arrangement in the tubular reactor: (1) interchange of disks with one and four holes and (2) interchange of disk segments. Gas flow 1 $m^3_{STP}\,h^{-1}$. Disks are of 25 mm in diameter, the gap between disks is 1 mm.

Table 1
Comparison of the catalytic performance of the TCP to that of the traditional catalyst pellet

Reaction temperature (°C)	270	300	330	350
First order kinetic constant (s^{-1}) Cu-Zn-Zr catalyst	24.2	36.1	45.1	62.2
Effectiveness factor of catalyst usage				
Traditional pellet, 5 mm × 5 mm	0.41	0.37	0.36	0.34
TCP-220-380	0.47	0.44	0.35	0.29
TCP-170-380	0.53	0.46	0.36	0.39
TCP-170-410	0.60	0.48	0.40	0.40
TCP-220-440	0.39	0.38	0.28	0.24
TCP-170-440	0.51	0.40	0.33	0.33

CO content in dry gas 12 vol.%, steam:gas ratio 0.6, atmospheric pressure. The figures in the TCP notation mean the conditions of its preparation: pressure (MPa) and sintering temperature (°C).

Table 2
Comparison of the catalytic performance of the reactor TCP-1 with square TCP

	Reaction temperature (°C)			
	270	300	330	350
Effectiveness factor of catalyst usage TCP-170-440-square "unarranged"	0.45	0.41	0.33	0.25
Arranged in the reactor TCP-1	0.30	0.25	0.24	0.20

CO content in dry gas 12 vol.%, steam:gas ratio 0.6, atmospheric pressure, gas velocity 0.4 $m^3_{STP}\,h^{-1}$.

copper loading is needed to prepare strong plates. The plates discussed below contain 20–25 vol.% (50–55 wt.%) of metallic copper. The density of the WGSR catalyst loading is approx. 1.1 g cm^{-3}.

3.3. Catalytic activity studies of TCP in the gradientless reactor

The prepared TCP have rather high porosity (>55 vol.%), which makes the diffusion constrains rather mild. Their WGSR catalytic performance was studied in the circulating-flow gradientless reactor and the first order kinetic constants were calculated from the experimental data. The ratios of the observed kinetic constants to those observed on the fine catalyst powder (0.25–0.5 mm), i.e. effectiveness factors of the catalyst usage are compared in Table 1 to the corresponding values for a traditional cylindrical catalyst pellet (5 mm × 5 mm). It is evident from Table 1, that high values of pressure and sintering temperature worsen the catalytic activity of TCP. We suppose that the effect of sintering temperature is accounted for by the comparatively low thermal stability of the catalyst. Indeed, according to the data of Ref. [12], the Cu-Zn-Zr catalyst we used is rather stable at 380 °C, however tends to loose activity during the thermal treatment at above 400 °C. The value of pressure applied during the catalyst plate formation seems to affect the pore structure of the TCP, including the pores within the grains of Cu-Zn-Zr catalyst. The higher is the pressure, the smaller are the pores and the lower is the effectiveness factor of catalyst usage. Therefore, both these values should be minimized, provided they are enough to ensure the mechanical strength of the TCP. Basing on the results of Table 1, we suppose, that the optimal conditions of TCP preparation include pressing at 170 MPa and sintering at 400–410 °C.

3.4. Catalytic activity studies of TCP arranged in TCP reactors

The shape of the TCP and the way of its arrangement in the reactor may play significant role for the TCP reactor performance. Fig. 4 shows the calculated gas velocity fields for two different TCP shapes, firmly arranged in a reactor tube. In Fig. 4(1), disks with one hole are interchanged with those having four holes; in Fig. 4(2), all plates are disk segments interchanging symmetrically (like it was described above for reactor TCP-2, Fig. 1). The velocity of gas mixture is considered as 1 $m^3_{STP}\,h^{-1}$. The model accounted even heat generation at the surface of TCP. One can see that gas flow in the chink between two TCP elements is non-uniform. In fact, only forefront of the TCP in Fig. 4(1) is washed by the gas flow, while at the backside gas is stagnant. It forces one to expect twice worse perfor-

Table 3
Reaction conditions and the observed performance of the reactor TCP-2

Point no.	P^a	Dry gas flow, ($m^3_{STP}\,h^{-1}$)	Steam:gas	GSHV wet gas (h^{-1})	Feed gas composition (% of dry gas)			Residual CO (% of dry gas)
					CO	CO_2	CH_4	
1	atm.	1.1	0.51	6300	11.9	10.1	0.04	1.0
2	atm.	1.1	0.63	6900	11.9	10.2	0.07	0.9

[a] Pressure of the reaction mixture at the outlet of the reactor.

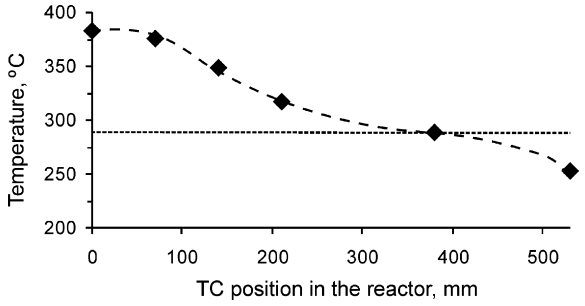

Fig. 5. The experimental temperature profile during the catalytic tests of the reactor TCP-2.

mance of the arranged TCP comparing to that of an "unarranged" one.

In contrast, the both sides of a TCP are well washed in Fig. 4(2), which presents modelling of the TCP reactor with the catalyst plates of a disk segment shape. Stagnant zones and zones with recurrent gas flow are much less extensive and cover only peripheral parts of the TCP backside.

These expectations from the mathematical modeling agree well with the experimental data on the catalytic tests in the TCP reactors arranged with TCP. The details of experimental procedure and reactor configuration are given in Section 2. As it is follows from Table 2, the performance of the TCP-1 reactor is almost twice less than the performance of "unarranged" TCP. The square TCP used in these tests is a good one-dimensional model for reactor configuration shown in Fig. 4(1).

Table 3 shows the results of the catalytic tests of reactor TCP-2 operating at the realistic fuel gas feed and optimized temperature profile, which is shown in Fig. 5. The composition at the reactor outlet (0.9% of residual CO in the wet gas) corresponds to the equilibrium composition at 289 °C (dotted line in Fig. 5).

The results of the catalytic tests evidently show that TCP can be efficiently used for WGSR in compact apparatuses with controlled temperature profile. Using the TCP reactor conversion of the fuel gas containing 12% of CO down to 1% of residual CO can be performed in one stage at GSHV of above 6000 h^{-1}. The pressure drop at TCP-2 reactor during the experimental run was reasonably small and equal to 35 kPa. The reactor outlet was kept at atmospheric pressure.

4. Conclusions

Thermal conductive catalyst plates for compact WGSR reactors were prepared and studied. High thermal conductivity of 2.5–5 W $(m\,K)^{-1}$ can be achieved, while the effective catalytic activity of TCP is even higher than that of the commercial size catalyst grains. TCP can be efficiently used for temperature sensitive exothermic reactions in compact apparatuses with controlled temperature profile. Using the TCP reactor WGSR of the fuel gas containing 12% of CO down to 1% of residual CO can be performed in one stage at GSHV of above 6000 h^{-1}. The TCP shape and the way of arrangement are important for the reactor performance and should be in the focus of our future studies.

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