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Hydrogen Synthesis by Hydrogen Sulphide Decomposition in Catalytic Membrane Reactor

S. R. KHAIRULIN[1], A. V. SALNIKOV[1], M. A. KERZHENTSEV[1], Z. R. ISMAGILOV[1,2]

[1] *Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia*

[2] *Federal Research Centre of Coal and Coal Chemistry, Siberian Branch of the Russian Academy of Sciences, Kemerovo, Russia*

E-mail: sergk@catalysis.ru

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Abstract

A number of ceramic membrane reactors (CMR) of various designs and compositions for high-temperature hydrogen sulphide decomposition were studied. Two CMR types with the layered structure were used: the first type included catalyst layer, membrane support, and membrane layer, while the second one was composed of catalyst layer, membrane support, an intermediate layer, and membrane layer. It is demonstrated that the pore structure and the thickness of the membrane layer have a significant effect on permeability for H_2 and H_2S. Due to the high H_2/H_2S separation coefficient (more than 2.5), a significant improvement of the parameters of H_2S decomposition in CMR in comparison with the flow reactor with a granulated catalyst is observed. The H_2S conversion (with the formation of H_2) reaches 87 % at 900 °C in the CMR of the optimal composition prepared using the optimal method.

Keywords: reactor, catalytic membrane, hydrogen sulphide, decomposition

INTRODUCTION

Hydrogen sulphide (H_2S) is formed as a by-product of various chemical processes, such as petroleum production and petrochemical processes [1, 2], hydrodesulphurization of hydrocarbons [1], processing heavy petroleum [3], bitumen [4] and coal [4]. It is very toxic and causes corrosion [5], so its processing is necessary to prevent its emission into the atmosphere.

Hydrogen sulphide is usually utilized with the help of a well-known Claus process which involves H_2S oxidation with the formation of water and elemental sulphur in a two-stage reaction [6]:

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O \quad (1)$$

$$2H_2S + SO_2 \rightarrow 3S + H_2O \quad (2)$$

Another method to process hydrogen sulphide is its direct oxidation [7–9]:

$$H_2S + 1/2O_2 \rightarrow 1/nS_n + H_2O \quad (3)$$

which provides oxidation of hydrogen sulphide to elemental sulphur in one stage.

In spite of the fact that sulphur obtained in the Claus process and through direct oxidation of H_2S is a commercial product, these processes do not allow the full involvement of the potential of H_2S because hydrogen present in it is bound in the form of water vapour [10–12].

An alternative to oxidation processes is the decomposition of H_2S, which results in the possibility to obtain hydrogen in addition to sulphur, which is a highly relevant product:

$$H_2S \rightarrow H_2 + 0.5S_2 \quad (4)$$

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Many methods of H_2S decomposition are known [13, 14]. Thermal decomposition appears to be the most interesting method among them. This process holds high practical significance for the production of not only elemental sulphur but also hydrogen on an industrial scale. Sulphur is usually present in reaction products in diatomic state because decomposition of hydrogen sulphide is performed at high temperatures.

Thermodynamics of the thermal decomposition of H_2S is unfavourable for carrying out at low temperatures. in particular, at a temperature below 550 °C the equilibrium concentration of H_2 is below 1 %, at 900 °C – only 13 % [15].

Investigation of the decomposition of H_2S at different temperatures, pressure and initial concentration showed that reduced pressure and high temperature promote an increase in the yield of hydrogen [16]. The efficiency of H_2S decomposition increases substantially in the presence of heterogeneous catalysts.

Oxides [6, 15, 17, 18] and sulphides [19–21] of transition metals were studied as the solid catalysts of heterogeneous high-temperature decomposition of hydrogen sulphide. The authors of [22] studied more than 10 different oxides (Fe_2O_3, MnO_2, SiO_2, ZnO, CaO, *etc.*) in the reaction of H_2S decomposition. It was demonstrated that it is reasonable to use Fe_2O_3 as the catalyst for H_2S decomposition because of its ability to readily form sulphides, which are active in the reaction.

The reaction is equilibrium, so simultaneous separation of H_2 from other reagents will improve the productivity of the process due to the shift of equilibrium to the formation of reaction products. For this purpose, it is possible to use, for example, a membrane reactor with a catalyst bed. Different types of membrane reactors have been studied [23–27]. Hydrogen was separated from the products of thermal decomposition of H_2S with the help of porous membranes based on metals (Pd or V) [23, 24] or ceramic materials [25–27]. For instance, microporous membranes made of glass tubes of Vikor type with an average pore diameter of 45 Å and a tubular membrane made of aluminium oxide with an average pore diameter of 1020 Å were studied. With these membranes used for the direct decomposition of H_2S, the yield of H_2 increased by a factor of approximately two in comparison with the calculated data on the equilibrium for the process without hydrogen removal [27].

In the present work, we describe the results of the development and tests of composite membranes made of aluminium oxide with a supported catalyst based on iron oxide for the decomposition of hydrogen sulphide.

EXPERIMENTAL

Preparation and investigation of membrane catalysts

Catalytic membrane reactors (CMR) are ceramic tubes (15 mm long, with the outer diameter 4 mm, inner diameter 2 mm). A schematic representation of CMR under investigation is shown in Fig. 1. The catalyst layer was deposited on the external surface of the ceramic tube, while the membrane layer was deposited on its inner surface. The membrane is obtained according to sol-gel technology. Sol composition is $Al(OH)_3$ with pseudo-boehmite structure, modified with lanthanum additives, thus a membrane with the composition 5 % $La_2O_3/\gamma\text{-}Al_2O_3$ was obtained Tubes with membrane layer were heated to 550 °C at a rate of 100 °C/h, and then they were annealed at different temperatures (T_{an}, °C): 550 °C for 4 h, 700 or 900 °C for 2 h.

The thickness of the membrane layer (L, μm) was calculated as follows:

$$L = G \cdot 10^4 / S\rho \quad (5)$$

where G is the mass of the layer, g; S is the geometric surface of the layer, cm^2; ρ is the apparent density of the layer, g/cm^3.

The catalytic layer at the outer surface of the ceramic tube was deposited in the form of suspension with the composition 80 mass % catalyst (4.1 % Fe/$\alpha\text{-}Al_2O_3$) prepared according to the procedure described in [17, 18], and 20 mass % $Al(OH)_3$ with pseudo-boehmite structure, with subsequent drying, heating to 450 °C, and calcination at 450 or 550 °C for 2 h.

The phase composition of the catalysts was determined by means of X-ray phase analysis (XPA) with the help of an HZG-4 diffractometer

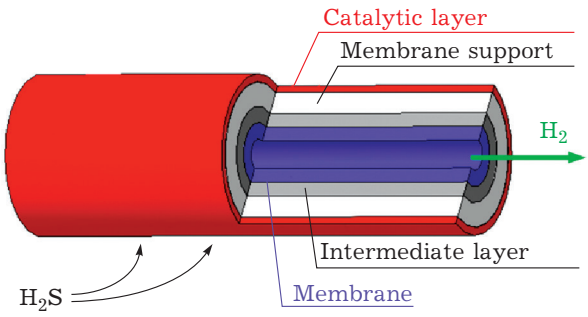

Fig. 1. Schematic representation of catalytic membrane reactors under investigation for H_2S decomposition.

(Freiberger Praezisionemechanik GmbH, Germany) with copper radiation within the angle region 10–70° over 2θ. Texture characteristics - specific surface area (S_{sp}, m^2/g), pore volume (V_{pore}, cm^3/g) and effective pore diameter (D_{eff}, Å) – were studied by means of low-temperature nitrogen adsorption using ASAP 2400 instrument (Micromeritics, USA). The morphology of spherical, block and membrane catalysts was studied by means of scanning electron microscopy (SEM) with the help of REM-100U microscope (Russia).

Membrane permeability and activity in the reaction of H_2S decomposition

Experimental data on permeability and catalytic activity were obtained at a temperature of 600–900 °C and pressure up to 1 MPa with the help of a specially built laboratory set-up (Fig. 2). The catalytic membrane reactor was placed in a shell made of stainless steel with the heater mounted on it and sealed with the help of graphite gaskets (Fig. 3).

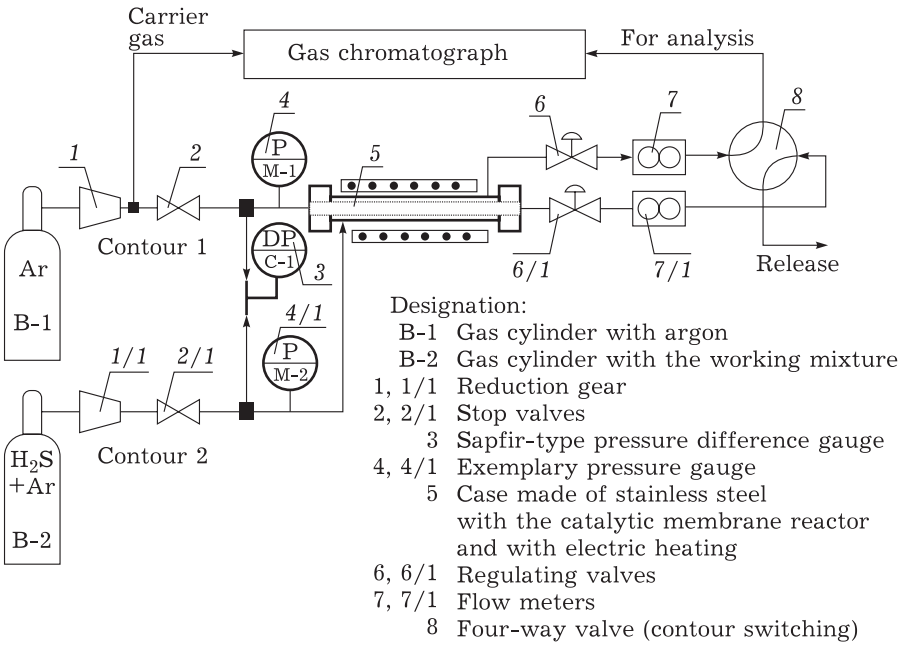

Fig. 2. Schematics of the laboratory set-up to determine permeability and to study H_2S decomposition in the catalytic membrane reactor.

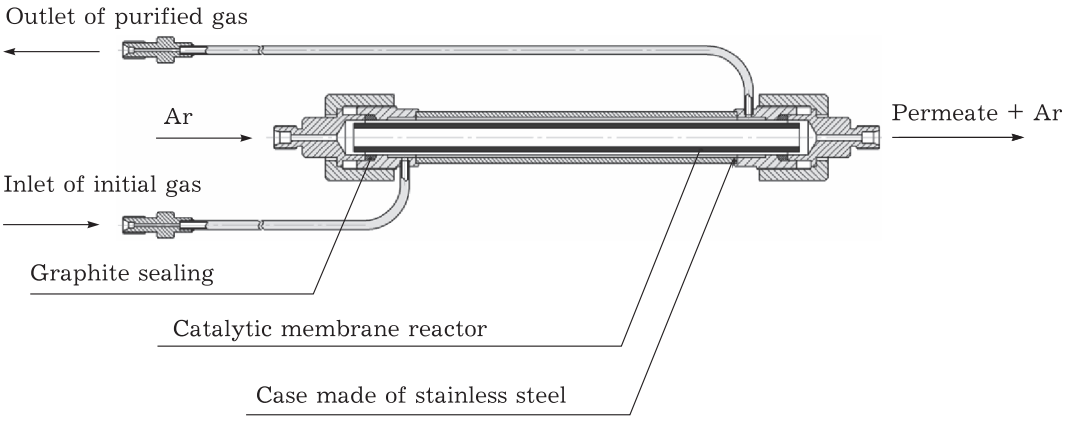

Fig. 3. Shell made of stainless steel with the catalytic membrane reactor for H_2S decomposition.

Membrane permeability was tested at room temperature in the gas mixture containing 1 vol. % H_2 + 1 vol. % H_2S + Ar. The reaction mixture was supplied into the external contour of the reactor at a necessary pressure. The composition of the permeate and the rate of gas flow after the membrane were determined.

Catalytic activity was tested by supplying the reaction mixture (1 vol. % H_2S in Ar) into the external contour of the reactor. Carrier gas Ar was supplied into the internal contour of the reactor. The pressure difference between the external and internal contours of the reactor was recorded with the help of a piezoelectric pressure gauge Sapfir (Russia). The composition of the reaction mixture and permeate was determined with the help of gas chromatograph Tsvet-500 (Russia) with a thermal conductivity detector. Sulphur formed as a result of the reaction was completely removed from the reactor with the gas flow within the temperature range under study, so sulphur did not form any deposits on the walls of the membrane reactor.

Permeability of reaction components through the membrane (K_p, mol/(s · m² · Pa)) was determined using equation [28, 29]:

$$K_p = \frac{V_p}{S_m \cdot \Delta P} \quad (6)$$

Here V_p is the molar rate of component flow through the membrane reactor, mol/s; S_m is the geometric surface of the membrane, cm²; ΔP is the pressure difference, Pa.

Transformation degree of hydrogen sulphide (X_{H_2S}, %) was calculated using the equation:

$$X_{H_2S} = \frac{V_1^0 C_{H_2S}^0 - V_1 C_{1H_2S} - V_2 C_{2H_2S}}{V_1^0 C_{1H_2S}^0} 100 \quad (7)$$

Here V_1^0 is the volume flow rate of the initial reaction mixture at the inlet of the reactor, cm³/s; V_1 is the volume flow rate at the outlet of the external contour of the reactor, cm³/s; V_2 is the volume flow rate at the outlet of the internal contour of the reactor after the membrane, cm³/s; $C_{H_2S}^0$ is H_2S concentration in the initial reaction mixture, mol/cm³; C_{1H_2S}, C_{2H_2S} are H_2S concentrations at the outlet of the external and internal contours of the reactor, respectively, mol/cm³.

In addition, the degree of hydrogen sulphide transformation was calculated from the amount of hydrogen formed during the reaction ($X_{H_2S(H_2)}$, %):

$$X_{H_2S(H_2)} = \frac{V_1 C_{1H_2} + V_2 C_{2H_2}}{V_1^0 C_{1H_2S}^0} 100 \quad (8)$$

Here C_{1H_2}, C_{2H_2} are H_2 concentrations at the outlet of the external and internal contours of the reactor, respectively, mol/cm³.

The coefficient of H_2 and H_2S separation (α) was calculated from the concentrations of H_2 and H_2S using equation [24]:

$$\alpha = \frac{C_{2H_2} C_{1H_2S}}{C_{1H_2} C_{2H_2S}} \quad (9)$$

RESULTS AND DISCUSSION

Physicochemical properties of catalytic membrane reactors

Analysis of the literature showed that the amount of works dealing with the development and systematic investigation of CMR for hydrogen sulphide decomposition is insufficient. The available data allow us to conclude that porous structure and the thickness of the membrane layer have a substantial effect on the efficiency of catalytic membranes. In the present work, we studied the CMR with membranes possessing different porous structures and thickness of the membrane layer.

The properties of ceramic tubes (membrane supports) used for making the CMR are presented in Table 1.

Depending on the calcination temperature, the total pore volume of the used tubes varied within the range 0.10–0.23 cm³/g, efficient pore diameter determined by means of BET procedure varied from 900 to 1100 Å. The image of the surface of the ceramic tube taken by means of SEM is shown in Fig. 4.

The major properties of the membrane layer are listed in Table 2. The effective pore diameter of the membrane layer composed of γ-Al_2O_3 increases from 60 to 360 Å with an increase in the calcination temperature from 550 to 900 °C. XPA data showed that an increase in the calcination temperature leads to a partial phase transition of γ-Al_2O_3 into δ-Al_2O_3. To enhance thermal stability, the membrane layer was modified by adding lanthanum oxide. It was established that the

TABLE 1

Properties of ceramic tubes used to prepare catalytic membrane reactors for H_2S decomposition

No.	Composition	T_{calc}, °C	S_{sp}, м²/г	V_{pore}, cm³/g	D_{eff}, Å
1	Al_2O_3-SiO_2	1000	6	0.23	900
2	Al_2O_3-SiO_2	1160	1	0.10	1100

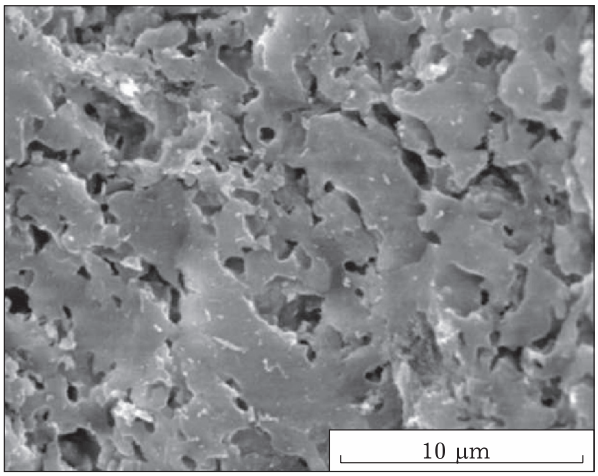

Fig. 4. SEM image of membrane support [30].

effective diameter of pores in the membrane layer with the composition 5 % $La_2O_3/\gamma\text{-}Al_2O_3$ calcined at 900 °C is three times smaller than that in non-modified $\gamma\text{-}Al_2O_3$, and is equal to 114 Å. X-ray phase analysis showed only the presence of the $\gamma\text{-}Al_2O_3$ phase, which confirmed the stabilizing effect of the La_2O_3 additive.

The prepared CMR differing in support, the calcination temperature and the thickness of membrane layer are listed in Table 3. Microphotographs of sample No. 7 (see Table 3) are shown in Fig. 5 as an example. One can see a well pronounced boundary between the porous support and a dense membrane. The thickness of the membrane layer was about 8 μm, while the calculated value is 9 μm. With an increase in the calcination temperature, an increase in the effective pore diameter was observed, accompanied by a decrease in specific surface area.

Taking into account the fact that the decomposition of hydrogen sulphide takes place at a high temperature (900 °C), we chose ceramic support calcined at 1160 °C as the initial material for CMR. The major characteristics of the synthesized CMR samples (CMR-1–CMR-3) composed of a membrane layer/membrane support/catalytic layer, and CMR-4 sample containing an additional intermediate layer are presented in Table 4.

For clarity, the synthesized CMR (with and without an intermediate layer) are shown schematically in Fig. 6.

As mentioned above, the membrane layer with the composition $La_2O_3/\gamma\text{-}Al_2O_3$ with the thickness within the range of 3–25 μm was annealed at different temperatures (550, 700 or 900 °C). The catalytic layer containing specially prepared catalyst 4.1 % $Fe/\gamma\text{-}Al_2O_3$ was deposited on the membrane support from the external side.

The CMR-4 sample containing an additional intermediate layer was manufactured to improve the selectivity of the membrane with respect to hydrogen, which is formed during the reaction. In this case, the efficient diameter of pores in the membrane layer was minimal (45 Å).

TABLE 2

Properties of membrane layer

Composition of membrane layer	$T_{calc,}$ °C	S_{sp}, m^2/g	D_{eff}, Å
$\gamma\text{-}Al_2O_3$	550	210	60
$\gamma\text{-}Al_2O_3$	700	180	120
$\gamma\text{-}Al_2O_3$	900	100	360
5 % $La_2O_3/\gamma\text{-}Al_2O_3$	550	200	60
5 % $La_2O_3/\gamma\text{-}Al_2O_3$	900	110	114

Permeability with respect to H_2 and Ar

Membrane permeability K_p was calculated as a tangent of the slope from experimental data plotted as $V_p/S_m - \Delta P$. Results of the determination of permeability of the membranes under inves-

TABLE 3

Synthesized catalytic membrane reactors for H_2S decomposition

Sample No.	Membrane support	Membrane layer	T_{calc}, °C	Thickness of membrane layer, μm	S_{sp}, m^2/g	D_{eff}, Å
1	$Al_2O_3\text{-}SiO_2$ (T_{calc} = 1000 °C)	$\gamma\text{-}Al_2O_3$	550	80	8	60
2	$Al_2O_3\text{-}SiO_2$ (T_{calc} = 1000 °C)	5 % $La_2O_3/\gamma\text{-}Al_2O_3$	550	120	9	63
3	$Al_2O_3\text{-}SiO_2$ (T_{calc} = 1000 °C)	5 % $La_2O_3/\gamma\text{-}Al_2O_3$	900	25	7	120
4	$Al_2O_3\text{-}SiO_2$ (T_{calc} = 1160 °C)	$\gamma\text{-}Al_2O_3$	550	80	3	60
5	$Al_2O_3\text{-}SiO_2$ (T_{calc} = 1160 °C)	5 % $La_2O_3/\gamma\text{-}Al_2O_3$	550	10	3	63
6	$Al_2O_3\text{-}SiO_2$ (T_{calc} = 1160 °C)	5 % $La_2O_3/\gamma\text{-}Al_2O_3$	700	4	2	83
7	$Al_2O_3\text{-}SiO_2$ (T_{calc} = 1160 °C)	5 % $La_2O_3/\gamma\text{-}Al_2O_3$	900	9	1	120

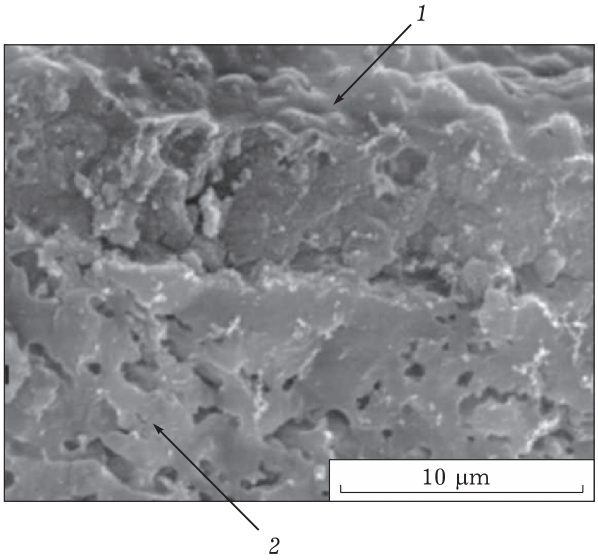

Fig. 5. SEM image of ceramic support with membrane layer deposited on it: *1* – membrane layer; *2* – support [30].

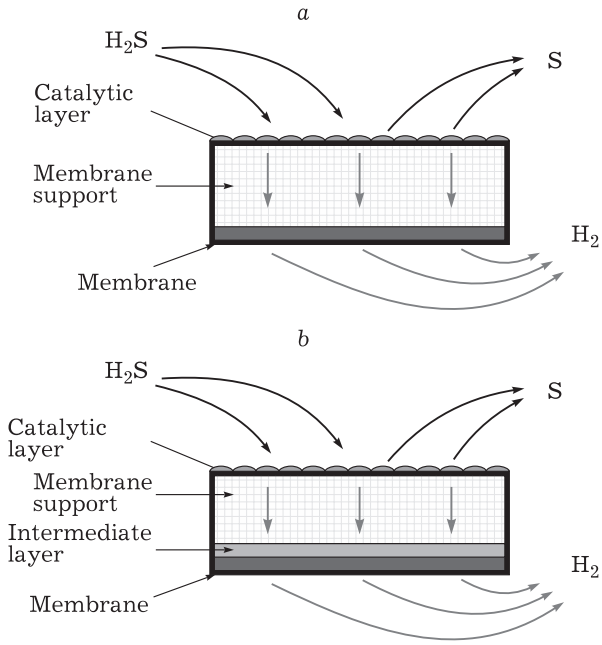

Fig. 6. Schematic representation of H_2S decomposition in the catalytic membrane reactor without an intermediate layer (*a*) and with the intermediate layer (*b*).

tigation (at room temperature) with respect to H_2, H_2S and Ar are shown in Fig. 7 [30].

The obtained permeability value K_p and the coefficient of H_2/H_2S separation (α) are presented in Table 5. It should be stressed that the permeability values for H_2 and N_2 that have been obtained with the mesoporous support α-Al_2O_3 coated with a layer of γ-Al_2O_3 were $7 \cdot 10^{-7}$ and $0.5 \cdot 10^{-7}$ mol/(cm^2 · Pa), respectively [31]. This is much lower than the coefficients calculated in this work.

Separation coefficients are close for all the studied membranes and are approximately equal to 2.5.

Catalytic activity in the reaction of H_2S decomposition

The parameters of the process of H_2S decomposition in the CMR are listed in Table 6. Hydrogen sulphide conversion calculated from the changes in its concentration and the conversion calculated from the concentration of the formed hydrogen are mainly close to each other; some deviations are observed for low conversion. Temperature dependences of the degree of hydrogen sulphide transformation are presented in Fig. 8. For comparison, process parameters in a flow reactor in the presence of granulated catalyst 4.1 % Fe/γ-Al_2O_3 are also shown in the same Figure.

For all CMR under investigation, the highest efficiency in H_2S decomposition is achieved at 900 °C. Results obtained for the samples without an intermediate layer and at the temperature of membrane layer calcination 500 and 950 °C are close to the data obtained in the flow reactor with granulated catalyst 4.1 % Fe/γ-Al_2O_3 (see Fig. 8, CMR-1 and CMR-3). The highest H_2S

TABLE 4

Physicochemical properties of the prepared catalytic membrane reactors for H_2S decomposition

Sample	Membrane layer			Intermediate layer			Catalytic layer
	T_{calc}, °C	L, μm	D_{eff}, Å	T_{calc}, °C	L, μm	D_{eff}, Å	L, μm
CMR-1	550	19	63	–	–	–	51
CMR-2	700	10	83	–	–	–	60
CMR-3	900	25	114	–	–	–	62
CMR-4	900	6	45	900	9	110	53

Note. Dash means the absence of a layer.

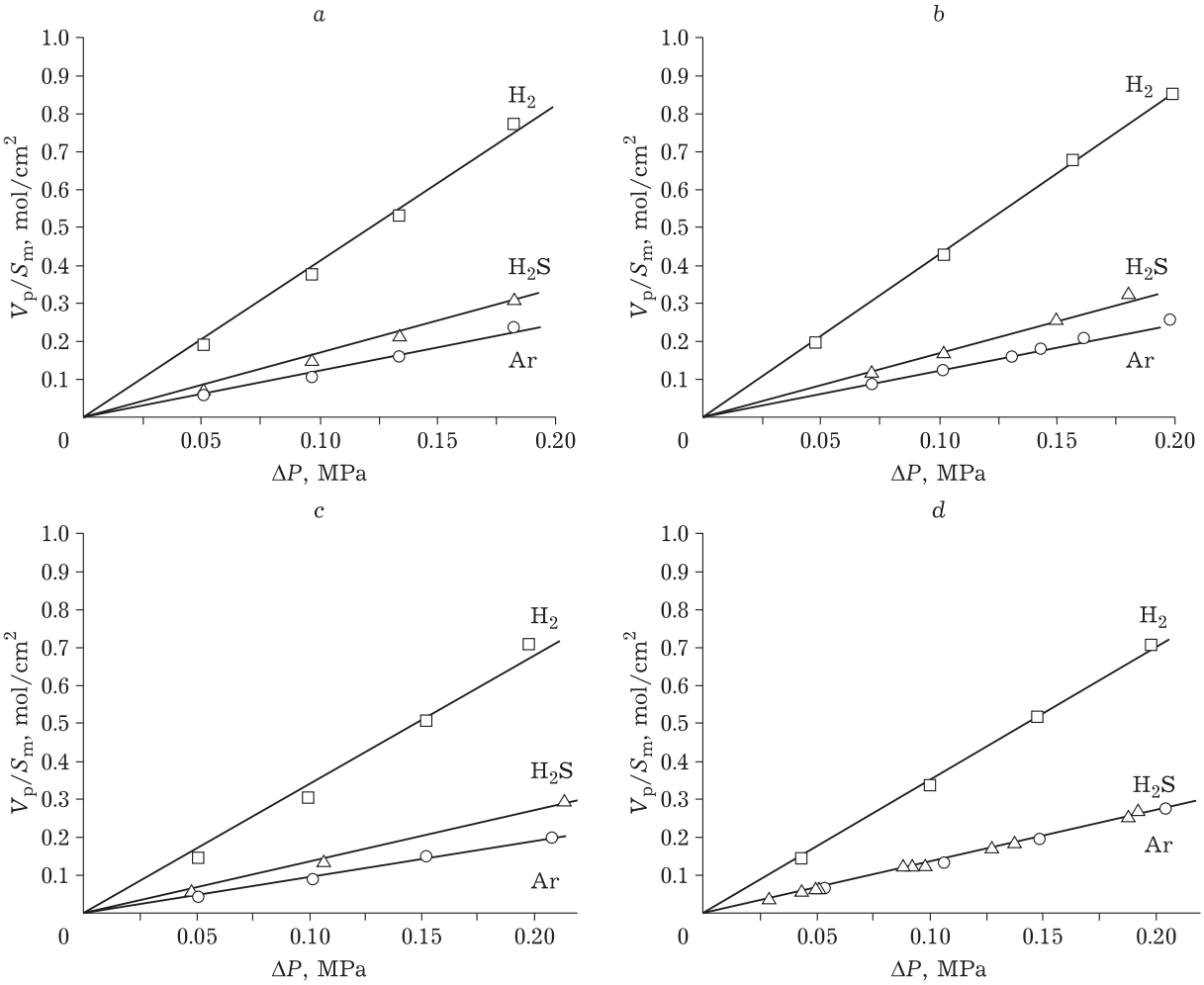

Fig. 7. Results of the determination of permeability with respect to H_2, H_2S and Ar at room temperature for CMR-1 (*a*), CMR-2 (*b*), CMR-3 (*c*) and CMR-4 (*d*) [30].

transformation degree in CMR containing no intermediate layer is observed for the sample annealed at 700 °C and is equal to 70 % at 900 °C (see Fig. 8, CMR-2). This is likely to be due to the efficient separation of H_2 and H_2S (α = 3–4). The coefficients of H_2 and H_2S separation at 900 °C

TABLE 5

Results of permeability tests of catalytic membrane reactors with respect to H_2, H_2S and Ar at room temperature

Sample	Permeability $K_p \cdot 10^7$, mol/(cm^2 · Pa)			α
	H_2	H_2S	Ar	
CMR-1	41	16	12	2.2
CMR-2	44	18	13	2.4
CMR-3	33	14	10	2.4
CMR-4	35	14	14	2.5

TABLE 6

Results of catalytic tests of the catalytic membrane reactors in H_2S decomposition

Sample	T, °C	X_{H_2S}, %	$X_{H_2S(H_2)}$, %	α
CMR-1	621	5	13	1.00
	716	38	24	1.14
	813	45	42	1.12
	913	39	44	1.65
CMR-2	630	46	11	3.82
	720	60	23	3.01
	820	44	50	3.00
	880	61	70	4.05
CMR-3	717	20	21	0.81
	838	49	45	1.15
	913	56	50	1.16
CMR-4	608	22	21	1.0
	702	46	52	0.78
	814	59	76	1.10
	913	67	87	1.63

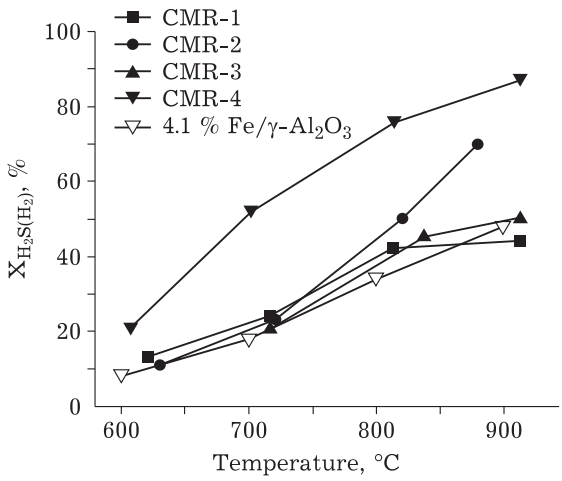

Fig. 8. Temperature dependences of the degree of H_2S transformation calculated from the amount of formed hydrogen ($X_{H_2S(H_2)}$) in the catalytic membrane reactors without an intermediate layer (CMR-1, CMR-2, CMR-3) and with the intermediate layer (CMR-4) and in the flow reactor with granulated catalyst (4.1 % Fe/γ-Al_2O_3).

were 1.65, 4.05 and 1.16 for samples CMR-1, CMR-2 and CMR-3, respectively.

The introduction of an additional intermediate layer into CMR provides an increase in the degree of H_2S transformation, which is 87 % at 900 °C (see Fig. 8, CMR-4). The presented data provide that the application of CMR leads to a substantial increase in the efficiency of hydrogen sulphide decomposition in comparison with the flow reactor with granulated catalyst.

CONCLUSION

Investigation of CMR with the layered structure of two types including in the first case a catalyst layer, membrane support and membrane layer, and in the second case a catalyst layer, membrane support, intermediate layer and membrane layer revealed that the porous structure and thickness of the membrane layer have a substantial effect on permeability and the coefficient of H_2 and H_2S separation. A high coefficient of H_2 and H_2S separation was achieved (more than 2.5), which provides an increase in the degree of H_2S transformation in CMR in comparison with a flow reactor with granulated catalyst. The degree of H_2S transformation (with the formation of hydrogen) is 87 % at 900 °C in the CMR with optimal composition and method of preparation.

Acknowledgements

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REFERENCES

1 Palma V., Vaiano V., Barba D., Colozzi M., Palo E., Barbato L., Cortese S., H_2 production by thermal decomposition of H_2S in the presence of oxygen, *Int. J. Hydrog. Energy*, 2015, Vol. 40, P. 106–113.
2 Gao B., Han X., Zhang H., Study on H_2S monitoring technique for high risk wellsite, *Procedia Engineering*, 2012, Vol. 45, P. 898–903.
3 Clark P. D., Hyne J. B., Tyrer J. D., Chemistry of organosulphur compound types occurring in heavy oil sands, *Fuel*, 1983, Vol. 62, P. 959–962.
4 Mohit N., Randhir S., Naveen K., Sushant U., Desulphurization of coke oven gas, *Int. J. Sci. Res. Rev.*, 2013, Vol. 2, P. 13–22.
5 Stanek J., Gift J., Woodall G., Foureman G., Hydrogen sulfide: Integrative analysis of acute toxicity data for estimating human health risk, in: Encyclopedia of Environmental Health, Elsevier, 2011, P. 124–139.
6 Pieplu A., Saur O., Lavalley J. C., Legendre O., Nedez C., Claus catalysis and H_2S selective oxidation, *Catal. Rev.*, 1998, Vol. 40, P. 409–450.
7 Batygina M. V., Dobrynkin N. M., Kirichenko O. A., Khairulin S. R., Ismagilov Z. R., Studies of supported oxide catalysts in the direct selective oxidation of hydrogen sulphide, *React. Kinet. Catal. Lett.*, 1992, Vol. 48, No. 1, P. 55–63.
8 Ismagilov Z. R., Khairulin S. R., Kerzhentsev M. A., Direct selective catalytic oxidation of H_2S, *Int. Hydrocarbon*, 1994, Vol. 431–432, P. 56–64.
9 Ismagilov Z. R., Khairulin S. R., Kerzhentsev M. A., Mazgarov A. M., Vildanov A. F., Development of catalytic technologies for purification of gases from hydrogen sulfide based on direct selective catalytic oxidation of H_2S to elemental sulphur, *Eurasian Chem.-Technol. J.*, 1999, Vol. 1, No. 1, P. 49–56.
10 Manenti F., Papasidero D., Ranzi E., Revised kinetic scheme for thermal furnace of sulfur recovery units, *Chem. Eng. Trans.*, 2013, Vol. 32, P. 1185–1290.
11 Zaman J., Chakma A., Production of hydrogen and sulfur from hydrogen sulphide, *Fuel Process Technol.*, 1995, Vol. 41, P. 159–198.
12 Galuszka J., Iaquaniello G., Ciambelli P., Palma V., Brancaccio E., Membrane-assisted catalytic cracking of hydrogen sulphide (H_2S), in: Membrane Reactor for Hydrogen Production Processes, London, Springer, 2011, P. 161–182.
13 Reverberi A. P., Клемељ J. J., Varbanov P. S., Fabiano B., A review on hydrogen production from hydrogen sulphide by chemical and photochemical methods, *J. Clean Prod.*, 2016, Vol. 136, P. 72–80.
14 De Crisci A. G., Moniri A., Xu Yu., Hydrogen from hydrogen sulfide: Towards a more sustainable hydrogen economy, *Int. J. Hydrogen. Energy*, 2019, Vol. 44, P. 1299–1327.
15 Reshetenko T., Khairulin S. R., Ismagilov Z. R., Kuznetsov V. V., Study of the reaction of high-temperature H_2S decomposition on metal oxides (γ-Al_2O_3, α-Fe_2O_3, V_2O_5), *Int. J.*

Hydrog. Energy, 2002, Vol. 27, No. 4, P. 387–394.
16 Kaloidas V., Papayannakos N., Hydrogen production from the decomposition of hydrogen sulphide. Equilibrium studies on the system $H_2S/H_2/S_i$, (i = 1, … ,8) in the gas phase, *Int. J. Hydrogen Energy*, 1987, Vol. 12, No. 6, P. 403–409.
17 Ismagilov Z. R., Podyacheva O. Y., Sakashita M., Tsykoza L. T., Shikina N. V., Ushakov V. A., Kuznetsov V. V., Tamura Sh., Fujimoto K., Development of Fe-based catalysts for purification of coke oven gases, *Eurasian Chem.-Technol. J.*, 2004, Vol. 6, No. 3, P. 213–219.
18 Podyacheva O. Y., Ismagilov Z. R., Tsykoza L. T., Sakashita M., Shikina N. V., Ushakov V. A., Kuznetsov V. V., Ovsyannikova I. A., Tamura S., Fujimoto K., Study of Fe-based catalysts in the purification of coke oven gases, *Eurasian Chem.-Technol. J.*, 2005, Vol. 7, No. 3–4, P. 205–211.
19 ˆFukuda K., Dokiya M., Kameyama T., Kotera Y., Catalytic decomposition of hydrogen sulphide, *Ind. Eng. Chem. Fundam.*, 1978, Vol. 17. P. 243–248.
20 Sugioka M., Aomura K., A possible mechanism for catalytic decomposition of hydrogen sulfide over molybdenum disulphide, *Int. J. Hydrog. Energy*, 1984, Vol. 9, P. 891–894.
21 Kaloidas V. E., Papayannakos N. G., Kinetic studies on the catalytic decomposition of hydrogen sulfide in a tubular reactor, *Ind. Eng. Chem. Res.*, 1991, Vol. 30, P. 345–351.
22 Yumura M., Furimsky E., Hydrogen sulphide adsorption and decomposition in the presence of manganese nodules, *Appl. Catal.*, 1985, Vol. 16, P. 157–167.
23 Zaman J., A simulation study on the thermal decomposition of hydrogen sulfide in a membrane reactor, *Int. J. Hydrog. Energy*, 1995, Vol. 20, P. 21–28.
24 Edlund D. J., Pledger W. A., Thermolysis of hydrogen sulfide in a metal-membrane reactor, *J. Membr. Sci.*, 1993, Vol. 77, No. 2–3, P. 255–264.
25 Akamatsu K., Nakane M., Sugawara T., Hattori T., Nakao S., Development of a membrane reactor for decomposing hydrogen sulfide into hydrogen using a high-performance amorphous silica membrane, *J. Membr. Sci.*, 2008, Vol. 325, No. 1, P. 16–19.
26 Badra C., Porous membrane reactors for hydrogen sulfide splitting, *Int. J. Hydrog. Energy*, 1995, Vol. 20, P. 717–721.
27 Kameyama T., Dokiya M., Fujishige M., Yokokawa H., Fukuda K., Production of hydrogen from hydrogen sulfide by means of selective diffusion membranes, *Int. J. Hydrog. Energy*, 1983, Vol. 8, P. 5–13.
28 Peureux J., Etude de reacteurs catalytiques a membrane. Caracterisation des transferts par mesures de permeabilite gazeuse. Application aux reactions triphasiques (Ph. D. Thesis), Lyon, 1994. 168 p.
29 Uzio D., Platinum/γ-Al_2O_3 catalytic membrane: Preparation, morphological and catalytic characterizations, *Appl. Catal. Gen.*, 1993, Vol. 96, No. 1, P. 83–97.
30 Khairulin S. R., Kuznetsov V. V., Podyacheva O. Yu., Ismagilov Z. R., Preparation and investigation of a catalytic membrane reactor for the catalytic decomposition of hydrogen sulphide [in Russian], *Alternativnaya Energetika i Ekologiya*, 2017, No. 22–27 (237–239), P. 13–23.
31 Yoon M.-Y., Kim E.-Y., Kim Y.-H., Whang C.-M., Gas permeation of SiC membrane coated on multi-layer γ-Al_2O_3 with a graded structure for H_2 separation, *Korean J. Mater. Res.*, 2010, Vol. 20, P. 451–456.