Fixed bed reactor design for gas phase chain reactions catalysed by solids : the oxidative coupling of methane

Citation for published version (APA):

Hoebink, J. H. B. J., Couwenberg, P. M., & Marin, G. B. M. M. (1994). Fixed bed reactor design for gas phase chain reactions catalysed by solids : the oxidative coupling of methane. *Chemical Engineering Science*, 49(24B), 5453-5463. <https://doi.org/10.1016/0009-2509%2894%2900323-8>, [https://doi.org/10.1016/0009-2509\(94\)00323-8](https://doi.org/10.1016/0009-2509(94)00323-8)

DOI:

[10.1016/0009-2509%2894%2900323-8](https://doi.org/10.1016/0009-2509%2894%2900323-8)

[10.1016/0009-2509\(94\)00323-8](https://doi.org/10.1016/0009-2509(94)00323-8)

Document status and date:

Published: 01/01/1994

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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0009-2509(94)00323-8

FIXED BED REACTOR DESIGN FOR GAS PHASE CHAIN REACTIONS CATALYSED BY SOLIDS: THE OXIDATIVE COUPLING OF METHANE

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(Received 9 May 1994; accepted for publication 20 September 1994)

Abstract—A multitubular catalytic fixed bed reactor for the oxidative coupling of methane is designed. A heterogeneous two-dimensional reactor model taking into account axial dispersion of mass and enthalpy is applied. A reaction network consisting of 36 gas phase radical reactions and 10 catalytic reactions, based upon experiments with an Sn/Li/MgO catalyst at atmospheric pressure, temperatures of 923–1,023 K and methane-to-oxygen ratios of 2–12, is used. Intrapellet concentration profiles of molecules and, even more so, of radicals are shown to affect the selectivity towards ethane and ethylene. The importance of homogeneous reactions in the void space between the catalyst pellets is highlighted. The reactor dimensions are determined by heat removal considerations.

1. INTRODUCTION

A useful classification by Froment and Bischoff (Froment and Bischoff, 1990) of models for the design of catalytic fixed bed reactors, makes distinctions in two respects: one-dimensional versus two-dimensional and pseudohomogeneous versus heterogeneous models. The choice between one- and two-dimensional models is commonly related to the development of serious radial temperature profiles, and may be made on the basis of the criterion derived by Mears (1971). In the two-dimensional pseudohomogeneous model the radial dispersion of heat and mass is described by the corresponding effective thermal conductivity and diffusion coefficient. An additional parameter accounts for the extra resistance against heat transfer near the wall. The two-dimensional heterogeneous model makes a distinction between a solid phase, consisting of the catalyst pellets, and a fluid phase, consisting of the voids between the pellets. The mass and heat transfer between both phases is described with transfer coefficients. Distinction between pseudohomogeneous and heterogeneous models usually deals with the occurrence of pronounced profiles inside the catalyst pellets. The relevance of internal temperature profiles can be estimated (Mears, 1971), while for concentration gradients the traditional concept of the Thiele or Weisz modulus (Weisz and Prater, 1954) was developed. If necessary, such gradients should be taken into account via the corresponding mass and heat balances inside a single catalyst pellet.

An analysis along the above lines is usually performed and is straightforward for reactions not involving intermediates in the gas phase. However, a particular situation arises when a reaction consists of a catalytic initiation followed by a chain of propagation steps in the fluid phase. The chain carriers, typically radicals, have usually a very large reactivity when compared to the corresponding molecules. The intrapellet gradients for molecules and chain carriers will be comparable, but their relevance for the local net production rate of species will be completely different, as the concentrations of the chain carriers may be several orders of magnitude lower than for the corresponding molecules. Hence, such a kinetic scheme always requires the use of a heterogeneous model, even if internal gradients seem negligible according to standard criteria. A typical example of such a reaction is provided by the oxidative coupling of methane (Aparicio *et al.*, 1991; Bistolfi *et al.*, 1992; Reyes *et al.*, 1993; Couwenberg *et al.*, 1994) and is used in the present work to illustrate the above considerations.

2. OXIDATIVE COUPLING OF METHANE

2.1 Process

The oxidative coupling of methane has drawn world-wide attention as a possible alternative route for the production of ethylene (Keller and Bhasin, 1982; Hinsen *et al.*, 1984; Baerns *et al.*, 1989). The reactions proceed essentially at atmospheric pressure, temperatures in the range of 900–1,100 K and methane-to-oxygen feed ratios of 4–10. For commercial operation a per pass methane conversion of 20–30% is desirable at a selectivity towards C₂ products,

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i.e. the fraction of methane converted to ethane plus ethylene, of 70–80%. Various reactor types were proposed (Chen *et al.*, 1992). As the reactions are very exothermal, fluidised bed reactors are often recommended for industrial application (Dautzenberg *et al.*, 1991; Edwards *et al.*, 1990; Mleczko *et al.*, 1992), although scaling-up of such reactors is not straightforward, especially if a new process has to be designed. Fixed bed reactor design seems much more developed. Also, in order to prevent non-selective reactions in the gas phase downstream of the catalyst bed, as well as to achieve safe operation in a cold-box separation section, a single-pass oxygen conversion of 100% is required, which asks for severe suppression of axial dispersion. The latter is more easily realised in fixed beds than in fluidised beds.

The use of a fixed bed would imply multitubular reactors with tube diameters as small as 0.01 m and a very large number of tubes to satisfy an ethylene production capacity on an industrial scale (Dautzenberg *et al.*, 1991). The heat management problem encountered with a fixed bed concerns the simultaneous demand for a feed temperature high enough to allow ignition but low enough to avoid runaway. It is obvious that a careful design justifies the use of two-dimensional models able to predict more precisely the hot spot temperature (Froment and Bischoff, 1990).

2.2 Chemistry

In the absence of a catalyst a typical elementary reaction network for the oxidative coupling of methane consists of 39 gas-phase reactions between 13 molecules and 10 radicals (Chen *et al.*, 1991, 1994a, 1994b). The maximum yield which can be obtained under isothermal conditions amounts to 9% at a methane-to-oxygen feed ratio of 3 (Reyes *et al.*, 1993). Many different catalysts were developed and tested to improve the selectivity and yield towards ethylene. Outstanding among them are lithium/magnesia catalysts, of which tin-promoted Li/MgO is one of the most promising (Korf *et al.*, 1989). A detailed kinetic scheme for the latter catalyst (Couwenberg *et al.*, 1994) combines the aforementioned gas-phase model with catalytic reactions.

The most important catalytic reaction during the oxidative coupling of methane consists of the production of methyl radicals (Ito *et al.*, 1985; Aparicio *et al.*, 1991; McCarty, 1992; Reyes *et al.*, 1993; Krylov, 1993) on the catalyst surface through the following catalytic cycle:

Catalytic methyl radical production

The catalytic radical production cycle provides a heterogeneous initiation, which is much faster than the homogeneous initiation. The produced methyl radicals react further in the gas phase, where they can either couple in the presence of a third body M to form ethane, reaction (2), or react further through branched chains (Chen *et al.*, 1991, 1994a, 1994b), typically by reaction (3). Such gas-phase reactions occur in the pores of the catalyst pellets as well as in the void space between the catalyst pellets.

Coupling

Branched Chain

In the branched chain a methyl radical is oxidised to carbon monoxide with the simultaneous production of three hydroxy radicals. With increasing residence time in the reactor the amount of radicals thus would increase, ultimately leading to selectivities comparable to the selectivities obtained in an empty reactor. However, it was found that the catalyst does not only produce but also quenches radicals (Tulenin *et al.*, 1992; Sanches-Marcano *et al.*, 1992), which is accounted for by the heterogeneous termination reaction (4).

Heterogeneous termination

The heterogeneous termination reaction reduces the accumulation of radicals with increasing residence time and thus keeps the non-selective gas-phase reactions under control.

The catalyst unfortunately also provides a route for the catalytic oxidation of methyl radicals via methoxy species towards carbon oxides and in particular to carbon dioxide, reaction (5).

Catalytic oxidation

The branched chain is the major contribution to the formation of carbon oxides in the interstitial gas phase, i.e. in the void space between the catalyst pellets. Inside the catalyst pellets the catalytic oxidation dominates the production of carbon oxides. Under isothermal conditions a maximum yield of 20% can be obtained at a methane-to-oxygen feed ratio of 2.

A kinetic network, consisting of 36 gas-phase chain reactions between 11 molecules and 9 radicals, coupled to 10 catalytic reactions has been applied in the current work. The gas-phase reactions and corresponding kinetic parameters were taken from Chen *et al.* (1994b) but their network was reduced by omitting the reactions involving C₃ components. The catalytic steps and the values used for the corresponding Arrhenius and van 't Hoff parameters are shown Table 1. Table 2 summarises the range of experimental conditions covered with this kinetic model.

3. REACTOR MODEL EQUATIONS

A two-dimensional heterogeneous model was used, including axial dispersion of mass to account for the influence of dispersion at the required high oxygen conversion. As the heterogeneous model distinguishes between two phases, continuity equations and enthalpy balances have to be considered on the reactor scale for both phases. The net production rates in the corresponding equations should be evaluated from the integration of similar balances on the pellet scale. The complete set of equations is given below for spherical pellets.

Reactor scale, interstitial gas phase

Continuity equations for each component A

$$-\varphi_m \frac{\partial \left(\frac{C_A}{\rho_f} \right)}{\partial z} + \rho_f D_{ea} \frac{\partial^2 \left(\frac{C_A}{\rho_f} \right)}{\partial z^2} + \rho_f D_{er} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \left(\frac{C_A}{\rho_f} \right)}{\partial r} \right) - a_v N_A^s + \epsilon_B R_{v,A}^f = 0 \quad (6)$$

Enthalpy equation

$$-\varphi_m c_p \frac{\partial T}{\partial z} + \lambda_{ea}^s \frac{\partial^2 T}{\partial z^2} + \lambda_{er}^s \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + h_f a_v (T_s - T) + \epsilon_B \sum_{i=1}^n R_{v,i}^f (-\Delta_f H_i) = 0 \quad (7)$$

Momentum equation

$$-\frac{dp}{dz} = f \frac{\rho_g u_z^2}{d_p} \quad (8)$$

Reactor scale, solid phase

Mass balance for each component A

$$N_A^s = -\rho_f D_e \frac{d}{d\xi} \left(\frac{C_{A,s}}{\rho_f} \right) \Big|_{\xi=d_p/2} \quad (9)$$

Enthalpy equation

$$-h_f a_v (T_s - T) + \lambda_{ea}^s \frac{\partial^2 T_s}{\partial z^2} + \lambda_{er}^s \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_s}{\partial r} \right) + a_v N_A^s (-\Delta_f H_i) = 0 \quad (10)$$

Boundary conditions on reactor scale

$$p = p^0, \quad C_A = C_A^0, \quad T = T^0, \quad \frac{\partial T_s}{\partial z} = 0 \quad \text{at } z = 0 \text{ and all } r \quad (11)$$

$$\frac{\partial C_A}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = 0, \quad \frac{\partial T_s}{\partial r} = 0 \quad \text{at } r = 0 \text{ and all } z \quad (12)$$

$$\frac{\partial C_A}{\partial r} = 0, \quad \lambda_{er}^s \frac{\partial T_s}{\partial r} = \alpha_w^s (T_w - T_s) \quad \text{at } r = d_t/2 \text{ and all } z \quad (13)$$

$$\frac{\partial C_A}{\partial z} = 0, \quad \frac{\partial T}{\partial z} = 0, \quad \frac{\partial T_s}{\partial z} = 0 \quad \text{at } z = L \text{ and all } r \quad (14)$$

Table 1. Catalytic reaction mechanism as well as kinetic and thermodynamic parameters on an Sn/Li/MgO catalyst[†]

	A	E _a c.q. Δ _r H/kJ mol ⁻¹
(1)	O ₂ + 2 * ⇌ 2 O *	2.6 10 ⁻³
(2)	CH ₄ + O * → CH ₃ * + OH *	1.9 10 ⁹
(3)	C ₂ H ₆ + O * → C ₂ H ₅ * + OH *	1.4 10 ⁹
(4)	C ₂ H ₄ + O * → C ₂ H ₃ * + OH *	1.4 10 ⁹
(5)	OH * + OH * ⇌ H ₂ O + O * + *	6.9 10 ⁹
(6)	CH ₃ * + O * → CH ₃ O *	3.6 10 ⁶
(7)	2 CH ₃ O * + 5 O * → 2 CO ₂ + 3 H ₂ O + 7 *	∞
(8)	CO + O * → CO ₂ + *	1.9 10 ⁹
(9)	CO ₂ + O * ⇌ CO ₃ *	5.0 10 ⁻⁵
(10)	4 HO ₂ * _{surface} → 3 O ₂ + 2 H ₂ O	1.0 10 ⁻²
		0.0

[†] Units: m³ g mol⁻¹ (1,9), m³ g m³ c s⁻¹ (2,3,4,6,8), mol m³ c s⁻¹ (5), m³ g m² c s⁻¹ (10). Reaction numbers in parentheses

Table 2. Range of experimental conditions covered to develop the kinetic model used for the reactor simulation

T	923–1,023 K
p	100–150 kPa
$\text{CH}_4/\text{O}_{2,0}$	2.0–12
$W/F_{i,0}$	1.0–12 kg s mol ⁻¹
X_{CH_4}	2.6–25%
X_{O_2}	9.6–96%

Pellet scale

Continuity equation for each component A

$$\rho_f \frac{D_{e,A}}{\xi^2} \frac{d}{d\xi} \left(\xi^2 \frac{d(C_{A,\xi})}{d\xi} \right) + R_{v,A}^c = 0 \quad (15)$$

Enthalpy equation

$$\frac{\lambda_e}{\xi^2} \frac{d}{d\xi} \left(\xi^2 \frac{dT_p}{d\xi} \right) - \sum_{i=1}^n R_{v,i}^c (-\Delta_f H_i) = 0 \quad (16)$$

Boundary conditions on pellet scale

$$d(C_{A,\xi}/\rho_f)/d\xi = 0, \quad dT_p/d\xi = 0 \quad \text{at } \xi = 0 \quad (17)$$

$$C_{A,\xi} = C_A, \quad -\lambda_e dT_p/d\xi = h_f(T_s - T) \quad \text{at } \xi = d_p/2 \quad (18)$$

The non-convective heat transport in both the axial and radial direction is assumed to occur through both the interstitial gas phase and the solid phase (Dixon and Cresswell, 1979; Dixon, 1985). To account for intrapellet temperature profiles, two solid temperatures were considered: T_p is the local temperature at a certain position, ξ , inside the catalyst pellet, and T_s is the average temperature of the catalyst pellet. The latter determines the heat transport by conduction through the solid phase on a reactor scale. Therefore, following Dixon and Cresswell, who discussed thoroughly the heat transfer parameters in a heterogeneous model (Dixon and Cresswell, 1979), the fluid-to-pellet heat transfer coefficient, h_f , contains a contribution from the interstitial gas phase and from the solid phase. All other heat transport parameters were also determined with the correlations recommended by the same authors. The interfacial mass transfer coefficient was calculated according to Dwivedi *et al.* (1977), and the effective dispersion coefficients according to Gunn (1987). Diffusion inside the pellets was based on the molecular diffusion coefficient, corrected for the pellet porosity and tortuosity. The applied values of the reactor and catalyst parameters are shown in Table 3. Table 4 presents typical values of the heat and mass transport parameters as evaluated from the correlations mentioned above. Temperature dependence of all parameters was incorporated in the model except for the heat conductivity of the catalyst.

Table 3. Values of the reactor and catalyst parameters

Property	Value	Units
ϵ_B	0.5	m _g ³ m _r ⁻³
d_i	0.01	m
φ_m	1.0	kg m ⁻² s ⁻¹
λ_e	1	W m ⁻¹ K ⁻¹
d_p	0.001	m
τ	5	—
ϵ_p	0.2	—

Table 4. Typical values of transport parameters, as calculated from the applied correlations

	Radial	Axial	Units
λ_v^s	0.266	0.266	W m ⁻¹ K ⁻¹
λ_e^f	0.171	0.545	W m ⁻¹ K ⁻¹
D_e	0.00027	0.003	m ² s ⁻¹
α_w^s	563		W m ⁻² K ⁻¹
α_w^f	178		W m ⁻² K ⁻¹
h_f	300		W m ⁻² K ⁻¹

4. NUMERICAL SOLUTION

The model equations on the reactor scale, eqs (6)–(18), form a set of elliptic partial differential equations. The flow simulation package Phoenix (Spalding, 1986), which implements the control-volume method for solving the heat transport and fluid flow equations, was applied (Patankar, 1980). Making use of the radial symmetry the radial direction was subdivided into 5 cells, while 50 cells were distributed unequally over the axial direction with a high concentration near the expected hot spot. The Phoenix equation solver was linked to a Fortran routine which calculated for each cell its physical properties, heat/mass transport parameters and net production rates. The latter were obtained by integrating the model equations on the pellet scale, eqs (15)–(18). Orthogonal collocation (Finlayson, 1972) using a symmetrical polynomial with seven collocation points was applied to integrate the equations on the pellet scale. All simulations were carried out on a Silicon Graphics Power Challenge computer.

5. RESULTS AND DISCUSSION

Preliminary simulations with the model were performed to study the relevance of the various phenomena, incorporated in the model, for the oxidative coupling of methane. The main incentive in this respect was to reduce the quite considerable computing (CPU) time required for a single simulation.

Following Chen *et al.* (1991), the pseudo-steady-state approximation was applied for the radicals in the interstitial gas phase, i.e. eq. (6) was reduced to $\epsilon_B R_{v,A}^f = a_v N_A^3$ for the radicals. As shown in the model equations, interfacial mass transfer resistance was neglected. This simplification is justified at industrial conditions, as far as reacting molecules are concerned. For all but one of the radicals it was verified

that gradients outside the pellet could be neglected as well, even when low Sherwood numbers were assumed (Couwenberg *et al.*, 1994). The radical $\text{HO}_2^\bullet$, however, is produced in the gas phase and involved in the heterogeneous termination reaction at the external surface. Omitting the external mass transfer resistance therefore causes some overestimation of the quenching of radicals at the external surface. Temperature differences inside the pellets were shown to be small compared to the absolute temperature level because of the relatively good heat conducting properties of the catalyst. Therefore the pellet scale enthalpy equation (16) was not considered during further calculations and was replaced by $T_p = T_s$. The contribution of axial dispersion was neglected at the reactor inlet only, as expressed by the boundary conditions in eq. (11). This was justified, as expected, because of the low level of axial dispersion in fixed beds and the low conversion at the bed entrance. In the remainder of the bed, dispersion effects were included in the calculations. After these simplifications a typical CPU time amounted to 10 h for one simulation.

5.1 Pellet scale

Figure 1 shows, for pellet diameters of 0.25 mm and 2 mm, the concentration profiles in the catalyst for oxygen and methyl radicals, as obtained by integration of the pellet-scale balances, eqs (15)–(18). These results concern typical bulk gas concentrations and

temperatures found in the hot spot region of the fixed bed (see next section). The temperature difference between bulk gas and pellet was about 7 K. The results shown are representative for the behaviour of the other molecules and radicals.

For pellets with a diameter of 0.25 mm the oxygen concentration profile is quite flat. For pellets with a diameter of 2 mm the gradient is very steep and oxygen is completely consumed in the pellet centre. The methyl radicals show very pronounced gradients for both pellet diameters, even when the gradients of stable molecules are relatively small. Figure 1 clearly indicates the relevance of the radical gradients with respect to the absolute concentration level; the rate of reaction steps involving radicals will change drastically along the pellet coordinate, while steps not involving radicals are almost unaffected.

For pellet diameters of 0.25 mm the methyl radical concentration rises from the external surface to the centre of the pellet, as to be expected. For pellets with a diameter of 2 mm the concentration shows a maximum near the outer surface. Obviously there is a net production of radicals in the outer shell of the catalyst pellet and a net consumption deeper in the pellet. The local methyl radical concentration inside large pellets is dominated by a balance between the production through initiation, reaction (1), and the consumption via coupling, reaction (2), and catalytic oxidation, reaction (4). The lower oxygen concentration inside the catalyst pellet leads to a lower local

Fig. 1. Oxygen (circles) and methyl radical (plusses) profiles inside catalyst pellets with diameters of 0.25 mm (dotted curves) and 2 mm (full curves) at typical bulk gas conditions, corresponding with the hot spot in the packed bed. Note the different scales.

concentration of adsorbed oxygen. It causes a smaller production rate of methyl radicals and a relatively similar or even larger decrease of the rate of their catalytic oxidation. The coupling reaction rate, however, is not directly dependent on the oxygen concentration and is hardly affected. The coupling reaction rate is second-order in methyl radicals, so it consumes a greater fraction of the produced radicals and leads to a lower methyl radical concentration.

The same phenomena appear in Fig. 2, obtained at the same bulk gas conditions. Figure 2 shows the pellet-scale selectivity towards C_2 products as a function of the pellet diameter. This selectivity is defined as

$$S_{C_2} = \frac{2N_{C_2}|_{\xi=d_p/2}}{2N_{C_2}|_{\xi=d_p/2} + N_{CO_x}|_{\xi=d_p/2}} \quad (19)$$

Since methyl radical oxidation is more affected than coupling by lower oxygen concentrations, the selectivity increases with increasing diameter. Even in the absence of intrapellet oxygen concentration gradients, Couwenberg *et al.* (1994) have shown that the concentration gradients of the surface-produced radicals are kinetically significant. Figure 2 also shows by extrapolation to a pellet diameter of zero that a pseudohomogeneous reactor model would predict a selectivity which would be 10% too low, emphasizing the need for a heterogeneous fixed bed reactor model.

5.2. Reactor scale

For a methane-to-oxygen feed ratio of 10, Fig. 3 presents the methane and oxygen conversion, as well as the integral C_2 selectivity in the centre of the bed as a function of the axial reactor coordinate. From axial reactor coordinates higher than 0.5 m the quantities shown are equal to the corresponding radially averaged conversions and selectivity. The corresponding temperature profiles in the solid phase along the reactor coordinate at two radial positions in the bed are shown in Fig. 4. In the hot spot region, the gas-phase temperatures, not shown, are about 7 K below the solid temperatures; the differences are smaller elsewhere. The reactor tube with a diameter of 0.01 m is cooled via the wall with a medium at constant temperature. The small tube diameter is necessary to avoid runaway (Dautzenberg *et al.*, 1991; Wijngaarden and Westerterp, 1992). At the total feed flow rate of $1 \text{ kg m}^{-2} \text{ s}^{-1}$ the pressure drop amounted to 50 kPa for pellets with a diameter of 10^{-3} m . Even when the industrial application consists of an add-on unit to a naphtha cracker (Hoebink *et al.*, 1994) with a yearly capacity of 50,000 tons of ethylene, some 600,000 tubes with a diameter of 0.01 m are required.

Major but not complete oxygen conversion has been achieved directly behind the hot spot. Similar calculations, although not shown, were made with a pseudohomogeneous model and revealed underestimates of the reactor length at all conversions. The underestimation becomes larger with increasing

Fig. 2. Selectivity towards C_2 products as a function of the pellet diameter. See Fig. 1 for conditions.

Fig. 3. O_2 conversion, CH_4 conversion and C_2 selectivity in the bed centre versus the axial reactor coordinate. Conditions: $T_0 = 950$ K, $T_w = 920$ K, $d_t = 0.01$ m, $d_p = 0.001$ m, $CH_4/O_2|_0 = 10$, $p_0 = 150$ kPa, total flow rate $1 \text{ kg m}^{-2} \text{ s}^{-1}$.

Fig. 4. Axial temperature profile of the solid phase in the bed centre (upper curve) and at the wall (lower curve). See Fig. 3 for conditions.

pellet diameter, and is always serious for typical industrial pellet diameters.

The C_2 selectivity reaches a maximum in the hot spot. The lower downstream values are not only caused by consecutive reactions of O_2 with the C_2 products, but also by the lower downstream temperatures, which change the relative rates of selective and non-selective reactions. The ratio of C_2 formation to CO_x formation is favoured by high temperatures, because of an increased radical formation at high temperatures and a hardly activated catalytic oxidation of methyl radicals, see Table 1. This maximum selectivity cannot be fully exploited due to the incomplete oxygen conversion in the hot spot. The positive effect of higher temperatures in methane coupling is in contrast with the original intent leading to the development of tin-promoted Li/MgO catalyst. This intent was to improve the yield towards C_2 products by lowering the reaction temperature in order to suppress interstitial gas-phase reactions (Korf *et al.*, 1989).

The hot spot temperature amounts to about 200 K above the feed temperature and is considerably below the maximum adiabatic temperature rise of about 730 K, when taking into account complete combustion and the stoichiometric limitation by oxygen. At lower flow rates the hot spot moves to the reactor inlet and becomes more pronounced, since the interfacial heat transfer rate decreases due to a lower heat transfer coefficient, while the reaction rates proceed at similar concentration levels. The radial temperature profile is rather steep in the hot spot region in spite of the small tube diameter.

Figures 5 and 6 illustrate the different behaviour of the gas and catalyst phases, which can only be

accounted for by applying a heterogeneous model. The net production rate of C_2 products per unit reactor volume, shown in Fig. 5 in the bed centre as a function of the axial reactor coordinate, is much larger in the solid than in the interstitial gas phase. This holds especially in the neighbourhood of the hot spot. The net production rate of carbon oxides (see Fig. 6) is also different in both phases, notably near the hot spot, but the difference is less pronounced than for C_2 formation. Selective and non-selective reactions occur at comparable rates in the interstitial gas phase, while their catalytic counterparts favour C_2 production. The non-selective routes in the catalyst pellet and in the gas phase are completely different, as the former results mainly from catalytic oxidation and the latter from branched chains. In the catalyst pellet mainly CO_2 is produced, while CO production is dominant in the interstitial gas phase. The distinction between the two phases becomes even more important when reactors with a high volume ratio of interstitial gas and catalyst phase are applied for this process. As such these results plead against the use of fluidised bed reactors and certainly riser reactors, which were proposed as well (Tjatjopoulos *et al.*, 1994). Even at contact times in the order of 10^{-4} – 10^{-3} s, typical for riser reactors, the ratio of C_2 formation to CO_x formation is favoured by a low interstitial gas-to-catalyst ratio.

The performed simulations show a C_2 yield of only 8%, i.e. comparable to obtainable yields in the absence of catalyst (Reyes *et al.*, 1993). But these simulations correspond to the much higher methane-to-oxygen ratio of 10 in the feed, leading to stoichiometric limitation. Even at the small tube

Fig. 5. Rate of C_2 formation, $\text{mol m}_r^{-3} \text{s}^{-1}$, in the bed centre as a function of the axial reactor coordinate inside the catalyst pellets (full curve) and in the interstitial gas (dotted curve). See Fig. 3 for conditions.

Fig. 6. Rate of CO_x formation, $\text{mol m}^{-3} \text{s}^{-1}$, in the bed centre as a function of the axial reactor coordinate inside the catalyst pellets (thick curve) and in the interstitial gas (thin curve). See Fig. 3 for conditions.

diameter considered, lower methane-to-oxygen ratios were found to result in runaway. This is mainly caused by the high activity of the Sn/Li/MgO catalyst, $10\text{--}15 \text{ mol m}^{-3} \text{s}^{-1}$ at the reactor inlet conditions, and illustrates that because of heat transfer limitations a highly active methane coupling catalyst offers no advantages (Chen *et al.*, 1992). Dilution of the catalyst with inert material, in order to lower the volumetric heat production in the catalyst bed, does not seem attractive. It increases the ratio of interstitial gas to catalyst phase, leading to more pronounced contributions of the non-selective gas-phase reactions. Whether or not that approach would favour the C_2 yield should be the subject of further simulations. The current model is a useful tool to design and optimise a fixed bed reactor involving both catalytic and gas-phase reactions.

6. CONCLUSIONS

The design of fixed bed reactors for gas-phase chain reactions catalysed by solids requires the application of heterogeneous models in order to account fully for the involved chemistry. Intrapellet gradients of radicals, even if they are small, can have a large impact on the production rates. The ratio of interstitial gas phase to catalyst phase may be an important design variable. Further catalyst development should aim at improving the selectivity of the oxidative coupling of methane.

Acknowledgement—Financial support by the Commission of the European Communities in the framework of the Joule program, subprogram Energy from Fossil Sources,

Hydrocarbons, No. JOUF-0044-C, is gratefully acknowledged.

NOTATION

a_p	external pellet surface area per unit reactor volume, $\text{m}_p^2 \text{m}_r^{-3}$
c_p	specific heat at constant pressure, $\text{J kg}^{-1} \text{K}^{-1}$
C_2	ethane plus ethylene, —
C_A	molar concentration of species A , mol m_f^{-3}
$C_{A,s}^s$	molar concentration of species A , at the external pellet surface, mol m_f^{-3}
d_t	tube diameter, m
d_p	pellet diameter, m
$D_{e,A}$	effective diffusion coefficient in catalyst for species A , $\text{m}_f^3 \text{m}_p^{-1} \text{s}^{-1}$
D_{ea}	effective axial diffusion coefficient, $\text{m}_f^3 \text{m}_r^{-1} \text{s}^{-1}$
D_{er}	effective radial diffusion coefficient, $\text{m}_f^3 \text{m}_r^{-1} \text{s}^{-1}$
$-\Delta_f H_i$	heat of formation of species i , $\text{J mol}^{-1} i$
h_f	fluid-to-pellet heat transfer coefficient, $\text{W m}_p^{-2} \text{K}^{-1}$
n	number of molecules and radicals, —
N_A^s	molar flux of species A at the external catalyst surface, $\text{mol m}^{-2} \text{s}^{-1}$
p	pressure, Pa
r	radial reactor coordinate, m
$R_{v,A}^c$	net catalytic production rate of species A per unit catalyst volume, $\text{mol m}_c^{-3} \text{s}^{-1}$
$R_{v,A}^f$	net gas phase production rate of species A per unit gas phase volume, $\text{mol m}_f^{-3} \text{s}^{-1}$
S	selectivity, —
T	fluid temperature, K

T_p	solid temperature on pellet scale, K
T_s	solid temperature on reactor scale, K
T_s^s	solid temperature at the external pellet surface, K
T_w	wall temperature, K
u_s	superficial gas velocity, $m_f^3 m_r^{-2} s^{-1}$
X	conversion, —
Y	yield, —
z	axial reactor coordinate, m,

Greek symbols

α_w^f	wall-to-bed heat transfer coefficient of fluid, heterogeneous model, $W m^{-2} K^{-1}$
α_w^s	wall-to-bed heat transfer coefficient of solid, heterogeneous model, $W m^{-2} K^{-1}$
ϵ_B	void fraction of packing, $m_f^3 m_r^{-3}$
ϵ_p	pellet porosity, $m_f^3 m_p^{-3}$
λ_{ea}^f	effective axial thermal conductivity, fluid, $W m^{-1} K^{-1}$
λ_{er}^f	effective radial thermal conductivity, fluid, $W m^{-1} K^{-1}$
λ_{ea}^s	effective axial thermal conductivity, solid, $W m^{-1} K^{-1}$
λ_{er}^s	effective radial thermal conductivity, solid, $W m^{-1} K^{-1}$
λ_e	effective thermal conductivity of catalyst pellet, $W m^{-1} K^{-1}$
λ_g	thermal conductivity of fluid, $W m^{-1} K^{-1}$
ρ_f	fluid density, $kg_f m_f^{-3}$
σ	stoichiometric number, —
τ	pellet tortuosity, —
ξ	pellet coordinate, m,
φ_m	superficial mass flow velocity, $kg m_r^{-2} s^{-1}$

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