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The effect of hydrogen removal during methane steam reforming in membrane reactors in the presence of hydrogen sulphide

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Abstract

The steam reforming of methane in a membrane reactor has been simulated with emphasis on the effect of hydrogen removal by the membrane on the poisoning effects due to traces of H_2S. The performance of the membrane reactor under these conditions has been compared with that of fixed-bed reactor operation for temperatures in the range 773–873 K. Removal of hydrogen increases the tendency to poisoning from H_2S. This effect can be reduced by operating at higher temperatures when H_2S poisoning is dominant. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The current world-wide abundance of natural gas has led to continuing interest in its conversion to chemical products such as ammonia, methanol and hydrogen. The predominant method for achieving these conversions is from the formation of synthesis gas, and for which the main process is by steam reforming of natural gas [1].

In methane steam reforming the following reversible reactions occur:

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \tag{2}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2 \tag{3}$$

Reactions (1) and (3) are endothermic, whereas reaction (2) is exothermic. The conversion of methane is limited by thermodynamic equilibria and is favoured by high temperature and low pressure. However, high pressure is required in the associated ammonia and methanol plants and to compensate for this high applied pressure an increase in temperature is required. Consequently, the energy consumption for steam reforming is relatively high.

An attractive option to break the equilibrium limitation in the above reactions is the use of selective membranes to remove the product hydrogen from the reaction mixture and, hence, drive each reactant to the product side. The effect has been demonstrated by many workers including Uemiya, et al. [2], Adris, et al. [3], Chai, et al. [4], Shu, et al. [5] and Barbieri, et al. [6]. However, only limited attention has been directed to any possible disadvantage caused by removal of hydrogen from the reaction mixture during the process of steam reforming [7]. Potential effects due to removal of hydrogen, include increased carbon deposition on the catalyst [7] and an adverse effect on the activity of the nickel catalyst due to poisoning by sulphur compounds in the feed stream.

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It has been pointed out by Rostrup Nielsen [1,8] and Bartholomew [9] that the adsorption of hydrogen sulphides on nickel catalyst is very strong at low temperatures and the fractional surface coverage depends on the value of p_{H_2S}/p_{H_2}. Removal of the produced hydrogen will favour the adsorption of hydrogen sulphide, so that catalyst activity and stability will be affected and may well restrict any advantages arising from the use of a membrane reactor for methane steam reforming.

Sulphur compounds are generally present in natural gas in the form of organic sulphide and/or hydrogen sulphide. Purification involves conversion of the organic sulphide to H_2S which is then removed in an absorbent fixed bed. Usually, this process ensures that sulphur is removed to a tolerable level. Because sulphur adsorbs so strongly on nickel, its presence on a catalyst surface usually causes substantial loss of activity in many important reactions, particularly in methane steam reforming. The reasons for this are twofold:

1. sulphur adsorption on the nickel surface prevents the further adsorption of reactant molecules; and
2. the reconstruction of the Ni surface may modify or decrease the adsorption rates of reactant gases.

Adsorption of H_2S on nickel is very rapid; this high adsorption rate suggests that no barrier to adsorption and dissociation occurs until saturation of the surface is approached. Accordingly, sulphur poisoning of nickel is not likely to be limited by rates of adsorption and reaction on the surface. Thus, surface coverages of sulphur can be predicted by equilibrium thermodynamics and by mass-balance and mass-transfer considerations under the conditions of interest. At steady state, the concentration difference between H_2S in the bulk phase and in the catalyst pellet may be very small; thus sulphur poisoning effects can be correlated with the H_2S concentration in the bulk phase, which is the important parameter in practical operations.

Most previous investigators [8,10,11,12] agree that H_2S completely dissociates on a nickel surface even below room temperature. Rostrup Nielsen [8] suggested a one-site mechanism at high temperatures in the range 825–925 K,

$$H_2S\ (\text{gas}) + \text{Ni} = \text{Ni} - \text{S} + H_2\ (\text{gas}) \tag{4}$$

based on the value of one obtained for the power, *n*, in the Langmuir expression

$$\theta_s = \frac{A(p_{H_2S}/p_{H_2})^n}{1 + B(p_{H_2S}/p_{H_2})^n} \tag{5}$$

He also found that the sulphur uptake is a function of the ratio p_{H_2S}/p_{H_2}. A saturation layer developed at values of this at ratios above 5×10^{-6} while at a ratio of 10^{-3}, a bulk sulphide (Ni_2S_3) was formed.

Simulations of sulphur poisoning in the steam reforming process have been given by Christiansen and Andersen [13] and Rostrup Nielsen [14]. Their analysis indicates a rapid breakthrough of sulphur for different inlet concentrations of sulphur and a slow approach to equilibrium on the catalyst. The transient profiles of sulphur poisoning were calculated with fixed conversion and fixed axial temperature profiles. Based on their simulations, the fractional sulphur coverage on the catalyst is always >0.5 along the reformer tube even for H_2S concentrations of <0.02 ppm in the feed. This decrease in catalyst activity caused by sulphur poisoning must be compensated by increasing the reaction temperature in order to keep the outlet conditions fixed.

In view of the foregoing, removal of hydrogen will cause the ratio p_{H_2S}/p_{H_2} to increase, favouring an increase in surface coverage by hydrogen sulphide on the nickel catalyst used for steam reforming. Consequently, the application of a membrane reactor for the process of steam reforming may have some disadvantages in terms of retention of catalyst activity. The aim of the present paper is to use a mathematical model for the membrane reactor to analyse this effect.

2. Model development

2.1. Intrinsic reaction kinetics

There is a large amount of literature that deals with reaction kinetics of methane steam reforming (Akers and Camp [15]; Bodrov, et al. [16]; Ross and Steel, [17]; De Deken, et al. [18] and Xu and Froment [19]. Here, we use the intrinsic kinetics data obtained experimentally on ICI catalyst 57-4 from laboratory studies in this Department [20]. The intrinsic kinetic rate expressions determined for reactions (1), (2) and (3) are given, respectively, by

Table 1
Rate data used in simulations

Parameter	Dimension
$k_1 = 6.741 \times 10^{12} \exp(-25162/T)$	kmol/kg cat h bar$^{0.25}$
$k_2 = 2.172 \times 10^{12} \exp(-1852/T)$	kmol/kg cat h bar
$k_3 = 1.245 \times 10^{7} \exp(-13158/T)$	kmol/kg cat h bar$^{0.25}$
$K_{CO} = 5.127 \times 10^{-11} \exp(16839/T)$	1/bar
$K_H = 5.680 \times 10^{-9} \exp(11234/T)$	1/bar
$K_W = 9.251 \exp(-1912/T)$	dimensionless

$$r_1 = \frac{k_1 p_{CH_4} p_{H_2O}^{0.5} p_{H_2}^{-1.25} (1 - p_{CO} p_{H_2}^{3} / p_{CH_4} p_{H_2O} K_{p1})}{\mathrm{Den}^2} \quad (6)$$

$$r_2 = \frac{k_2 p_{CO} p_{H_2O}^{0.5} p_{H_2}^{-0.5} (1 - p_{CO_2} p_{H_2} / p_{CO} p_{H_2O} K_{p2})}{\mathrm{Den}^2} \quad (7)$$

$$r_3 = \frac{k_3 p_{CH_4} p_{H_2O} p_{H_2}^{-1.75} (1 - p_{CO_2} p_{H_2}^{4} / p_{CH_4} p_{H_2O}^{2} K_{p3})}{\mathrm{Den}^2} \quad (8)$$

where,

$$\mathrm{Den} = 1 + K_{CO} p_{CO} + K_H p_{H_2}^{0.5} + K_W \frac{p_{H_2O}}{p_{H_2}} + K_{H_2S} \frac{p_{H_2S}}{p_{H_2}}$$

The intrinsic kinetic parameters, except for K_{H_2S}, for these rate expressions were obtained from experiments and $K_{H_2S} = 55 \exp(10720/T)$ (Christiansen [13]) and are listed in Table 1.

2.2. Mass balance equations for a membrane reactor

From the Langmuir adsorption, the H_2S coverage on the catalyst is given by

$$\vartheta_S = \frac{K_{H_2S} (p_{H_2S}/p_{H_2})}{1 + K_{CO} p_{CO} + K_H p_{H_2}^{0.5} + K_W (p_{H_2O}/p_{H_2}) + K_{H_2S} (p_{H_2S}/p_{H_2})} \quad (9)$$

A dense Pd/Ag composite membrane reactor with a jacket (shell) for the removal of hydrogen is used in this investigation. The catalyst (57-4) is loaded in the tubeside of the reactor. Reactants enter into the tubeside and sweep gas enters the shellside in co-current with the reactants. The dense Pd/Ag composite membrane is permeable only to hydrogen.

In order to derive the equations presenting this type of reactor, the following assumptions have been made:

1. Steady-state operation.
2. Isothermal conditions prevail.
3. Negligible pressure drop.
4. Plug flow on both, tubeside and shellside.
5. Hydrogen permeability is the same as the pure gas value.
6. No interphase and intraparticle mass-transfer limitations.

From these assumptions, mass balance equations can be written for all components as follows:

In the tubeside,

$$\frac{\mathrm{d}N_{it}}{\mathrm{d}z} = \Omega \rho_B \sum_{j=1}^{3} \nu_{ij} r_j \quad i = 1,\ 2,\ 3,\ 4 \quad (10)$$

$$\frac{\mathrm{d}N_{5t}}{\mathrm{d}z} = \Omega \rho_B \sum_{j=1}^{3} \nu_{ij} r_j - 2\pi R f_{H_2} \left(\left(\frac{N_{5t}}{\sum_{i=1}^{5} N_{it}} p_t \right)^{0.5} - \left(\frac{N_{5s}}{\sum_{i=1}^{5} N_{is}} p_s \right)^{0.5} \right) \quad (11)$$

where $i = 1, 2, 3, 4$ and 5 for CH_4, H_2O, CO, CO_2 and H_2, respectively, and ν_{ij} the stoichiometric coefficient of component i in the reaction j, f_{H_2} the permeability of hydrogen, which is dependent on the half-power of the hydrogen pressure [21].

In the shellside, only one mass balance equation for hydrogen is needed, i.e.

$$\frac{\mathrm{d}N_{5s}}{\mathrm{d}z} = 2\pi R_2 f_{H_2} \left(\left(\frac{N_{5t}}{\sum_{i=1}^{5} N_{it}} p_t \right)^{0.5} - \left(\frac{N_{5s}}{\sum_{i=1}^{5} N_{is}} p_s \right)^{0.5} \right) \quad (12)$$

The initial conditions for equations (10) and (11) are

$$z = 0, \quad N_{it} = N_{it0} \text{ and } N_{is} = N_{is0} \quad (13)$$

Equations (9)–(12) were solved using the fourth-order Runge–Kutta method.

Table 2
Input basic data for the simulation study

Contact time W/F_{CH_4} (kg cat h/kmol)	37.1	feed composition	$CH_4 > 99.9\%$ (vol), (balance H_2S)
Membrane area/reactor volume (m^{-1})	400	shellside pressure (bar)	1.0
Thickness of the palladium layer (total pressure on tube side total pressure on tube side (μm)	50	tubeside pressure (bar)	1.2
Steam/methane ratio	3	reaction temperature (K)	773–873

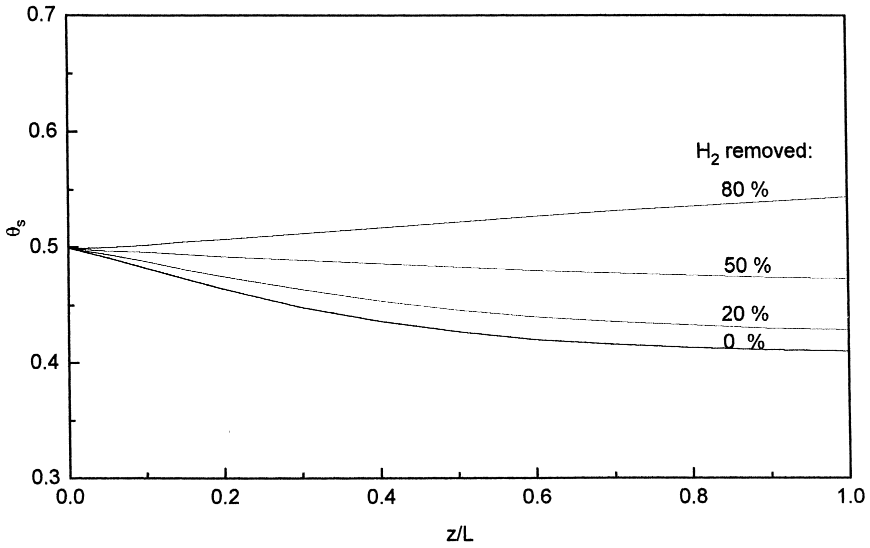

Fig. 1. Effect of H_2 removal on axial profiles of H_2S coverage on catalyst. $T=773$ K $Y_{H_2S}=0.04$ ppm, $P_t=1.2$ bar, $H_2O/CH_4=3$, $W/F_{CH_4}=37.1$ g h/mol.

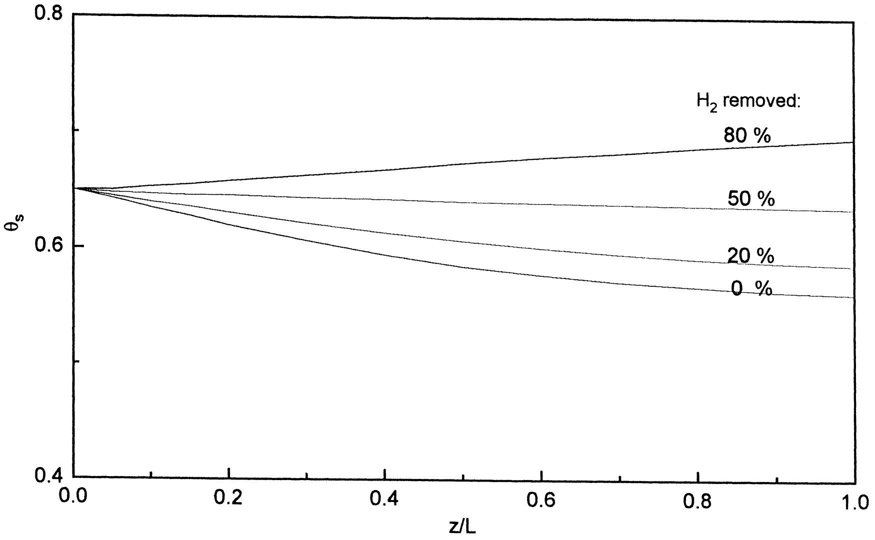

Fig. 2. Effect of H_s removal on axial profiles of H_2S coverage on catalyst. $T=823$ K, $Y_{H_2S}=0.2$ ppm, $P_t=1.2$ bar, $H_2O/CH_4=3$, $W/F_{CH_4}=37.1$ g h/mol.

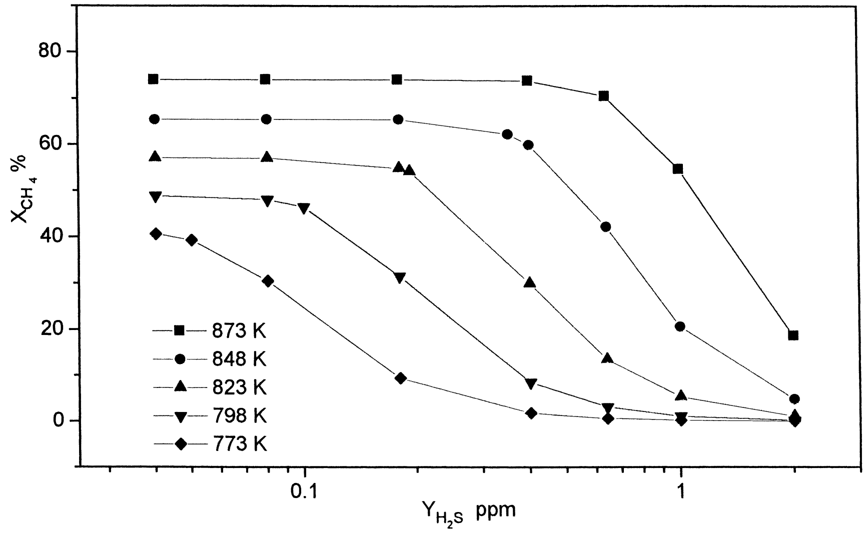

Fig. 3. Effect of H_sS concentration on methane conversion. $P_t = 1.2$ bar, $H_2O/CH_4 = 3$, $W/F_{CH_4} = 37.1$ g h/mol.

3. Results and discussion

In this simulation study, the effects of the removal of hydrogen produced on the catalyst by H_2S poisoning, on the performance of the membrane reactor have been investigated. Table 2 shows the basic data used for this investigation.

3.1. *The effects of hydrogen removal on the catalyst activity and the performances of the membrane reactor*

For comparing the membrane reactor with a fixed-bed reactor, f_{H_2} is set to zero in order to simulate the performance of the fixed-bed reactor, but

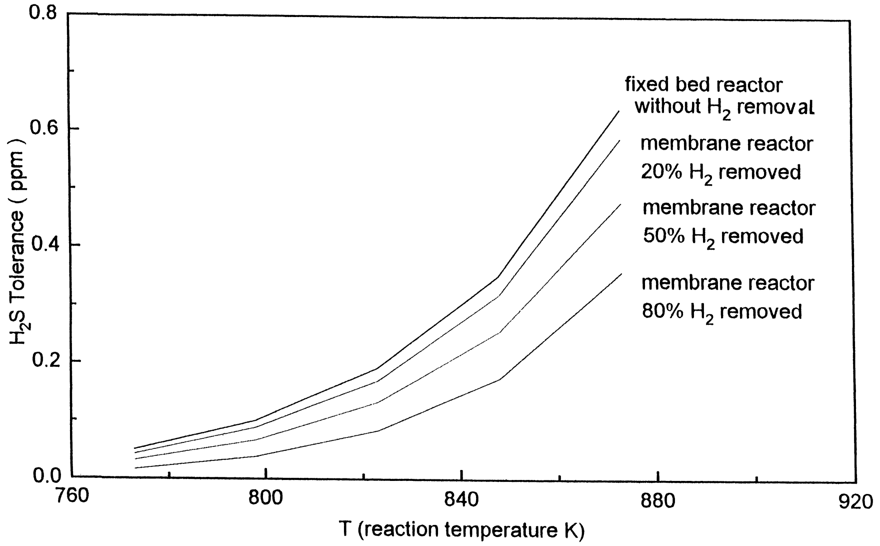

Fig. 4. Relation between H_2S tolerance and reaction temperature, for $W/F_{CH_4} = 95\%$, $X_{CH_4\,max}$, $P_t = 1.2$ bar, $H_2O/CH_4 = 3$, $W/F_{CH_4} = 37.1$ g h/mol.

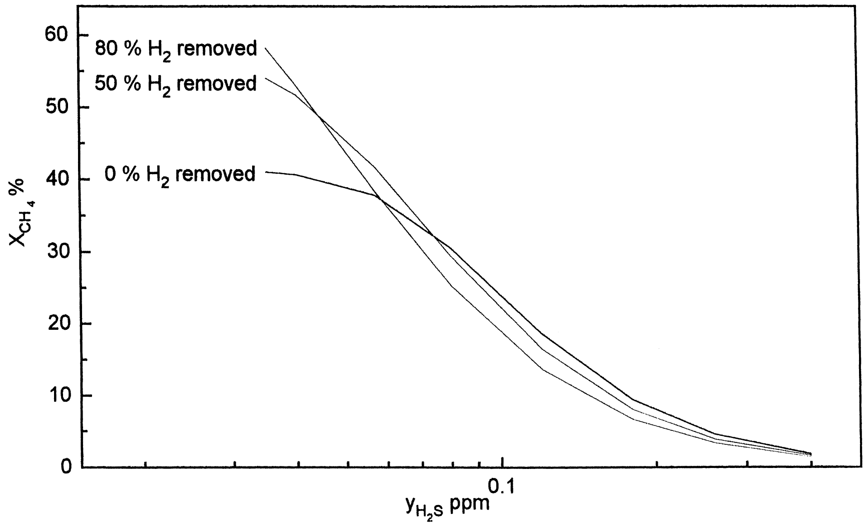

Fig. 5. Comparison of effect of H_2S concentration on performance of fixed-bed and membrane reactors, $T = 773$ K, $P_t = 1.2$ bar, $H_2O/CH_4 = 3$, $W/F_{CH_4} = 37.1$ g h/mol.

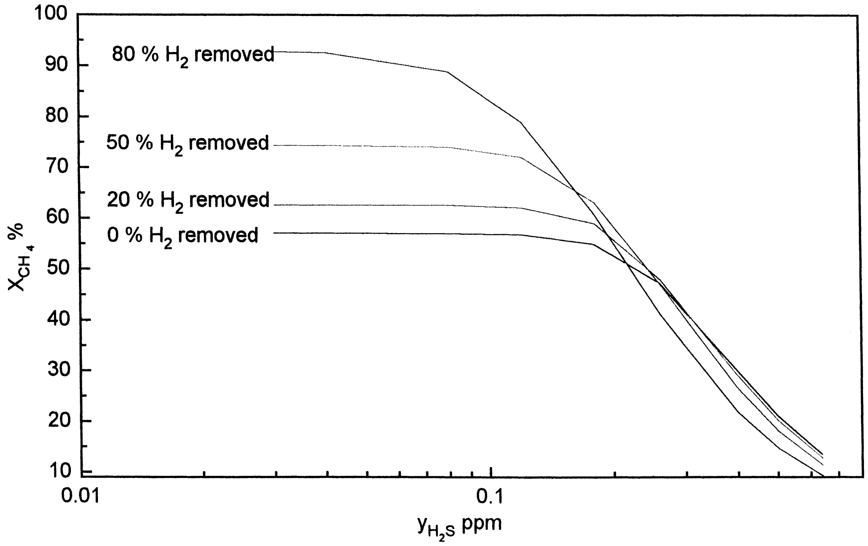

Fig. 6. Comparison of effect of H_2S concentration on performance of fixed-bed and membrane reactors, $T = 823$ K, $P_t = 1.2$ bar, $H_sO/CH_4 = 3$, $W/F_{CH_4} = 37.1$ g h/mol.

keeping other conditions the same as in the membrane reactor. In all cases for the membrane reactor, the sweep gas flows co-current to the reacting gas.

The effects of the extent of hydrogen removal on the catalyst poisoning are presented in Figs. 1 and 2. It can be seen from these figures that the H_2S coverage drops continuously along the reformer tube for cases where no hydrogen removed (i.e. fixed-bed reactor) and for low degrees of hydrogen removal; however, at 80% hydrogen removal the H_2S coverage increases along the tube length. Consequently, at high levels of H_2 removal catalyst poisoning by H_2S is more serious than at low percentages of hydrogen removal due to the increased value of p_{H_2S}/p_{H_2}.

Under the conditions studied, the limitations of different H_2S contents range from 0.04 to 0.4 ppm for cases without hydrogen removal as shown in Fig. 3. As can be seen, higher reaction temperatures can tolerate higher H_2S concentrations in methane.

Defining $X_{CH_4\,max}$ as the maximum conversion of methane which can result at given temperatures and pressures when H_2S poisoning is absent, the amount of H_sS which can be tolerated to give 95% of $X_{CH_4\,max}$ for different extents of hydrogen removal may be estimated. Fig. 4 shows a plot of this H_2S tolerance level for 95% $X_{CH_4\,max}$ vs. temperature. From this figure it can be seen that H_2S tolerance increases with increasing temperature and the tolerance also increases when hydrogen removal is less.

As catalyst poisoning by H_2S is sensitive to the ratio p_{H_2S}/p_{H_2}, hydrogen removal may result in a decrease in methane conversion using a membrane reactor compared with a fixed-bed reactor at higher H_2S concentrations. Figs. 5 and 6 show the variation of the methane conversions with different percentages of hydrogen removal and different H_2S contents for operating temperatures of 773 and 823 K, respectively. At higher H_2S contents, there is no advantage in employing a membrane reactor due to hydrogen removal resulting in more serious catalyst poisoning. To obtain benefit from the membrane reactor, the H_2S content has to be decreased to a limiting value depending on the conditions of operation. Based on Figs. 5 and 6, in general, the limiting value will decrease with increase of the proportion of hydrogen removed and increase with reaction temperature increase.

4. Conclusions

Simulations of the steam reforming of methane in a catalytic membrane reactor have been made in order to assess the effect of poisoning by small amounts of hydrogen sulphide. The results have been compared with fixed-bed operation. In general, the removal of hydrogen by means of the selective hydrogen permeable membrane increases the tendency to poisoning by H_2S. These effects can be minimised to some extent by operating at higher temperatures when H_sS poisoning is present. For successful catalytic membrane reactor performance for methane steam reforming, a high degree of sulphur removal from the feed stream would appear to be necessary.

5. Notation

A	constant in Eq. (5)
B	constant in Eq. (5)
Den	denominator in Eqs. (6)–(8)
f_{H_2}	permeability of hydrogen (kmol/m^2 h bar$^{0.5}$)
f_{CH_4}	feed rate of methane (kmol/h)
k_j	rate constants for reactions j, $j=1$,3 (kmol/kg cat h bar$^{0.25}$), $j=2$ (kmol/kg cat h bar)
K_{pj}	equilibrium constants for reaction, j, $j=1$, 3 (bar^2), $j=2$
K_m	threshold constant for methane decomposition (bar)
L	reactor length (m)
n	power term in Eq. (5)
N_i	flux of component i (kmol/h)
p_i	partial pressure of component i (bar)
P_t	total pressure on tube side
r_j	reaction rate for reaction j (kmol/kg cat h)
R_2	outer radius of membrane (m)
T	temperature (K)
W	weight of catalyst (kg)
Y_{H_2S}	concentration of H_2S (ppm)
X_{CH_4}	maximum conversion of CH_4 in absence of H_2S
Z	distance along reactor (m)

6. Greek letters

ν_{ij}	stoichiometric coefficient of component i, in reaction j
ρ_B	catalyst bulk density (kg/m^3)
θ_s	fractional H_sS coverage on catalyst,
Ω	cross sectional area of reaction tube (m^2)

Subscripts

t	tubeside of membrane reactor
s	shellside of membrane reactor

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References

[1] J.R. Rostrup Nielsen, Catalytic Steam Reforming, Springer, Berlin, 1984.

[2] S. Uemiya, N. Sato, H. Ando, T. Matsuda, E. Kikuchi, Appl. Catal. 2 (1991) 223–230.

[3] A.M. Adris, S.S.E.H. Elnashaie, R. Hughes, Can. J. Chem. Eng. 61 (5) (1991) 1061–1070.

[4] M. Chai, M. Machida, K. Eguchi, H. Arai, Chem. Lett. 1 (1993) 41–44.

[5] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Appl. Catal. A: Gen. 119 (2) (1994) 305–325.

[6] G. Barbieri, V. Violante, F.P. Di Maio, A. Criscuoli, E. Drioli, Ind. Eng. Chem. Res. 36 (8) (1997) 3369–3374.

[7] S. Laegsgaard Jorgensen, P.E. Hojlund Nielsen, P. Lehrmann, Catal. Today 25 (1995) 303.

[8] J.R. Rostrup Nielsen, J. Catal. 11 (1968) 220–227.

[9] C.H. Bartholomew, G.D. Weatherbee, G.A. Jarvi, J. Catal. 60 (1979) 257–269.

[10] J.L. Oliphant, R.W. Foeler, R.B. Pannel, C.H. Bartholomew, J. Catal. 51 (1978) 229–242.

[11] C.F. Ng, G.A. Martin, J. Catal. 54 (1978) 384–396.

[12] R.W. Fowler, C.H. Bartholomew, Ind. Eng. Chem. Prod. Res. Dev. 18 (4) (1979) 339–347.

[13] L.J. Christiansen, S.L. Andersen, Chem. Eng. Sci. 35 (1980) 314–321.

[14] J.R. Rostrup Nielsen, in: J.L. Figueiredo (Ed.), Progress in Catalyst Deactivation., Martinus Nijhoff, The Hague, 1982, 209 pp.

[15] W.W. Akers, D.P. Camp, AIChE J. 1 (1955) 471–475.

[16] N.M. Bodrov, L.O. Apelbaum, M.I. Temkin, Kinet. Catal. 8 (1967) 821–828.

[17] J.R.H. Ross, M.C.F. Steel, J.Chem. Soc., Faraday Trans. 1 (1972) 69.

[18] J.C. De Deken, E.F. Devos, G.F. Froment, Chem. Reaction Eng. ACS Symp. Ser. 1982, 196 pp.

[19] J. Xu, G.F. Froment, AIChE J. 35 (1989) 88–96.

[20] K. Hou, PhD Thesis, Salford University, 1998.

[21] E. Gobina, R. Hughes, J. Membrane. Sci. 90 (1994) 11.