### KINETIC-TRANSPORT MODELS OF BIMODAL REACTION SEQUENCES—I. HOMOGENEOUS AND HETEROGENEOUS PATHWAYS IN OXIDATIVE COUPLING OF METHANE

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Abstract—A reaction-transport model that combines gas-phase reactions occurring within interstitial and intrapellet voids with surface reactions occurring on catalytic sites was used to describe the oxidative coupling of methane in packed-bed reactors, a typical example of bimodal (homogeneous-heterogeneous) reaction systems. A kinetic model for gas-phase reactions was assembled from available literature data; it describes well experimental results in empty reactors. Simulations suggest that  $C_2$  yields greater than 8-9% are unattainable with  $CH_4/O_2$  mixtures in homogeneous reactors. Staging the introduction of the oxygen reactant along the reactor length minimizes secondary oxidation reactions by lowering the local  $O_2$  pressures, and leads to a slight increase in maximum yield (12% for 200 injection points) but also to much larger required reactor volumes. The introduction of an ideal catalytic function (methyl and ethyl radical formation without full oxidation) also increases maximum  $C_4$  yields by increasing the concentration of methyl radicals involved in bimolecular coupling steps. However,  $C_2$  yields greater than 30% require selective catalysts with very high turnover rates (> 100 s<sup>-1</sup>); higher rates become ultimately limited by intrapellet diffusion rates. Again, staging oxygen by multiple injection schemes increases attainable yields but requires larger reactor volumes and catalytic sites with low reaction or(< 1) in oxygen. For optimum conditions, staged oxygen injection techniques lead to  $C_2$  yields as high as 50%.

#### 1. INTRODUCTION

Oxidative coupling offers a potential route for the direct conversion of light alkanes  $(C_1-C_4)$  to more useful products. Such reactions often proceed via bimodal pathways that require formation of alkyl radicals at surfaces and subsequent coupling and oxidation reactions of these radicals in gas-phase reactions. The increased reactivity of the higher alkanes formed in this reaction limits the maximum attainable yields in bimodal catalytic schemes for oxidative coupling of methane to  $C_2^+$  hydrocarbons.

#### 1.1. Bimodal reaction networks

High-temperature heterogeneous catalytic processes such as alkane cracking and naphtha reforming often occur in parallel with corresponding homogeneous pathways. More interestingly, surfaces can also form intermediates required in free-radical and thermal reactions. For example, catalytic dehydrogenation of alkanes leads to triene intermediates that undergo cyclization to aromatic products in gasphase electrocyclic addition reactions [1]. In catalytically stabilized thermal (CST) combustion, gasphase reactions are sustained by the formation of OH and O radicals at a solid surface [2].

Partial oxidation [3] and oxidative coupling [4-6]of alkanes are also examples of bimodal reaction sequences. In catalytic oxidative methane coupling, methyl radicals formed on metal oxide surfaces undergo thermal recombination reactions to give ethane as the initial product, and ethylene and carbon oxides as secondary products [4-6]. Oxidative coupling overcomes the thermodynamic barriers in methane dehydrodimerization (pyrolysis) reactions by kinetic coupling of the dehydrogenation and water formation steps. The latter lowers thermal efficiency compared to methane pyrolysis and consumes valuable  $H_2$  but allows  $CH_4$  reactions to occur at lower temperatures and with greater control of secondary polymerization reactions and much lower tar and coke yields.

Here, we develop a general framework for the description of bimodal reactions in convection-controlled reactors and apply it to the oxidative coupling reactions. A later paper will address the role of diffusive transport on the rate and selectivity of the oxidative coupling chemistry [7]. Such a report expands our previous description of transport effects [8] and offers a much more detailed analysis than a recent study of transport restrictions which is based on a four-species kinetic model [9]. Our diffusional model also allows us to explain the selectivity gains observed experimentally [10] as catalysts become limited by intrapellet diffusion of the oxygen reactant.

#### 1.2. Oxidative coupling of methane

Keller and Bhasin [11] first showed that catalysts can convert methane to a mixture of  $C_2^+$  hydrocarbons and carbon oxides (CO<sub>x</sub>) with much higher rate and selectivity than free-radical thermal pathways. Later studies identified several preferred catalysts consisting of promoted basic metal oxides [12–16]. Kinetic studies later suggested that methyl radicals are generated at surfaces [17]:

$$CH_4 + O^{-}(s) [or O^{2-}(s)] \longrightarrow CH_3^{-}$$
  
+ OH(s) [or O<sub>2</sub>H(s)], (s) = surface site (1)

desorb, and then recombine in the gas phase:

$$CH'_3 + CH'_3 + M \longrightarrow C_2H_6 + M^* \qquad (2)$$

in a step that becomes limited by relaxation of excited intermediates and energy transfer at low pressures. Spectroscopic evidence has confirmed the presence and the reactive nature of gas-phase  $CH_3$  species in homogeneous and catalytic oxidative coupling of methane [3-6, 18-21].

Homogeneous reactions of methane are initiated by thermal dissociation:

$$CH_4 \longrightarrow CH'_3 + H'$$
 (3)

or by oxygen-assisted dissociation:

$$CH_4 + O_2 \xrightarrow{------} CH_3 + O_2 H^2. \tag{4}$$

Rates are higher for  $C_2H_6$  than for  $CH_4$  because of the lower dissociation energy of their C-H bonds [22]. The presence of a catalyst leads to higher initiation rates, to subtle selectivity changes, and to the preferred formation of CO<sub>2</sub> instead of CO [23].

In oxidative coupling of methane,  $C_2$  selectivity decreases as  $CH_4$  conversion increases, an obstacle to the efficient use of this conversion chemistry. This inherent difficulty in reactions of very stable species, such as methane, arises because intermediate products (e.g.  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$ ) are often more reactive than the reactants ( $CH_4$ ) and continue to convert to thermodynamically favored products ( $CO_x$ ). This indirect thermodynamic effect of the weaker C-H bond energy in intermediate products is difficult to circumvent by either catalytic or homogeneous processes. The sequential nature of the reaction scheme, whether proceeding entirely via homogeneous pathways or with heterogeneous radical generation:



inherently limits the yields (i.e. the exit concentration) of unstable (reactive) intermediate products. In the kinetic scheme described in eq. (5), only  $CO_x$  species are truly stable products that cannot reenter the available reaction paths. All other species ( $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ) are intermediate products that can react further to more stable  $CO_x$  species through reaction pathways not significantly different from those used in the activation of methane and which lead to the formation of these intermediate products.

The competitive consumption of  $C_2$  products to  $CO_x$  [24] leads to the decrease in  $C_2$  selectivity

observed as the level of methane conversion increases; yields above 25% have not been reported [3, 24-26], even after exhaustive testing of many catalytic materials. Recent reports [27, 28] clearly suggest the crucial role of secondary reactions in controlling  $C_2$  yields during oxidative methane coupling. It appears that alternate chemistry occurring at much lower temperatures, significant increases in catalytic methyl formation rates, or novel reactor designs, will be required in order to increase  $C_2$  yields above presently achievable values.

Structural properties of catalytic materials also affect selectivity and yields in bimodal chemical reactions. Heterogeneous steps depend on surface area and site density; homogeneous steps, in contrast, depend on intrapellet and interpellet porosity. Moreover, the intermediate nature of the desired products and the high surface areas and turnover rates required for high heterogeneous radical generation rates often lead to intrapellet transport restrictions. Therefore, the pore size and tortuosity of catalyst pellets, and the effective diffusivities that these properties control, become crucial parameters in the design of novel catalytic materials.

Here, we present a detailed model that includes both homogeneous and heterogeneous kinetics. This model describes the effects of reactor configuration and of the chemical and structural properties of catalytic materials on  $C_2$  selectivity and yield. Our reaction-transport model consists of: (1) a homogeneous kinetic model consisting of 145 reversible reactionsteps, which describes available gas-phase reaction data without adjustable parameters, (2) heuristic kinetic models for surface-catalyzed reactions, and (3) pellet and reactor equations that describe the concentrations of 28 reactive species involved in homogeneous-heterogeneous reactions.

This reactor model is used to explore the underlying basis for inherent yield limitations, the role of heterogeneous radical generation steps, and the effect of controlled oxygen injection and of surface kinetics on  $C_2$  yields and selectivity. In the second paper in this series [7], we explore in detail the role of intrapellet diffusion constraints, which not only inhibit heterogeneous radical generation but can also lower oxygen concentrations within catalyst pellets.

#### 2. OXIDATIVE COUPLING REACTION NETWORKS

#### 2.1. Homogeneous kinetic model

The homogeneous kinetic model was assembled from elementary steps reported previously for gasphase reactions of light alkanes [29–34]. The model includes 145 reversible steps involving 28 reactive species. Elementary kinetics were used for most reactions, except those involving collisional activation or relaxation with third bodies (Appendix A). The stoichiometry and rate constants for each step are shown in Table 1. Reverse rates were calculated from equilibrium data [34] whenever reverse rate constants were not directly available. Reactions of  $C_3^+$  hydrocarbons were excluded from the kinetic network because  $C_3s$  are minor reaction products at typical oxidative coupling conditions. Reported rate and equilibrium constants were not adjusted in any way in order to improve the agreement between simulations and experimental data.

Individual reaction steps in the homogeneous kinetic model are shown in Table 1. Homogeneous methane conversion proceeds by free-radical reactions that involve chain initiation, transfer, and termination processes. Primary initiation occurs initially by dissociation of methane in activating collisions with a third body (7; all numbers refer to reaction steps in Table 1) or by hydrogen abstraction using  $O_2$  (1). As the concentration of radicals increases, faster chain transfer (2-6) and secondary initiation steps (8) become the preferred pathways for methyl radical formation.

Methyl radicals undergo bimolecular coupling reactions (9–11) to give ethane and oxidative processes with O<sub>2</sub>, O, HO<sub>2</sub>, and OH (19–29, 138, 139) to give methoxy and formaldehyde species that ultimately convert to  $CO_x$  (30–35). Hydrogen abstraction from formaldehyde leads to formyl radicals (50–56) that react further to form CO (57–61) and CO<sub>2</sub> (62–65). Formaldehyde also decomposes very rapidly on reactor walls (144). Methylene radicals formed from CH<sub>3</sub> (81) and ethylene (49) react further in non-oxidative hydrogen transfer reactions (72–74).

Ethyl radicals form in reactions of ethane with the same species that convert methane to methyl radicals (12–18). They also undergo sequential hydrogen abstraction events to form ethylene (36–42, 71),  $C_2H_3$  radicals (43–46, 136), and acetylene (127–129, 132).  $C_2$  radicals and reactive products lead to  $CH_3$  (47, 48, 75) and to CO and oxy-radicals (49, 66, 67, 76–80, 126, 130–134).  $C_2$  oxy-radicals dehydrogenate to HCCO (109–112, 118–124) and decompose to formaldehyde and CO (107, 108, 111, 113). Dihydrogen forms in hydrogen atom coupling (84) and in several hydrogen abstraction reactions (e.g. 4, 11, 12, 22...). Free-radical reactions of  $H_xO_y$  species are also included in the homogeneous kinetic model (85–106).

#### 2.2. Surface reaction model

A model catalytic function is used to explore the effects of heterogeneous radical generation on attainable  $C_2$  yields. This catalytic function catalyzes (irreversible) hydrogen abstraction reactions with stoichiometry:

$$CH_4 + 1/4 O_2 \xrightarrow{k_s, CH_3} CH_3 + 1/2 H_2 O \qquad (6)$$

proceeding at a rate given by

$$r_{\mathrm{CH}_3} = k_{\mathrm{s, CH}_3} \cdot [L] \cdot [\mathrm{CH}_4] [\mathrm{O}_2]^{\mathrm{s}}$$
(7)

where  $k_{s,CH}$ , is the kinetic constant for methyl radical formation, [L] is the density of active sites, and n is the oxygen pressure order [20, 21]. Similarly, ethyl radicals are assumed to form in similar surface-

catalyzed H-abstraction steps:

$$C_2H_6 + 1/4O_2 \xrightarrow{k_a, C_2H_5} C_2H_5 + 1/2H_2O$$
 (8)

at a rate given by  $r_{0,n} = k$ 

$$c_{2H_3} = k_{s, C_2H_3} [L] [C_2H_6] [O_2]^*.$$
 (9)

These simple kinetics are used to explore the effect of site density [L], site reactivity  $(k_i)$  or selectivity  $(k_{s,CH_1}/k_{s,C_2H_2})$ , and oxygen pressure order on C<sub>2</sub> attainable yields. They describe a hypothetical surface capable of oxidative activation of alkanes to form alkyl radicals, but which does not catalyze undesirable full oxidation reactions of alkanes or alkyl radicals.

The volumetric rates of heterogeneous methyl and ethyl radical generation  $(r_i; i = CH_3, C_2H_5)$  can also be expressed in terms of intrinsic properties of the catalyst:

$$\mathbf{r}_i = 10^6 \cdot \mathbf{s}_g \cdot \boldsymbol{\rho}_{p'} [L] \cdot \boldsymbol{\nu}_i \tag{10}$$

where  $r_i$  is in units of  $\mu$ mol/m<sup>3</sup> s.  $S_g$  is the BET surface area (m<sup>2</sup>/g),  $\rho_{ir}$  is the particle density (g/cc), [L] is the density of active sites (sites/m<sup>2</sup>), and  $v_i$  is the site turnover rate (molecules/sites). For illustration purposes, we choose typical values of site density ([L] ~ 10<sup>19</sup> sites/m<sup>2</sup>), surface area ( $S_g \sim 10 \text{ m}^2/\text{g}$ ), and particle density ( $\rho_r \sim 2 \text{ g/cc}$ ) to express  $r_i$  solely in terms of site turnover rates:

$$r_i = 3.32 \cdot 10^8 \cdot v_i \tag{11}$$

where  $r_i$ s are given by eqs (7) and (9). The site reactivity of catalysts are compared on the basis of a standard turnover rate ( $v_o$ ):

$$v_0 = v_{CH_3}$$
 [at 1073 K, 0.667 bar CH<sub>4</sub>, 0.333 bar O<sub>2</sub>]  
(12)

defined as the turnover rate for methyl radical generation at a specified value of operating conditions. Such a procedure completely defines the value of  $k_{3,CH_3}$  in eq. (7).

Ethyl radical generation rates are described by relating its rate constant  $(k_{s,C_2H_3})$  to that for methyl radical formation  $(k_{s,CH_3})$ :

$$k_{s, C_2H_5} = \gamma \cdot k_{s, CH_3} \tag{13}$$

where  $\gamma$  is a constant. The effects of a catalytic function on maximum C<sub>2</sub> yields will be examined by varying  $v_0$  from 0.01 to 100 (molecules/sites), *n* from 0 to 1, and  $\gamma$  from 0 to 4. Typical experimental catalytic turnover rates are less than 10 (molecules/sites), reflecting expected limits imposed by slow diffusive arrival of reactants at more reactive sites.

#### **3. REACTOR-PELLET EQUATIONS**

Here, we develop a general mathematical framework that couples diffusion and (gas-phase and surface) reactions within catalyst pellets with (gas-phase) reactions and convection within interpellet voids. In isothermal plug-flow reactors with negligible change in the total number of moles, the mass conservation of

Reaction	Forward rate	Equilibrium constant	Reference
			LW)
1 CH <sub>4</sub> + O <sub>2</sub> ≠ CH <sub>5</sub> + HO <sub>2</sub>	$40.35 \exp(-28,040/2)$	exp(	55
2 CH <sub>4</sub> + HO, ≠ CH <sub>5</sub> + H,O <sub>2</sub>	$20 \exp(-y00/T)$	$r_1 \exp(-2\pi m v_1 r)$	22
$3 \text{ CH}_{4} + \text{OH}_{2} \approx \text{CH}_{4} + \text{H}_{5} \text{O}_{1}$	$1.92 \times 10^{-7} T^{2.4} \exp(-1060/T)$	$\exp(7150/7 + 2.01)$	- - -
4 CH, $+$ H $\neq$ CH, $+$ H,	$2.25 \times 10^{-6} T^3 \exp(-4406/T)$	$\exp(-574/T + 3.60)$	<u>s</u>
$S CH, + C, H, \neq CH, + C, H_c$	$8.6 \times 10^{-14} T^{4.14} \exp(-6322/T)$	$\exp(-2527/T-0.67)$	
$\xi CH + CH, \neq CH, + CH$	$1.44 \times 10^{-12} T^{4.02} exp(-2754/T)$	$\exp(1163/T + 0.82)$	<u>ک</u>
	$2 \times 10^5 \exp(-44.503/T)$	800 T - 3.01	[62]
	$10.2 \times 10^{-3} T^{1.5} \exp(-4330/T)$	$\exp(-1570/T + 4.40)$	[34]
	Ren T - 0.64	$\exp(45,665/T-36.76)$	[ <b>3</b> 4]
	1 8 exp( = \$248/T)	$\exp(-5997/T-2.50)$	Z
N CD3 + CH3 + C2M5 + M = CH + CH + CH + H	$1 \times 10^4 \exp(-16.117/T)$	$\exp(28,423/T-4.30)$	[31, 34]
II (U <sup>3</sup> + (U <sup>3</sup> + C <sup>1</sup> ) + C <sup>1</sup> + U <sup>2</sup>	$5.54 \times 10^{-10} T^{3.5} evn(-2600/T)$	$\exp(1953/T + 4.27)$	E
17 C <sup>2</sup> U(+ U ← C <sup>2</sup> U) + U <sup>2</sup> さ ク U + OU + OU + O U + H O	2 2 2 2 10 <sup>-3</sup> 71.04 ern(	$\exp\left(9677/T + 2.68\right)$	5
		exp(958/T + 5.07)	<b>7</b>
	d0.35  ern(-25.600/T)	$\exp(-25.659/T + 5.17)$	[34]
	0.00  and  -750/T	exn(-7110/T + 3.68)	[34]
	$6.03 \times 10^{-10} T^{3.3} \text{ and } - 5285/T$	extn(3690/T + 1.49)	<u></u>
バ しっぽ。+ しっこ。# しっこ。+ ヘッル4	$\frac{1}{1} \sqrt{107} \frac{1}{100} \frac{1}{100}$	exn(-5) 642/T + 34.26)	[31, 34]
	$\int r/correct = \int dv s nt x T$	evn(35 107/T - 2.73)	[34]
19 CH <sub>3</sub> + 0 ≠ CH <sub>2</sub> O + H	(270) 		1451
20 CH <sub>3</sub> + O <sub>2</sub> ≠ CH <sub>3</sub> O + O	$(r/nt)/(+t) = ) dx_{2} = (r/nt) \times 26^{-1}$	τουία - 1440 (- 1446) 	
21 CH <sub>3</sub> + HO <sub>2</sub> ≠ CH <sub>3</sub> O + OH	19.87	CAP(12,120/1 1,04/)	
22 CH <sub>3</sub> + OH ⇔ CH <sub>2</sub> O + H <sub>2</sub>			145
23 CH <sub>3</sub> + O <sub>3</sub> ≠ CH <sub>2</sub> O + OH	52.5 exp(-17,300/T)		[36] [46]
24 CH <sub>3</sub> + O <sub>2</sub> = CH <sub>3</sub> O <sub>2</sub>	$9.03 \times 10^{-6} T^{-13.04} \exp(-8567/T)$	$(0) = \frac{1}{2} - \frac{1}{2} $	t
25 $CH_3 + HO_3 \neq CH_3O + H_2O$	$4.63 \times 10^{\circ} T^{-1.764} \exp(-1049/T)$	$\exp\left(62,202/F-2.46\right)$	12
26 $CH_1 + C_2H_3 \neq CH_4 + C_2H_3$	0.39	$\exp(33,551/T = 3.86)$	
27 CH, + C,H, ≠ CH, + C,H	$0.18 \exp(-8700/T)$	exp(-9698/T - 1.51)	
28 CH, + CH, ∂ ≠ CH, + CH, 0	24.09	$\exp(42,982/T-2.85)$	<u></u>
29 CH, + HCO = CH, + CO	120.46	$\exp(44,752/T-5.09)$	Ŧ
$30 \text{ CH}, 0 + \text{M} \neq \text{CH}, 0 + \text{H} + \text{M}$	$3.9 \times 10^{25} T^{-6.63} \exp(-16.740/T)$	$\exp(-11.817/T + 30.73)$	<b>x</b> ]
31 CH, $0 + H \neq CH, 0 + H$ ,	19.87	$\exp(42,408/T+0.75)$	<u>-</u>
32 CH, $0 + 0 \neq CH$ , $0 + 0H$	6.023	$\exp(41_413/T + 1.55)$	- - -
33 CH,0 + OH ≠ CH,0 + H,0	18.07	$\exp(50,132/T-0.84)$	[46]
34 CH.0 + 0, ≓CH.0 + HO,	$0.066 \exp(-1310/T)$	$\exp(14,796/T + 1.64)$	<u></u>
35 CH $0 + C\dot{0} \neq C\dot{1}$ , + CO,	$15.66 \exp(-5940/T)$	$\exp(17,999/T - 1.01)$	5 5 5
36 C,H, + M ≠ C,H, + H + M	$1.10^5 \exp(-15.636/T)$	$\exp(-19,195/T+28,18)$	<b>1</b>
$37 C, H, + O, \neq C, H, + HO,$	$0.84 \exp(-1950/T)$	$\exp\left(6788/T-0.92\right)$	<u></u>
38 C,H, + HÓ, ≓ C,H, + H,O,	0.3	$\exp(25,337/T-2.40)$	2 2 2 2 2 2
19 C.H. + OH = C.H. + H, Ô	24.1	$\exp(42,123/T - 3.40)$	
An C.H. + H $\approx$ C.H. + H.	1.8	$\exp(34,400/T-1.81)$	T.
41 $C, H, + C, H, \neq C, H, + C, H_{*}$	1,4	$\exp(32,446/T-6.08)$	<u>s</u> 2
42 $C, H, + C, H, \neq C, H, + C, H_{L}$	0.48	$\exp(36,137/T-4.59)$	<b>3</b>
$43 \text{ C,H}_{4} + \text{H} \neq \text{C,H}_{3} + \text{H}_{2}$	$1.33 \times 10^{-6} T^{1.53} \exp(-6160/T)$	$\exp(-1737/T + 2.78)$	[ <del>4</del> 6]

Table 1. Homogeneous kinetic model?

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[34]	exp(-27,612/T + 0.89)	$144.5 \exp(-28.500/T)$	90 $O_2 + H_2 \neq HO_2 + H$
[ <b>7</b> 4]	exp(- 82/0/1 + 2/3) ern (25 981/T - 29 09)	$1.00 \times 10^{-1}$ $\frac{1}{13} \times 10^{-11} T$	$\begin{array}{c} \begin{array}{c} \begin{array}{c} 0 \\ 0 \\ 0 \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $
[34]	$\exp(60,870/T-31.91)$	$1.88 \times 10^{-11} \exp(900/T)$	ο Ο + Ο + Μ + Ο 2 + Μ X8 Ο + Η ‡ΟΗ + Ο
[45]	$\exp(7724/T-1.59)$	$6.4 \times 10^{-6} T^2 \exp\left(-1490/T\right)$	80 H, + OH # H,O + H 91 O - O - M - O - M
[.44] [.34]	axp(-295/T + 0.79)	$1.08 \times 10^{-6} T^{2.6} \exp(-2980/T)$	85 H <sub>2</sub> + 0 $\approx$ 0H + H
[31]	0.04	10.0 • • • • • • • • • • • • • • • • • • •	83 CH + U2 # HCU + U 84 H + H + M # H, + M
[31]	$0.0^{\pm}$	40.0	82 CH + 0 = CO + H
[34]	$\exp(63,867/T - 32.01)$ $^{322} \exp(-3040/T^{3})$	4.56 × 10° T = *-1 exp ( = 721/T) 801 35 erb ( = 7550/T)	∞ ∪, π + π + m ≠ ∪, π, + m 81 CH, + H ≠ CH, + H,
ξ <u>Ξ</u>	0.04	10.0	79 C <sub>2</sub> H + O ≠ CO + CH
<b>3</b> 2	$\exp\left(7.618/T + 0.34\right)$	24	78 $C_1H + O_1 \neq CO_1 + HCO^2$
[3]	$87.1 \exp(-36.300/T)^3$	2017 1606	$77 C_{3}H_{4} + 0 \neq CH, 0 + CH, 0 + CH,$
5	$\exp(6920/T + 31.59)$	24.1	75 $C_2H_5 + HO_2 \neq CH_5 + CH_2O + OH_7$ 75 $C_1U + O = CU CHO + CH_2O + OH_7$
[ <del>3</del> 4] [71]	exp(4577/JT + 2.41) err(31.046/T6.17)	114,4	$74 \text{ CH}_3 + \text{CH}_3 \neq C_2 \text{H}_4 + \text{H}$
	0.0	40.0	72 CH2 + H ≠ CH + H2 72 CH2 + A # - A # - A # - A # - A # - A # - A # - A # - A # - A # - A # - A # - A # - A # - A # - A # - A # - A
	$m_{rem}^{24}$ 074/T $= 5.41$	1.13(300/T) <sup>0.5</sup>	71 $CH_3 + C_2H_3 = CH_4 + C_3H_4$
[34]	$\exp(-64,908/T-5.53)$	32.0	<sup>10</sup> CH <sub>2</sub> + CH <sub>2</sub> ∓ C <sub>2</sub> H <sub>2</sub> + H <sub>2</sub> 70 CH, + O ≠ CH + OH
32	$288 \exp(-34,850/T)^{2}$	$(9.95 \exp(-4500/T))$	$\underset{n}{68}$ CH <sub>2</sub> + O <sub>2</sub> = CH <sub>2</sub> O + O
[32]	$(11.75 \exp{(-11,100/T)^{\ddagger}})$	52.5 exp(	w С <sub>2</sub> m <sub>2</sub> + О≓ С <sub>2</sub> mO + H 67 С.Н. + ОН ⇒СН. + СО
	$\exp(30,129/T-2.65)$	$150.6 \exp(-11,900/T)$	$65 \text{ CO} + HO_2 \neq CO_2 + OH$
5	$\exp(3513/T - 2.56)$	$2.53 \exp(-24,000/T)$	$64 \text{ CO} + \text{O}_3 \neq \text{CO}_2 + \hat{\text{O}}$
[ <del>3</del> 4]	$\exp(11,783/T-5.29)$	0.07 exp (0.00091 <i>T</i> ) 6 24 x 10 <sup>10</sup> exp(151077 )	63 CO + O + M ≠ CO, + M
5	$\exp(16,566/T-0.61)$	$51.2 \exp(-850/T)$	61 HCO + O₂ ≠ CO + HO₃ 23 CO + OⅡ + 20 + HO₃
[34] [34]	$\exp\left(44_{3}I8/I$ - 1.49) $\exp\left(43.182/T$ - 0.69)	30.12	$60 HCO + O \neq CO + OH$
[34]	$\exp\left(-\frac{9417/T}{28.49}\right)$	$5.11 \times 10^9 T^{-2.14} \exp\left(-10,278/T\right)$	28 HCO+M # H + CO + M 59 HCO+H # CO ≠ H
<u>4</u>	$\exp(-13/30/1 + 3.09)$ $\exp(51.901/T - 3.09)$	30.11	$57 \text{ HCO} + \text{OH} \neq \text{CO} + \text{H}_2\text{O}^2$
4	$\exp\left(-\frac{1207}{7}+\frac{2.20}{2}\right)$	$2 \exp(-5870/T)$ 20 5 $\exp(-18.600/T)$	$\begin{array}{c} 50 \ \text{CH}_20 + \text{HO}_1 \approx \text{HCO} + \text{H}_20_2 \\ 56 \ \text{CH}_20 + \text{O}_2 \approx \text{HCO} + \text{HO}_2 \end{array}$
145 145	$\exp(8430/T - 0.80)$	$5.54 \times 10^{-9} T^{2.61} \exp(-2950/T)$	$54 \text{ CH}_2 \text{ O} + \text{CH}_3 \neq \text{HCO} + \text{CH}_4$
	$\exp\left(7856/T + 2.79\right)$	$2.2 \times 10^{-4} T^{4.1}$ exp ( $-1510/T$ ) 18 erg ( $-1550/T$ )	$52 \text{ CH}_{2}^{1}\text{O} + \Pi \neq \Pi \text{CO} + \Pi_{2}^{1}$ $53 \text{ CH}_{2}^{1}\text{O} + \text{O} \neq \Pi \text{CO} + \text{OH}$
F (5)	$\exp(15,580/T + 1.20)$	$3.43 \times 10^{-3} T^{1.18} \exp{(225/T)}$	51 CH <sub>2</sub> O + OH $\approx$ HCO + H <sub>2</sub> O
[32] [20 34]	u. /9 exp ( = 06UU/ / ]* exn ( = 45 730/7 ± 37 78)	$5 \times 10^{4} \exp(-38,489/T)$	SO $CH_2O + M \neq HCO + H + M$
[32]	$0.91 \exp(-8200/T)^{4}$	$2 \exp(-500/T)$	48 C2H4 + UH ⊉CH3 + CH20 49 C2H4 + O ⊉ CH2O + CH
t t	$\exp(14,630/T + 4.37)$	$1.3 \times 10^{-4} T^{1.55} \exp(-215/T)$	47 $C_2H_4 + 0 \neq CH_3 + HCO^2$
	$\exp(5987/T + 1.19)$	$1.0 \times 10^{-3} T^{-1.2} \exp(-2100/T)$ 42 1 ever (29 000/T)	$46 \text{ C,H}_{4} + 0.4 \text{ C,H}_{3} + 10.46  $
[34]	$\exp(-1163/T - 0.82)$	$6.63 \times 10^{-12} T^{3.7} \exp(-4780/T)$	44 $C_2H_4 + CH_5 \neq C_2H_5 + CH_4$

### Kinetic-transport models of bimodal reaction sequences-I

(Contd.)
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Tab

Reaction	Forward rate	Equilibrium constant	Reference
			55
91 02 + UH = HO2 + U	$22.5 \exp(-26,300/L)$	$(-20,010) = \frac{1}{20}$	<u>z</u> :
$92 \text{ H}_{1}\text{O}_{2} + \text{H} \rightleftharpoons \text{H}_{2} + \text{H}\text{O}_{2}$	$48.2 \exp(-4000/T)$	$\exp(905/7 + 7/500)$	<b>x</b>
93 H <sub>2</sub> O <sub>2</sub> + OH ≠ HO <sub>2</sub> + H <sub>2</sub> O	$1.75 \exp(-160/T)$	$\exp(16/787/T - 0.99)$	34
94 $H_2O_3 + O \rightleftharpoons OH + HO_2$	$9.6 \times 10^{-6} T^2 \exp(-2000/T)$	$\exp(8068/T + 1.39)$	[34]
95 H <sub>2</sub> O <sub>2</sub> + M <b>⇔</b> OH + OH + M	$1.28 \times 10^{21} T^{-4.86} \exp(-26,795/T)$	$\exp(-26,186/T+33.21)$	[34]
<b>96</b> $H_2C + H \neq H_2 + OH$	$6.2 \times 10^{-5} T^{1.9} \exp(-9265/T)$	$\exp(-7724/T + 1.59)$	[34]
97 $H_2O + O \neq OH + OH$	$4.6 \times 10^{-3} T^{1.3} \exp(-8605/T)$	$\exp(-8719/T + 2.39)$	[34]
$98 \text{ OH} + H + M \neq H_2 \text{ O} + M$	0.0227 - 2	$\exp(61,319/T - 31.58)$	[34]
99 OH + HO <sub>2</sub> $\rightleftharpoons$ H <sub>2</sub> $\dot{O}$ + O <sub>2</sub>	14,455/ <i>T</i>	$\exp(35,336/T-2.48)$	<u>4</u>
$100 HO_{2} + H \neq H_{2}O + O$	30.0	$\exp(27,065/T + 0.24)$	[31, 34]
101 $HO_2 + H \neq OH + OH$	$168.6 \exp(-440/T)$	$\exp(18,346/T+2.64)$	[¥]
$102 H_2 \tilde{O}_2 + O_2 \approx HO_2 + HO_2$	$54.2 \exp(-20,000/T)$	$\exp(-18,549/T+1.49)$	F
103 H <sub>2</sub> + O <sub>2</sub> ≠ OH + OH	$17.0 \exp(-23,900/T)$	$0.5 \exp(-14,600/T)^{4}$	[32]
$104 H_2O_3 + H \neq H_2O + OH$	$24.1 \exp(-2000/T)$	$\exp(35,133/T + 1.64)$	34
105 O + H + M ≠ OH + M	$4.7 \times 10^{-6} T^{-1}$	$\exp(52,599/T-29.18)$	[ <b>1</b> 4]
106 HO <sub>2</sub> + M $\neq$ O + OH + M	$5 \times 10^{-8} \exp(-34,254/T + 31.82)$	5 x 10 <sup>- 8‡</sup>	[34, 33]
$107 \text{ CH}_{3}\text{CO} + \text{M} \approx \text{CH}_{3} + \text{CO} + \text{M}_{3}$	$3.63 \times 10^3 \exp(-29,650/T)$	$1.17 \times 10^{-11} \exp(8350/T)^{2}$	[32]
108 CH <sub>2</sub> CO + OH $\approx$ CH <sub>2</sub> O + HCO	28.2	$16.2 \exp(-8050/T)^{4}$	[32]
109 CH <sub>2</sub> CO + OH $\approx$ C <sub>2</sub> HO + H <sub>2</sub> O	$7.6 \exp(-1500/T)$	$1.0 \exp(-7850/T)^{4}$	[32]
110 CH <sub>2</sub> CO + $O \approx C_2 HO$ + OH	$50.11 \exp(-4000/T)$	$0.62 \exp{(-1650/T)^{2}}$	[32]
111 CH <sub>2</sub> CO + O $\approx$ CH <sub>2</sub> O + CO	19.95	$25.12 \exp(-51,750/T)^{4}$	[32]
112 CH <sub>2</sub> CO + H $\approx$ C <sub>2</sub> HO + H <sub>2</sub>	$75.9 \exp(-4000/T)$	$2.04 \exp(-2650/T)^{4}$	[32]
113 CH <sub>2</sub> CO + H $\approx$ CH <sub>3</sub> + CO <sup>-</sup>	$10.96 \exp(-1700/T)$	$0.89 \exp{(-18,500/T)^4}$	[32]
114 $C_2HO + O_2 \neq CO + CO + OH$	$1.5 \exp(-1250/T)$	$3.16 \times 10^{-13} \exp(-45,600/T)^{4}$	[32]
115 $C_1HO + O \neq CO + CO + H$	1.2	$3.9 \times 10^{-12} \exp(-52,600/T)^3$	[32]
116 $C_{1}HO + H \neq CH_{2} + CO$	109.6	$51.3 \exp{(-15,500/T)^3}$	[32]
117 $C_2HO + OH \neq HCO + H + CO$	10.0	$1.5 \times 10^{-11} \exp(-8950/T)^{2}$	[32]
118 CH, CHO ≠ CH, + HCO	$2 \times 10^{13} \exp(-39.550/T)$	$1.9 \exp(2050/T)^{4}$	32
119 CH <sub>3</sub> CHO + $O_3 \neq CH_3CO + HO_2$	$19.9 I^{u_1} \exp(-21,100/T)$	$204 \exp(-2530/F)$	25
$120 \text{ CH}_{3}\text{CHO} + \text{H} \neq \text{CH}_{3}\text{CO} + \text{H}_{2}$	$39.3 \exp(-2100/T)$	16.2 exp (	[32]
121 CH, CHO + UH ≓ CH, CU + H₂U im cui cuio i cui co i cui	10.0 5 ( 000(T)	22.4 CXP(-11,500/7)	[26]
	0.095 and 1 Juni 7 Juni	1 555) (	[26]
$124 \text{ CH} \text{ CHO} \pm \text{ HO} \pm \text{ HO} \pm \text{ CH} \text{ CO} \pm \text{ HO}$	1.7 Arr(-5350/T)	$15 \exp(-700/T)^{4}$	
$125 \text{ CH}_{10} + \text{M}_{2} \text{ CH}_{1} + \text{CO} + \text{M}_{2}$	$1.2 \times 10^3 \exp(-630^3/T)$	$exn(-5548/T \pm 31.24)$	[30] 34]
126 C.R. + HO. ⇒ CH.CHO + OH	$6.02 \times 10^{-3} \exp(-4000/T)$	$2.95 \times 10^{-3} \exp(-27.550/T)^{\ddagger}$	[32]
$127$ C,H, + M $\neq$ C,H, + H + M	$2.8 \times 10^{29} T^{-7.49} \exp(-22.917/T)$	$\exp(-20.619/\dot{T}+29.70)$	5
128 C,H, + H ≠ C,H, + H,	96.4	$\exp(32.976/T - 0.28)$	3
129 $C_{i}H_{i} + O_{i} \neq \hat{C}_{i}H_{i} + \hat{H}O_{i}$	0.12	$\exp(5365/T + 0.61)$	[ <del>3</del> 4]
130 C <sub>2</sub> H <sub>3</sub> + O <sub>2</sub> ≈ HCO + CH <sub>2</sub> O	$4 \exp(150/T)$	$9.5 \exp(-42,300/T)^{\ddagger}$	[32]
131 $C_{2}H_{3} + 0 \neq CH_{3}CO + H_{2}$	33,11	$2089 \exp(-42,600/T)^{2}$	[32]
132 $C_1H_3 + OH \neq C_2H_1 + H_2O$	30.12	$\exp(40,700/T - 1.87)$	<b>F</b>
133 $C_2H_3 + OH \approx CH_3CHO$	30.20	$7.4 \times 10^{42} \exp(-57,500/T)$	[32]

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34 C,H, + 0 <del>a</del> CH, + C0	$120.5 \exp{(-3300/T)}$	$\exp(24,945/T + 2.24)$	[34]
35 CH, + OH æ CH + H,O	$0.27 T^{0.7} \exp(-12,990/T)$	0.0*	(m) (m)
36 C,Ĥ₄ + O æ C,H, + ÔH	25.3 exp(- 2514/T)	$\exp(-2733/T + 3.58)$	[31, 34]
37 C,H, + C,H, ⊉ Č,H, + C,H,	0.96	$\exp\left(34,713/T-3.07\right)$	[34]
38 CH, + OH ≓ CH, + H,O	$1.55 \times 10^{-6} T^{2.1} \exp(-1203/T)$	$\exp(5100/T + 0.27)$	[31, 34]
39 CH,+OH	$2 \times 10^{4} \exp(-13,832/T)$	$\exp(-6216/T - 4.27)$	[31, 34]
40 HCO + O ⇔ CO, + H	30.12	$\exp(54,965/T-5.99)$	[34]
41 C,H, + H <b>≠</b> C,H + H,	$60.23 \exp{(-11,220/T)}$	$\exp(-10,274/T+2.03)$	[ <del>4</del> 6]
42 C,H, + OH ≠ C,H + H,O	$1.45 \times 10^{-8} T^{2.68} \exp(-6060/T)$	$\exp(-2549/T + 0.44)$	4
43 CH,O, + CH, ≠ CH,O + CH,O	24.09	$\exp\left(17,896/T-2.36\right)$	[ <del>1</del> 6]
44 CH.O # CO + H.	I × 10 <sup>3</sup>	0.0 <sup>4</sup>	Ð
45 $CH_3^+ + C_2H_6 \neq C\dot{H}_4 + C_2H_5$	$5.48 \times 10^{-13} T^4 \exp(-4169/T)$	$\exp(2527/T + 0.68)$	[34]
<sup>+</sup> All rates in units of $\mu$ mol/m <sup>3</sup> s.			
<sup>‡</sup> Denotes kinetic constant for reverse read	ction.		
*Fast reaction, assumed irreversible.			

reactive species i = 1, ..., N is described by

$$U_0 \frac{\mathrm{d}C_i(z)}{\mathrm{d}z} = \varepsilon \sum_{j=1}^G R_{ij}(R_0, z) - a_v D_i \frac{\partial c_i}{\partial r}(R_0, z)$$
(14)

with initial conditions:

$$C_i(z=0) = C_{i0}.$$
 (15)

The right-hand side of eq. (14) accounts for the rate of reaction of component *i* within bed interstices and within pellets, respectively.  $C_i(z)$  is the molar concentration of species *i* at position *z* in the reactor,  $R_{ij}(R_0, z)$  is the rate of reaction of species *i* in reaction *j* within bed voids at position *z*, and  $D_i$  and  $\partial c_i/\partial r$  are the effective diffusion coefficient and the concentration gradient of species *i*, respectively.  $U_0$ ,  $\varepsilon$ ,  $a_v$  and  $R_0$  are the interstitial gas velocity, bed void fraction, bed surface area to volume ratio, and pellet radius, respectively. The above definition of gas velocity makes the bed residence time equal to  $L/U_0$ , where *L* is the reactor length.

The steady-state mass conservation equations and associated boundary conditions for the *i*th species within the pellets are

$$\nabla D_i \nabla c_i(r, z) + \Phi \left[ \sum_{j=1}^G R_{ij}(r, z) + \sum_{k=1}^S L_{ik}(r, z) \right] = 0$$
(16)

 $c_i(R_0, z) = C_i(z)$ 

(17)

$$\nabla_{\mathcal{C}}(0, -) = 0 \tag{18}$$

$$\mathbf{v}c_t(\mathbf{0}, \mathbf{z}) = \mathbf{0} \tag{18}$$

where  $c_i(r, z)$  is the molar concentration of component *i* at radial position *r* within a pellet and axial position *z* in the reactor, and  $R_{ij}$  and  $L_{ik}$  are the rates of reaction of component *i* in reactions *j* and *k* within pellet voids and at catalyst surfaces, respectively. *G* and *S* are the number of homogeneous and surfacecatalyzed steps, and  $\Phi$  is the pellet porosity. Equation (17) requires that concentrations at the pellet surface  $[C_i(R_0, z)]$  be the same as those within bed interstices  $[C_i(z)]$  at all axial positions in the reactor. Equation (18) ensures that concentration profiles are symmetric with respect to the center of the pellet.

Equations (14)-(18) provide a general model that describes concentration gradients in both the pellet and the reactor characteristic dimensions. Computer simulations for this general case will be described elsewhere [7]. Here, we explore cases in which the reactor is either empty (i.e. no catalyst pellets) or contains pellets that catalyze homogeneous-heterogeneous reactions without diffusional inhibition.

If we neglect intraparticle diffusional constraints, eqs (14) and (16) can be combined using Green's theorem to give

$$U_{0} \frac{\mathrm{d}C_{i}}{\mathrm{d}z} = \varepsilon \sum_{j=1}^{6} R_{ij} + (1-\varepsilon) \Phi \left( \sum_{j=1}^{6} R_{ij} + \sum_{k=1}^{5} L_{ik} \right)$$
(19)

$$C_i(0) = C_{i0}$$
 (20)

for spherical pellets; its solution describes the behavior of reactors where homogeneous-heterogeneous reactions occur in kinetic-limited pellets (Section 5). These equations describe changes in the concentration of reactive species as reaction proceeds along the reactor length. They include homogeneous reactions within the interpellet and intrapellet void volume  $[\varepsilon + (1 - \varepsilon)\Phi]$  and surface-catalyzed steps, expressed per unit of intrapellet volume  $[(1 - \varepsilon)\Phi]$ . Equations (19) and (20) form a set of coupled nonlinear ordinary differential equations that can be solved using standard numerical methods.

The above system of equations for homogeneous-heterogeneous conditions reduces to the homogeneous case by simply requiring that the interpellet volume fraction ( $\varepsilon$ ) become unity. This leads to

$$U_0 \frac{\mathrm{d}C_i}{\mathrm{d}z} = \sum_{j=1}^{\mathbf{G}} R_{ij} \tag{21}$$

$$C_i(0) = C_{10} \tag{22}$$

an equation whose solution describes the behaviour of homogeneous reactors (Section 4). The models described in this section extend previous descriptions that couple the gas-phase reactions with surfacecatalyzed steps [35].

#### 4. HOMOGENEOUS BEACTOR SIMULATIONS

#### 4.1. Comparisons with experimental data

Solutions of the homogeneous reactor equations [(21) and (22)] are compared in Fig. 1 with previously reported experimental data for methane/oxygen reactions in empty vessels [23, 36]. Predicted  $C_2$  selectivities are in excellent agreement with data by Droege *et al.* [36] at 1073 K, and CH<sub>4</sub>/O<sub>2</sub> ratios of 3 [Fig. 1(a)] and 5 [Fig. 1(b)], and I bar total reactant pressure. At lower temperatures (1023 K) and reactant pressures (0.7 bar), the model also describes experimental selectivities reported by Lane and Wolf [23] [Fig. 1(c)].

Simulations are also consistent with experimental results obtained in our laboratory at 923 K, 0.145 bar CH<sub>4</sub>, 0.07 bar O<sub>2</sub>, and 0.785 bar He (Fig. 2) in a gradientless recirculating batch reactor [37]. The model overestimates the C<sub>2</sub> selectivity slightly, especially at low conversion, but describes ethylene content and qualitative conversion trends quite accurately [Fig. 2(a)]. Detailed selectivity comparisons [Fig. 2(b)] show that the homogeneous kinetic model underpredicts the rate of C<sub>2</sub> conversion to CO, especially at low conversions. The poorer agreement at lower reaction temperatures is expected because reported homogeneous kinetics are usually obtained at temperatures well above 1000 K.

At short residence times and low methane conversions, methyl radicals are produced primarily by reactions of methane with oxy-radicals and ethane is the predominant initial product [Fig. 2(b)]. Methyl radicals combine with each other to produce ethane or



Fig. 1. Comparison of model predictions and experimental homogeneous selectivities: (a) bed residence time effect on  $C_2$  selectivity: (------) model predictions; ( $\bullet$ ) data from reference [36] (1073 K, 0.75 bar CH<sub>4</sub>, 0.25 bar O<sub>2</sub>); (b) bed residence time effect on  $C_2$  selectivity; (-----), model predictions; ( $\bullet$ ) data from reference [36] (1073 K, 0.833 bar CH<sub>4</sub>, 0.167 bar O<sub>2</sub>); and (c) bed residence time effects on  $C_2$  selectivity: (------) model predictions; ( $\bullet$ ) data from reference [23] (1023 K, 0.467 bar CH<sub>4</sub>, 0.233 bar O<sub>2</sub>, 0.30 bar diluent).

react with molecular oxygen to form  $CO_x$ . At longer residence times, ethane selectivity decreases, while ethylene and carbon monoxide selectivities increase [Fig. 2(b)]. Ethylene selectivity reaches a maximum and then decreases suggesting its intermediate role in a consecutive reaction sequence that ultimately leads to stable  $CO_x$  products [eq. (5)]. In the present example, ethylene never disappears from the exit stream because oxygen reactants are depleted before their complete conversion to CO [Fig. 2(b)].

Even at very low methane conversion,  $C_2$  selectivities are less than 100%, suggesting that CO formation can also occur by direct oxidation of CH<sub>4</sub> or CH<sub>3</sub> radicals [Fig. 2(b)]. C<sub>2</sub> selectivity decreases as conversion increases, leading to a maximum C<sub>2</sub> yield (moles of carbon in C<sub>2</sub>/moles CH<sub>4</sub> converted) at



intermediate  $CH_4$  conversions (and axial positions) in the reactor. This behavior is consistent with consecutive reactions involving  $C_2$  as an intermediate reactive product; it suggests that reactor backmixing, which increases the effective concentration of reactive  $C_2$  products, would also markedly lower  $C_2$  selectivity. Yield is defined as the product of selectivity and conversion; yields increase initially with increasing conversion, but reach a maximum and then decrease as conversion increases further because of secondary oxidation of  $C_2$  species.

We conclude that the gas-phase model describes experimental measurements well, especially at higher temperatures, where the kinetic constants used in the simulations were obtained (Table 1). These constants were obtained from compilations of gasification, combustion and partial oxidation literature data (>1000 K); their extrapolated values at lower temperatures are undoubtedly less accurate.

#### 4.2. Reactant concentration effects on C<sub>2</sub> yields

Homogeneous reactor model simulations were used to explore maximum  $C_2$  yields as the temperature and the reactant concentrations were varied. For completeness, we are studying mixtures with wide ranges of  $CH_4/O_2$  ratios. Operation under certain oxygen-rich compositions cannot be attained in practice because they lie within the explosion limits. Methane and oxygen conversions increase with increasing reactor residence time [Fig. 3(a)]. An initial induction period is observed; it reflects the onset of faster secondary initiation and chain transfer reactions and the initial build-up in the concentration of  $HO_2$ , OH, O, and H radicals formed by slower primary initiation steps (using  $O_2$  and M). The sigmoidal shape of the curves is typical of autoignition processes, which involve fast chain transfer steps after slow and highly endothermic free-radical initiation reactions.

Reactor residence times required for a given oxygen conversion are inversely proportional to oxygen partial pressure [Fig. 3(a), 1073 K, 0.5 bar CH<sub>4</sub>], suggesting that primary initiation processes controlling the induction period are approximately first-order in oxygen concentration. The induction period is very sensitive to the rate of heterogeneous radical generation and radical quenching reactions, as we shall discuss in more detail later in Section 5.



Fig. 3. Oxygen concentration effects on methane conversion rate and selectivity (1073 K, 0.5 bar CH<sub>4</sub>, 0.1-0.5 bar O<sub>2</sub>);
(a) oxygen consumption rate vs bed residence time; (b) C<sub>2</sub> yields vs oxygen conversion; and (c) C<sub>2</sub> yields vs methane conversion.

The effects of oxygen and methane concentrations on the yield of C<sub>2</sub> hydrocarbons are shown in Fig. 3(b) and (c). At low oxygen concentrations,  $C_2$  yields continue to increase as conversion increases. The slope of this curve (proportional to the  $C_2$  selectivity) decreases with increasing conversion because C<sub>2</sub> products convert to more stable CO<sub>x</sub> molecules in secondary reactions. At higher oxygen concentrations [e.g.  $CH_4/O_2 = 1$ , Fig. 3(b) and (c)], such secondary reactions occur more rapidly and C<sub>2</sub> yields ultimately decrease at high methane conversion levels. Thus, maximum yields are obtained at intermediate values of oxygen conversion. At low oxygen concentrations, the maximum yield occurs at the reactor exit after almost complete conversion of the oxygen reactant [Fig. 3(c)].

Surprisingly, the maximum  $C_2$  yields that can be achieved from  $CH_4/O_2$  mixtures depend only weakly on inlet oxygen concentration (1073 K, 0.5 bar  $CH_4$ , 0.1-0.5 bar  $O_2$ ) [Fig. 3(c)]. These maximum yields reflect the steady-state concentration of reactive intermediates ( $C_2$ ) that exists when the formation and conversion rates of these  $C_2$  intermediates become equal. Because homogeneous formation and conversion rates of  $C_2$  molecules depend similarly on oxygen pressure, steady-state concentrations of these intermediates are nearly independent of oxygen pressure [Fig. 3(c)].

Very low oxygen concentrations  $(CH_4/O_2 \ge 5)$  inhibit secondary oxidation reactions but also limit the level of methane conversion that can be achieved within the reactor. Therefore, staging the introduction of oxygen could maintain reasonable high C2 selectivities while avoiding unreacted methane in the reactor effluent; however, C<sub>2</sub> selectivities actually decrease slightly as the oxygen concentration decreases, as shown by the decreasing value of the initial slopes in Fig. 3(c). As oxygen levels decrease, the rate of bimolecular methyl radical recombination reaction is more strongly influenced by the decrease in methyl radical generation rates than the corresponding rate of hydrogen abstraction from ethane to give ethylene and CO. Thus, ethane formation rates decrease faster than the rate of conversion of ethane to CO products, as oxygen levels decrease, leading to lower values of C<sub>2</sub> yields.

As oxygen disappears from the reactant stream, much slower non-oxidative homogeneous (pyrolysis) reactions continue to occur and contribute to the observed methane conversion products. This leads to the slight upturn observed in  $C_2$  yield-conversion curves as oxygen is depleted [Fig. 3(c)]; this occurs at lower methane conversion as the inlet oxygen levels decrease. Such pyrolysis reactions are very slow at oxidative coupling conditions and generally become significant only at much higher temperatures and longer-bed residence times. These pyrolysis reactions make it difficult to estimate maximum attainable  $C_2$  yields from yield-conversion plots because they cause a continuous but very slow increase in  $C_2$  yields with increasing bed residence time, even after oxygen is depleted. This increase requires extremely long residence times at normal oxidative coupling conditions and it is not of practical interest. In our estimates of maximum yields, we have chosen a true maximum in yield--conversion curves or, in the absence of one, the yield obtained at 85% oxygen conversion, in order to avoid conditions that favor selective but extremely slow methane pyrolysis reactions.

# 4.3. Temperature and reactant concentration effects on maximum $\mathbf{C}_2$ yields

The maximum  $C_2$  yields that can be achieved in a homogeneous plug-flow reactor depend on temperature and on the inlet concentration of reactants. The effects of temperature and of  $CH_4/O_2$  ratio are shown in Fig. 4 (at a constant CH<sub>4</sub> pressure of 0.5 bar). Maximum yields occur at different methane conversion levels and reactor residence times as temperature and reactant concentrations change. This figure shows that maximum  $C_2$  yields increase (~3-9%) with increasing temperature (873-1123 K) but become nearly independent of  $CH_4/O_2$  ratios for values up to 10; higher ratios lead to complete oxygen depletion before any significant methane conversion occurs and, therefore, to lower  $C_2$  yields [see Fig. 3(c)]. The temperature effects reflect methyl radical generation rates that increase faster with increasing temperature than oxidation reaction rates, an effect that leads to higher steady-state methyl radical concentrations and favor bimolecular coupling steps as temperature increases. The weak dependence of  $C_2$  yields on  $CH_4/O_2$  ratio is consistent with the similar  $O_2$  pressure dependence of the  $C_2$  production and consumption steps.

The individual effects of methane and oxygen partial pressures on maximum  $C_2$  yields are shown in Fig. 5(a) (1073 K). This figure again shows that maximum yields are nearly independent of oxygen pressure except at very low pressures, when oxygen is depleted before significant methane conversion occurs. The net effect of total pressure of reactants is, therefore, not very pronounced and is further illus-



Fig. 4. Temperature and methane/oxygen ratio effects on maximum C<sub>2</sub> yields [0.5 bar CH<sub>4</sub>, no diluent].



Fig. 5. Methane and oxygen concentration effects on maximum  $C_2$  yields [1073 K, no diluent]; (a) methane and oxygen concentration effects; and (b) total pressure effects  $(CH_4/O_2 = 2)$ .

trated in Fig. 5(b) at a fixed  $CH_4/O_2$  ratio. This figure shows that maximum  $C_2$  yields go through a maximum (~8%) for an intermediate value of total pressure (~1.5 bar). The rising portion of this curve occurs because the rate of methyl radical generation increases as pressure increases; the subsequent gradual decrease arises because full oxidation is slightly favored over coupling reactions as total pressure increases at constant  $CH_4/O_2$  ratio. Overall, the results presented in Figs 4 and 5 are consistent with available homogeneous oxidative coupling data [23, 36, and this study], which suggest that yields greater than about 10% cannot be achieved throughout a wide range of temperatures and pressures in the absence of heterogeneous methyl radical generation sites.

#### 4.4. Controlled oxygen injection in homogeneous reactors

Our simulations show that oxidation of  $C_2$  products occurs primarily by reaction with molecular oxygen and with oxygen-containing species. Therefore, controlling the amount of oxygen in the gas phase and, consequently, the oxy-radical concentration, should improve the yields. The concept of controlled injection is not new but has not been explored systematically in the literature. Here, we explore the case in which the oxygen reactant is introduced sequentially along the reactor length, while keeping the total amount of oxygen added throughout the reactor equal to that in a cofeed process. Under these conditions, the oxygen pressure at each of  $N_p$  injection points becomes

$$P_i = P_{O_2} / [1 + (N_p - 1)\alpha]$$
(23)

where  $P_{O_2}$  is the total oxygen pressure equivalent to a cofeed process and  $\alpha$  is the oxygen conversion achieved in each stage before additional oxygen is introduced into the reactor;  $\alpha = 0.85$  is used in all simulations, in order to minimize conditions that favor slow methane pyrolysis reaction. In effect, staging the introduction of oxygen minimizes its local concentration but continues to provide a steady supply of a critical reactant and chemical potential to drive the conversion of methane.

Somewhat surprisingly, the introduction of oxygen at five points along the reactor length actually decreases the maximum  $C_2$  yields that can be achieved [Fig. 6(a), CH<sub>4</sub>/O<sub>2</sub> = 1]. As we discussed previously, a moderate decrease in O<sub>2</sub> concentration initially lowers the rate of methyl radical generation to a greater extent than the rate of  $C_2$  consumption (ethyl radical generation), leading to a lower steadystate C<sub>2</sub> concentration. However, as we continue to increase the number of injection points along the reactor ( $N_{e} = 100$ ) and, consequently, lower the local oxygen concentration level, maximum attainable  $C_2$  yields become greater than those in cofeed homogeneous reactors. At such low oxygen concentrations, C<sub>2</sub> selectivities remain relatively high (slope of  $C_2$  yield vs conversion) up to higher  $CH_4$  conversion levels and the continuous introduction of  $O_2$  allows successive increments in methane conversion without the rapid loss of selectivity typical of cofeed reactors. Overall, we find that increasing the number of O<sub>2</sub> injection points along the reactor initially decreases C<sub>2</sub> yields slightly [Fig. 6(b), 1073 K, 0.667 bar CH<sub>4</sub>, 0.333 bar O<sub>2</sub>], but ultimately leads to modest yield improvements (from 8 to 12%) as the number of injection points becomes very large and the reactor begins to resemble an O<sub>2</sub>-permeable wall reactor.

An unavoidable and costly consequence of oxygen staging is an almost proportional increase in the residence time (and reactor volume) required to achieve a given methane conversion and C<sub>2</sub> yield as the number of injection points  $(N_p)$  increases [Fig. 6(c)]. This occurs because the kinetic driving force for the overall conversion reaction decreases markedly as we decrease local oxygen concentrations by increasing the number of  $O_2$  injection points along the reactor. A 100-fold reactor volume increase is required to implement staging schemes that lead to even minor improvements in homogeneous C<sub>2</sub> yields (9.6%,  $N_p = 40$  [Fig. 6(b) and (c)]. Thus, it appears that oxygen staging for yield improvements is an impractical approach in homogeneous reactors. Reactor designs such as noncatalytic oxygen-permeable wall reactors and high conversion backmixed reactors appear to be equally impractical. Applications of staging and of these related types of reactors, however, may become feasible in the presence of a high-activity



Fig. 6. The effect of staged oxygen injection on homogeneous  $C_2$  yields (1073 K, 0.5 bar CH<sub>4</sub>, 0.5 bar O<sub>2</sub>); (a) cofeed vs staged oxygen injection ( $N_p = 5$ ,  $N_p = 50$ ); (b) maximum  $C_2$  yield vs  $1/N_p$ ; and (c) required residence time vs  $1/N_p$ .

catalytic function that decreases the residence times required to achieve a given methane conversion level in oxidative coupling reactors. In the sections that follow, we explore the benefits of a catalytic function in oxidative coupling processes.

#### 5. HOMOGENEOUS-HETEROGENEOUS REACTOR SIMULATIONS

In this section, we describe yield and selectivity trends in plug-flow reactors that combine gas-phase reactions with surface-catalyzed steps. We assume that active surface sites catalyze the formation of methyl and ethyl radicals only [reactions (6) and (7)]. Therefore, this analysis offers an optimistic view of the oxidative methane coupling process because deleterious oxidation reactions at surfaces are excluded; this optimistic model allows us to explore an ideal catalytic function that establishes an absolute upper limit on attainable yields. The present analysis is also restricted to kinetic-limited conditions without intrapellet diffusional inhibition, where mass conservation of species are described by eqs (19) and (20); this restriction will be relaxed in a later report [7]. The absence of diffusional inhibition leads to uniform reactant and product concentrations across a catalyst pellet. In such cases, the characteristic time scale for reactant diffusion is much shorter than that for chemical reaction.

## 5.1. Effects of catalyst properties on maximum $C_2$ yields

The  $C_2$  yield of combined homogeneous and heterogeneous reactions is controlled by three kinetic parameters that describe the catalyst: the turnover rate (v), the ratio of kinetic constants for ethyl and methyl radical generation ( $\gamma$ ), and the oxygen pressure order (n). Our simulations explore how these parameters affect product yields in methane coupling; they also suggest catalyst properties that lead to maximum  $C_2$  yields.

Figure 7 shows maximum  $C_2$  yields as a function of site turnover rate, a property that reflects the intrinsic activity of surface sites (curve A). These calculations assume no ethyl radical generation (y = 0) and firstorder kinetics for oxygen pressure (n = 1) at catalytic surfaces. At low turnover rates ( $\nu < 0.1 \text{ s}^{-1}$ ), the presence of a catalyst increases the maximum C<sub>2</sub> yields obtained in homogeneous reactors only slightly. Significant yield improvements occur only for turnover rates greater than about 10 s<sup>-1</sup> even on ideal selective catalysts, which generate only methyl radicals without catalyzing detrimental full oxidation reactions or even ethyl radical formation. Figure 7 illustrates that, even for this selective catalytic function, high yields (> 30%) require very high turnover rates  $(> 30 \text{ s}^{-1})$ , presently unattainable at reasonable temperatures on available catalytic materials. Also, high turnover rates are likely to introduce diffusional limitations because pore structures in which



Fig. 7. The effect of an ideal methyl generation catalytic surface on maximum  $C_2$  yields; (curve A) maximum yields; (curve B) catalyst effectiveness factor (1073 K, 0.667 bar  $CH_4$ , 0.333 bar  $O_2$ , n = 1,  $\gamma = 0$ ).

sites are contained limit our ability to transport reactants into pellets where they are rapidly consumed by very active sites. This renders most active sites within pellets unavailable for reaction and leads to average reaction rates much lower than within kinetic-limited pellets. A simple analysis of diffusion/reaction (Appendix B) gives an effectiveness factor (percentage of kinetic rate attained) shown as curve B in Fig. 7 in which we assume oxygen to be the diffusion-limited component. It shows that as turnover rates increase, oxygen has a lower probability of reaching interior sites before reaction occurs (and  $\eta < 100\%$ ); kinetic turnover rates greater than 50 s<sup>-1</sup> are unlikely to be practically exploited because of intrapellet diffusion limitations.

Heterogeneous methyl radical generation increases the local steady-state concentration of methyl radicals involved in bimolecular coupling reactions. An ideal catalyst function that selectively generates methyl radicals from methane (but not ethyl radicals from ethane) has only a secondary effect in the rate of ethane consumption to  $CO_x$  precursors. It increases secondary conversion of  $C_2$  only through pathways or radicals that benefit from a higher concentration of methyl radicals in the reactor. However, it seems unlikely that a catalytic function that activates methane will not also activate ethane because of the similar activation pathways required and of the lower energy of C-H bonds in ethane compared with methane. Catalytic sites that also form ethyl radicals from ethane reduce the benefit of a catalytic function on  $C_2$  yields by providing pathways for the activation of desired  $C_2$  molecules to more reactive precursors to full oxidation products.

In Fig. 8, we illustrate the effect of ethyl radical generation on maximum yields. Curve A is for methyl radical generation only ( $\gamma = 0$ ) and curves B and C correspond to two levels of ethyl radical formation described by the parameters  $\gamma = 2$  and  $\gamma = 4$ , respectively; the latter value reflects the relative reactivity of  $C_2H_6$  and  $CH_4$  in homogeneous hydrogen abstraction reactions. This figure shows that maximum yields decrease as the value of  $\gamma$  increases because ethane converts more rapidly to more reactive ethylene,

acetylene, and oxygen-containing intermediates, effective precursors to  $CO_x$ . Curves B and C represent more realistic situations that, however, still neglect direct oxidation of any species at catalytic surfaces. Even without direct oxidation, very high turnover rates are required to achieve yields above 25% when  $\gamma = 2$  or 4. These results are consistent with experimental measurements obtained for a wide range of catalysts and conditions; yields greater than about 25% have not been experimentally observed [3, 24-26]. Our simulations confirm that gas-phase reactions are a major obstacle to higher C<sub>2</sub> yields; homogeneous pathways limit attainable C<sub>2</sub> yields in oxidative coupling processes even on ideal selective catalysts.

Figure 9 illustrates the effect of oxygen pressure order of heterogeneous methyl radical generation rates on maximum C<sub>2</sub> yields. The curves A, C, and D were obtained for a surface reaction order of 0.5 and y-values of 0, 2, and 4, respectively. Curve B for first-order methyl radical generation rates is shown for comparison purposes ( $\gamma = 0, n = 1$ ). The increased yields with lower oxygen pressure order reflect the increasing ability of the catalyst to maintain a high rate of formation of methyl radicals as the oxygen pressure decreases with increasing conversion. These results suggest that low kinetic orders in oxygen concentration for heterogeneous methyl radical formation lead to higher  $C_2$  yields; preferably, they should be much smaller than the order of gas-phase reactions of reactive  $C_2$  products to  $CO_x$  in order to maximize the benefit of the heterogeneous function as methane (and oxygen) conversion increase along the reactor length. As we will show later, such low reaction orders also maximize the benefits of staged oxygen injection in catalytic reactors.

#### 5.2. Effect of radical quenching on C<sub>2</sub> yields

It is well known that peroxy-radicals, formed by slow initiation from reactants (1), are primary chainbranching centers in methane coupling processes. Once formed, peroxy-radicals participate in degenerate branching reactions that lead to intermediate products (e.g.  $H_2O$  and  $H_2CO$ ) and take part in sub-



Fig. 8. The effect of an ideal methyl and ethyl generation catalytic surface on maximum  $C_2$  yields: (curve A) n = 1, y = 0; (curve B) n = 1, y = 2; (curve C) n = 1, y = 4 (1073 K, 0.667 bar CH<sub>4</sub>, 0.333 bar O<sub>2</sub>).



Fig. 9. The effect of an ideal methyl generation catalytic surface on maximum  $C_2$  yields: (curve A) n = 0.5,  $\gamma = 0$ ; (curve B) n = 1,  $\gamma = 0$ ; (curve C) n = 0.5,  $\gamma = 2$ ; (curve D) n = 0.5,  $\gamma = 4$ .

sequent chain transfer and propagation reactions. The initial increase in the concentration of products lead to the induction period and self-accelerating behavior shown in Fig. 3(a) because of a build-up in the concentration of chain-branching precursors. In particular, the formation of  $H_2O_2$  is an important step, because this species decomposes in activated collisions with a third body (95) giving rise to hydroxyl groups that are very effective methyl radical initiators (3). However, this decomposition step can be readily intercepted by H<sub>2</sub>O<sub>2</sub> collisions with basic or inert surfaces that promote chain termination of these active centers. These radical quenching reactions cause the overall conversion to decrease and lengthen the induction period required in methane conversion [38-41].

In this section, we show how a different type of catalytic function, one that destroys chain transfer gas-phase centers, can be introduced into the reactor in order to control the rate and selectivity of homogeneous reactions. In some sense, this catalytic function acts as a staging mechanism that decreases the apparent  $O_2$  concentration within the reactor by scavenging oxy-radicals and, thus, reversing some of the homogeneous radical generation and transfer steps. In the process, however, it also decreases markedly the rate of homogeneous methane conversion and the local concentrations of methyl radicals required in bimolecular coupling reactions.

The effect that radical quenching has on  $C_2$  yields can be simulated by simply adding to the network of gas-phase reactions the following surface reaction:

$$H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O \tag{24}$$

which can occur at reactive sites on the reactor walls or at solid surfaces within catalyst pellets or solid inert materials [38, 39]. Following our previous description of surface-catalyzed reactions (Section 2.2), we use the following kinetic expression:

$$r_{\rm H_2O} = 58422 \cdot v_{\rm H_2O_2} \cdot [\rm H_2O_2] \ (\mu \rm{mol/m^3 s}) \qquad (25)$$

which describes the rate of radical quenching in terms of a turnover rate for chain termination at surfaces  $(v_{H_2O_2})$ . Figure 10 shows  $C_2$  yields vs residence time for various chain termination rates. This figure clearly shows the retarding effect of radical quenching on



Fig. 10. The effect of radical quenching on induction periods and maximum  $C_2$  yields.

methane conversion and its consequent effect on maximum  $C_2$  yields. These trends are consistent with experimental observations [38, 39, 41]. In particular, we have verified that by simply increasing the aspect ratio of an empty tube, while maintaining total reactor volume, leads to lower methane conversion due to the increased frequency of reactive collisions of  $H_2O_2$ with the reactor walls. Similar conclusions apply to reactors containing increasing amounts of inert solids.

#### 5.3. Controlled oxygen injection in catalytic reactors

In the previous section, we showed that yields greater than about 25% require extremely high activity and selectivity of active sites, levels that are difficult to reach on porous materials because of diffusional constraints. We also concluded that the control of secondary gas-phase oxidation reactions is a critical requirement for higher  $C_2$  yields. These results suggested that further improvements in catalyst activity or selectivity alone are unlikely to increase  $C_2$  yields significantly above levels already reported [4–6, 26]. Therefore, as we previously explored in homogeneous reactors, we consider the effects of staging the introduction of oxygen into a bimodal catalytic reactor.

Figure 11(a) and (b) shows  $C_2$  yields as a function of methane conversion for cofeed  $(N_p = 1)$  and staged oxygen injection ( $N_p = 10$  and  $N_p = 50$ ) on catalysts with heterogeneous oxygen pressure orders of 1 and 0.5, respectively. These simulations were carried out at 0.667 bar CH<sub>4</sub>, 0.333 bar O<sub>2</sub>, and T = 1073 K for a homogeneous-heterogeneous system with a turnover rate of 1 s<sup>-1</sup>, no ethyl radical generation ( $\gamma = 0$ ), and no diffusional constraints. Figure 11(a) shows that, for high values of oxygen pressure orders (n = 1). staging the introduction of the oxygen feed along 10 injection points does not improve C<sub>2</sub> yields attained in the cofeed mode  $(N_p = 1)$ . Increased yields are obtained, however, when oxygen concentrations are lowered further by continuing to increase  $N_p$ . Figure 11(b) shows that, for lower oxygen pressure orders (n = 0.5), the maximum yield increases as we move from a cofeed mode  $(N_p = 1)$  to a staged oxygen injection process, even for few injection points  $(N_p = 10)$ . This occurs because lower oxygen pressures do not significantly decrease the catalyst ability to produce methyl radicals and maintain high methyl radical concentrations, conditions that favor coupling reactions, even at low oxygen concentrations. Methyl radical generation at surface sites with weak dependence on oxygen concentration decreases more slowly than homogeneous ethyl radical formation and conversion to  $CO_x$  as oxygen concentration decreases.

Maximum  $C_2$  yields obtained as we increase the number of injection points are shown in Fig. 12(a). Curve A is for gas-phase reactions only and, as already shown in Fig. 6(b), shows only modest yield improvements over a cofeed process. Curves B and C describe the results for an ideal catalytic function for methyl radical formation only and oxygen pressure orders of 1 and 0.5, respectively. Clearly, the



Fig. 11. The effect of staged oxygen injection on homogeneous-heterogeneous  $C_2$  yields (1073 K, 0.667 bar CH<sub>4</sub>, 0.333 bar  $O_2$ ): (a) cofeed vs staged oxygen injection  $(N_p = 10, N_p = 50, n = 1.0)$  and (b) cofeed vs staged oxygen injection  $(N_p = 10, N_p = 50, n = 0.5)$ .

coupled homogeneous-heterogeneous systems show significant yield improvements, specially for catalysts with low oxygen pressure orders (curve C).

Because of the low oxygen concentrations that prevail in controlled injection reactors, the required bed residence time (or reactor volume) increases markedly with  $N_p$ . A very large increase in residence time (>100-fold) is required to cause significant yield improvements over a cofeed process. The least favorable case is for homogeneous reactors; the catalyst with the lowest oxygen pressure dependence is least affected by increased reaction times as oxygen introduction is staged along the reactor.

In the limit of a very large number of injection points, the reactor behaves as a permeable membrane, except that the oxygen concentration profile actually changes as  $O_2$  is consumed between injection points (in our simulations, a new oxygen addition is done only after the previous amount has reacted to 85% conversion). An alternate but closely related procedure for achieving high yields is to maintain a fixed, low oxygen, level throughout the reactor length, a process that could be achieved with an oxygen-permeable membrane or with a gradientless backmixed reactor. The results of a simulation of this system [43] are presented in Fig. 13. Here, we plot maximum C<sub>2</sub> yields as a function of oxygen concentration, expressed per unit of methane pressure (0.667 bar) at the reactor inlet. As expected, this figure closely resembles Fig. 11(a) (curves A-C) but also shows that maximum  $C_2$  yields go through a maximum at intermediate, but



Fig. 12. The effect of staged oxygen injection on maximum  $C_2$  yields and required bed residence times: (curvé A) homogeneous reactions, v = 0; (curvé B) heterogeneous,  $v = 1.0 \text{ s}^{-1}$ , n = 1.0,  $\gamma = 0$ ; (curve C) heterogeneous,  $v = 1.0 \text{ s}^{-1}$ , n = 0.5,  $\gamma = 0$  (1073 K, 0.667 bar CH<sub>4</sub>, 0.333 bar  $O_2$ ): (a) maximum  $C_2$  yields vs  $1/N_p$  and (b) required residence time vs  $1/N_p$ .



Fig. 13. The effect of a fixed oxygen concentration on maximum C<sub>2</sub> yields: (curve A) homogeneous reactions, v = 0 s<sup>-1</sup>; (curve B) heterogeneous, v = 1.0 s<sup>-1</sup>, n = 1.0,  $\gamma = 0$ ; (curve C) heterogeneous, v = 1.0 s<sup>-1</sup>, n = 0.5,  $\gamma = 0$ ; (curve D) heterogeneous, v = 1.0 s<sup>-1</sup>, n = 0,  $\gamma = 0$ .

very low  $(10^{-3}-10^{-4})$ , oxygen concentrations. In addition to curves A-C, which correspond to the conditions of those in Fig. 11(a), curve D for a zero oxygen pressure order is also included. Overall, this figure summarizes the benefits of low oxygen concentration for ideal catalytic functions. In practice, the required bed residence times would be very large and the maximum yields much lower because of the less selective nature of many catalytic materials.

#### 6. INTRINSIC AND PRACTICAL LIMITATIONS IN

#### C<sub>2</sub> YIELDS FROM OXIDATIVE COUPLING OF METHANE

In this section, we discuss how some of the apparent  $C_2$  yield limitations are not necessarily inherent in the homogeneous-heterogeneous nature of the reaction pathways and can be overcome by the selection of appropriate catalytic functions and reactor operation, albeit with a great difficulty.

The kinetic scheme of eq. (5) can also be described as a sequential reaction:

$$A \xrightarrow{r_1} B \xrightarrow{r_2} C$$

$$(CH_4/O_2) (C_2) (CO_x) (CO_x)$$
(26)

where the objective is to increase yields of **B**, the intermediate product in this sequence. Clearly, this requires that we selectively increase the rate of formation of **B**  $(r_1)$  or that we selectively inhibit its subsequent conversion to C  $(r_2)$ . A selective catalytic function achieves the first and, with certain restrictions, the controlled injection of oxygen achieves the second.

Clearly, the truly intrinsic  $C_2$  yield limits imposed by the presence of homogeneous pathways have not been reached in practice, as shown by  $C_2$  yields well above 50% attainable in controlled injection [Fig. 12(a)] and permeable wall (Fig. 13) reactors. The apparent experimental limits are not intrinsic consequences of the required involvement of homogeneous pathways in oxidative coupling and can be overcome with the use of selective catalysts.

Specifically, catalysts with high methyl radical generation turnover rates must not catalyze rapid secondary full oxidation or  $C_2$  activation reactions. Also, heterogeneous kinetics must differ in their kinetic oxygen order from corresponding homogeneous pathways; specifically, heterogeneous methyl radical generation rates must be less sensitive to changes in oxygen concentration than homogeneous oxidative processes than catalytic activation of  $C_2$  products. These are rather strict requirements, certainly difficult to achieve in practice; they cannot, however, be classified as intrinsic with our current knowledge of the surface chemistry of methyl radical formation pathways.

Undoubtedly, the best catalytic performance  $(\gamma = 0, n = 0)$  will remain unartainable given the similar surface pathways and kinetics for methane and ethane reactions and the fact that all reactions approach first-order kinetics at sufficiently low reactant concentrations. Clearly, the practice of controlled oxygen injection will require much more active and selective catalysts with heterogeneous oxygen pressure orders near zero. Yet, overcoming these limitations is not precluded by theory. The limitations may be difficult to overcome, perhaps even impossible, reactor designs may be complex and expensive to operate, and the catalysts may be unartainable with materials currently known, but the limitations are not intrinsic. The burden falls once again on catalysis to

provide the required solutions to control the rather unselective nature of homogeneous reaction pathways.

#### 7. CONCLUSIONS

In this work, we have developed a comprehensive reaction/diffusion/convection model that couples detailed gas-phase reaction networks within interstitial and intrapellet voids with surface-catalyzed steps in packed-bed reactors. This model is applied to the analysis of the oxidative coupling of methane, a typical and important example of a bimodal reaction involving strongly coupled homogeneous and heterogeneous reaction pathways.

An accurate homogeneous kinetic model assembled from literature data leads to predictions in excellent agreement with experimental data in homogeneous reactors. This gas-phase reaction network is combined with an ideal heterogeneous reaction model (methyl and ethyl radical generation without surface oxidation steps) in order to establish how the rate and specificity of the catalytic function affects methane conversion and  $C_2$  hydrocarbon yields.

Homogeneous reactor simulations over a wide range of temperature and inlet reactant pressures show that maximum  $C_2$  yields greater than about 8-9% cannot be obtained using  $CH_4/O_2$  feeds. These simulations are consistent with experimental findings. These yield values can only be slightly improved (up to ~12% for 200 injection points) if, instead of cofeeding  $CH_4$  and  $O_2$  at the reactor inlet, the oxygen reactant is introduced gradually along the reactor length in order to inhibit secondary oxidation reactions of  $C_2$  reactive products.

Homogeneous  $C_2$  yields can also be improved by the addition of a catalytic function. However, detailed homogeneous-heterogeneous reactor model simulations over a wide range of catalyst properties (such as activity, selectivity, and kinetics) show that yields greater than about 30% require catalysts with very high turnover rates, highly selective sites for methyl radical generation, and heterogeneous kinetics with low order in oxygen pressure. Further yield improvements can be obtained by staging the oxygen introduction through multiple injection ports. However, the resulting lower oxygen pressures require much longer residence times (targer reactor volumes) in order to achieve a given methane conversion and  $C_2$  yield.

Overall, the model presented here provides a powerful tool for scoping the behavior of chemically reacting systems where homogeneous reactions occur in parallel with surface-catalyzed chain initiation and propagation steps. In particular, it allowed us to mechanistically interpret existing data on oxidative coupling of methane as well as to systematically explore reaction conditions under which  $C_2$  yields can be maximized. Our results will be extended in later reports to describe intrapellet transport restrictions and to predict the effect of a catalytic function and of

reactant	concentration	cycling	in	related	bimodal	I
(homoge	neous-heteroge	encous) r	cac	tions.		¢

#### NOTATION

av	bed surface area per unit volume	
c	molar concentration within intrapellet	e
	voids	,
Cin	molar concentration at reactor inlet	
c	molar concentration within interpellet	
	voids	-
da	oxygen molecular diameter	
₩02 D	effective diffusivity within catalyst nellets	2
- Л.	molecular diffusivity	2
<i>ב</i> י, ה.	Knudeen diffusivity	1
<u>רי</u>	affactive orwen diffusivity	
	fugagity of reactive species	
, C	sumber of one phase reactions	
0 1.	number of gas-phase reactions	
K <sub>A</sub>	rate constant for consumption of com-	
	ponent A	
K - A	rate constant for formation of compon-	
	entA	
K <sub>B</sub>	rate constant for consumption of com-	
	ponent B	
$k_{f,l}$	kinetic constant for forward reaction	
$k_{r,i}$	kinetic constant for reverse reaction	
k <sup>app</sup>	pseudo first-order kinetic constant	
k <sub>s, CH3</sub>	kinetic constant for heterogeneous	
	methyl radical generation	
k <sub>s, C2H5</sub>	kinetic constant for heterogeneous ethyl	
	radical generation	
$k_i$	equilibrium constant	
L	reactor length	
Lik	rate of surface reaction of component i in	
	reaction k	
M <sub>O</sub>	molecular weight of oxygen	
л <sup>-</sup> х	oxygen pressure order for surface-	
	catalyzed reaction	
n.	catalyst site density	
Ň	total number of chemical species	
N <sub>n</sub>	number of injection points	
Р́	total pressure	
<b>P</b> :	oxygen pressure at injection point	
Po.	total oxygen pressure at reactor inlet	
- U2 7	catalyst nellet radial dimension	
T.c	forward rate of reaction	ł
, r.	irreversible rate of surface reaction	
· · · 7_	reverse rate of reaction	
'r Fre o	rate of radical quenching at surfaces	1
· H <sub>2</sub> O <sub>2</sub>	rate of fudical quotiening at summers	
r <sub>CH3</sub>	rate of methyl radical generation at cata-	
	lyst surface	[
r <sub>C2</sub> Hs	rate of ethyl radical generation at cata-	
_	lyst surface	
K <sub>0</sub>	catalyst pellet radius	1
К <sub>IJ</sub>	rate of gas-phase reaction of component	
_	in reaction j	
5	number of surface-catalyzed reactions	
<u>S</u> ,	BET surface area	1
T	absolute temperature	
U <sub>0</sub>	interstitial gas velocity	
Z	axial reactor dimension	

#### Greek letters

r	oxygen conversion between injection points
,	ratio of kinetic constants for ethyl to methyl radical generation at catalytic surfaces
;	bed void fraction
1	effectiveness factor
r V	stoichiometric coefficient
2 o	particle density
ŗ.	tortuosity factor
υ	turnover rate
Ð	pellet porosity
¥	Thiele modulus

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#### APPENDIX A: HOMOGENEOUS REACTION KINETICS

The homogeneous kinetic model consists of a network of reversible elementary steps that account for the formation and destruction of radicals and of reactive intermediate products; the network describes the consumption of reactants to form stable  $(CO_x)$  and reactive (e.g.  $C_2H_c$ ,  $C_2H_d$ ,  $H_2$ , CO, ...) products. Kinetic parameters were obtained primarily from Tsang [34] and Mackie *et al.* [32] compilations of literature data; but other sources [29-31, 33] were also used when required steps were not reported in these primary references.

Rate constants for monomolecular, bimolecular, and trimolecular reactions are in  $s^{-1}$ ,  $m^3/\mu$ mol s,  $m^6/\mu$ mol<sup>2</sup> s units, respectively. The forward reaction rates are given by

$$r_{f,i} = k_{f,i} \prod_{j} [f_j]^{r_j}$$
(A1)

where  $k_{f,i}$  is the forward rate constant,  $f_j$  is the fugacity or pressure of the reactants in the *j*th step, and  $v_j$  is their stoichiometric coefficient in the chemical reaction describing the elementary process. Their values are reported in Table 1. The reverse rates are given by

$$r_{r_{i}i} = k_{r_{i}i} \prod_{k} [f_{k}]^{\nu_{k}}$$
(A2)

with defining parameters similar to those in (A1), but with the reaction step proceeding in the opposite direction. Values of  $k_{r,i}$  or  $K_i = k_{f,i}/k_{r,i}$  are also reported in Table 1.  $K_i$ values were calculated from thermodynamic data [34].

Reaction steps involving collisional activation or relaxation with third bodies (M) obey complex pressure and temperature functions that are not adequately represented by law of mass action kinetics. For example, the steady-state rate of a collisionally activated step:

$$A + M \underset{k=-}{\overset{k_{A}}{\longrightarrow}} A^{*} + M \overset{k_{B}}{\longrightarrow} B + C + M$$
 (A3)

is given by

$$rate = \frac{k_{B}k_{A}[A][M]}{k_{-A}[M] + k_{B}}.$$
 (A4)

At low pressures ([M]  $\leq k_{\rm B}/k_{\rm -A}$ ), collisional activation of A limits the overall reaction rate and eq. (A5) becomes

$$rate = k_{A}[A][M]. \tag{A5}$$

At higher pressures ([M]  $\gg k_B/k_{-A}$ ), collisional processes are quasi-equilibrated and reactions of A\* limit the overall rate

rate = 
$$k_{\rm B} \frac{k_{\rm A}}{k_{\rm -A}}$$
 [A] (A6)

thus, the reaction becomes pseudo-monomolecular in spite of the bimolecular nature of the initial collisional activation step. The energy transfer efficiency of a third body (M) actually depends on its chemical identity. In this study, we assume transfer efficiencies equal to those of the most effective colliders in the reaction mixture.

All reaction steps containing M in Table 1 were analyzed using rate expressions similar to (A5). Most appeared to exhibit bimolecular behavior even at high pressures ( $P \le 10$ bar). Reaction steps (7), (9), (36), (80), (125), and (127) were corrected by using pressure and temperature functions for  $k_{\rm B}$  and  $k_{\rm B}k_{\rm A}/k_{-\rm A}$  given by Tsang [34] [for (9), (80), (127)] and Warnatz [30] [for (7), (36) and (125)].

#### APPENDIX B: EFFECTIVENESS FACTOR WITHIN CATALYST PELLETS

Here, we develop a relationship between catalyst effectiveness  $(\eta)$  and turnover rates  $(\upsilon)$  in order to illustrate how high volumetric activities, needed for improved yields, lead to diffusional inhibition within catalyst particles. High turnover rates lead to reaction time scales much shorter than time scales for intraparticle diffusion; the resulting radial concentration gradients within pellets affect reaction rates and selectivity. Both reactants and products may develop gradients within the particle, but we focus on oxygen as the limiting diffusion-hindered component; in effect, the diffusion sleving effect is more pronounced for O<sub>2</sub> than CH<sub>4</sub> [7]. This, therefore, restricts our analysis to the effect of oxygen depletion within pellets on methane conversion rates. The general case where all species are diffusion-hindered is described elsewhere [7].

At high turnover rates, oxygen consumption occurs primarily via reaction (6). The methane concentration is assumed to be uniform throughout the particle; therefore, the kinetics of this reaction, assumed to be an elementary step, becomes pseudo-first-order in oxygen concentration. The corresponding effectiveness factor ( $\eta$  = actual rate of reaction/rate of reaction at particle surface) for spherical particles then becomes where

where

$$\Psi^2 = k^{app} \cdot R_0^2 / D_{\Omega_2}^c \tag{B2}$$

and  $\Psi$  is the Thiele modulus which quantifies the ratio of characteristic diffusion to reaction times; the larger this ratio is, the more diffusion-hindered the reaction becomes.  $R_0$  is the radius of the catalyst pellet,  $k^{app}$  is the pseudo-first-order kinetic constant for reaction (6), and  $D_{\Delta_2}^{*}$  is the effective oxygen diffusivity within the catalyst pellet. According to eq. (7), the apparent kinetic constant becomes

 $\eta = \frac{3}{\Psi} \left( \coth \Psi - 1/\Psi \right)$ 

$$k^{\text{PP}} = k_{s, \text{ CH}} \cdot [\text{CH}_4]_0 \tag{B3}$$

where  $[CH_4]_0$  is the methane concentration at the pellet surface.

The effective oxygen diffusivity can be estimated from [42]

$$D_{\mathbf{O}_2}^* = \frac{\Phi}{\tau} \left( \frac{1}{\frac{1}{D_k} + \frac{1}{D_k}} \right)$$
(B4)

$$D_k = 9700 \times \frac{2\Phi}{S_g \rho_p} (T/M_{O_2})^{1/2}$$
(B5)

$$D_b = 0.00149 \frac{T^{3/2}}{M_{O_2}^{1/2} P d_{O_2}^2}.$$
 (B6)

Equations (B4)-(B6) are based on a simple model that estimates an effective diffusivity in terms of the properties of the pore structure (porosity  $\Phi_{p}$ , tortuosity  $\tau$ , BET surface area  $S_{gr}$ , and catalyst density  $p_{p}$ ), and the Bosanquet's approximation that averages contributions to diffusion from Knudsen  $(D_{k})$  and molecular  $(D_{b})$  transport mechanisms within a pore [42]. For illustration purposes, we choose the following typical parameters to obtain  $\eta$  as a function of v:

$$\Phi = 0.4; \tau = 1.8, S_g = 10 \text{ m}^2/\text{g}$$

$$\rho_p = 2 \text{ g/cc}, R_0 = 0.5 \text{ mm}, T = 1073 \text{ K} \qquad (B7)$$

$$P = 1 \text{ bar}, [CH_4]_0 = 0.667 \text{ bar}$$

which upon substitution in eqs (B1)-(B6) gives

$$\eta = \frac{3}{\sqrt{5.66v}} \left( \coth \sqrt{5.66v} - 1/\sqrt{5.66v} \right).$$
 (B8)

The variation of  $\eta$  (expressed on a percent basis) with v is presented graphically in Fig. 7;  $\eta$  is always less than one, thereby showing that, for high turnover rates, the rate of methane consumption is always less than the corresponding rate obtained in the absence of oxygen concentration gradients within catalyst pellets.

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(B1)