Design and optimization of catalysts and membrane reactors for the non-oxidative conversion of methane

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Abstract

Kinetic-transport simulations were used in order to explore the relevant thermodynamic and kinetic barriers in the non-oxidative conversion of CH\textsubscript{4} in a membrane reactor and the effects of continuous hydrogen removal and of catalytic sites on CH\textsubscript{4} conversion and on the attainable yields of useful C\textsubscript{2}–C\textsubscript{10} products. A sensitivity analysis of homogeneous CH\textsubscript{4} pyrolysis pathways showed that sites that activate methane to form methyl radicals or ethene and the conversion of ethene to aromatics increased pyrolysis rates, but led to impractical reactor residence times with or without H\textsubscript{2} removal. Catalysts, such as Mo/H-ZSM5, which increase the rate of both CH\textsubscript{4} conversion to ethene and of ethene aromatization are required in order to overcome the kinetic barriers in homogeneous pyrolysis pathways. Homogeneous models were modified by incorporating non-elementary catalytic steps with rate constants obtained from experimental residence time studies on Mo/H-ZSM5. Simulations using this homogeneous–heterogeneous kinetic model were used in order to determine the benefits of continuous H\textsubscript{2} removal on the yields of desired C\textsubscript{2}–C\textsubscript{10} hydrocarbons and on the required residence times and to obtain rigorous criteria for the design of catalysts and membranes for direct methane conversion reactions. Bifunctional catalysts able to catalyze the required steps and the removal of H\textsubscript{2} across ceramic membranes can lead to almost complete CH\textsubscript{4} conversion at \( \sim 1000 \) K at practical reactor residence times (\(< 100 \) s). This performance requires catalytic reactors with intermediate values of the ratio of characteristic reaction and permeation times (\( \delta = 1–10 \)), which in turn require the use of thin dense ceramic films (10–100 \( \mu \)m) in order to achieve these \( \delta \) values for practical reactor diameters.

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1. Introduction

The direct conversion of methane to fuels and petrochemicals remains a formidable challenge. With the exception of processes for producing synthesis gas intermediates via steam reforming and partial oxidation, direct CH\textsubscript{4} conversion reactions remain economically unattractive. For example, oxidative coupling of methane (OCM) (Keller & Bhasin, 1982; Ito & Lunsford, 1985; Tonkovich, Carr, & Aris, 1993; Jiang, Yentekakis, & Kelkar, 1999) yields < 25\% C\textsubscript{2} yields and significant lower yields of ethene, because ethane is the initial coupling product and the activation of C–H bonds in both methane and ethane occurs concurrently with unselective and highly exothermic reactions using O\textsubscript{2} co-reactants to form CO and CO\textsubscript{2} (Labinger, 1988; Reyes, Iglesia, & Kelkar, 1993). Non-oxidative reactions of methane to form aromatics occur on cation-modified zeolites at relatively low temperatures (\( \sim 1000 \) K) with low carbon and tar yields, because active sites activate methane within shape-selective environments that restrict chain growth and the formation of polynuclear aromatics (Wang, Tao, Xie, & Xu, 1993; Solymosi, Erdohelyi, & Szoke, 1995; Wang, Lunsford, & Rosyne, 1996; Lunsford, Rosyne, & Wang, 1995; Borry, Kim, Huffsmith, Reimer, & Iglesia, 1999). In contrast, homogeneous methane pyrolysis pathways require much higher temperatures and lead to high selectivities to acetylene and to large polynuclear aromatics. The highly endothermic nature of methane conversion to aromatics, however, leads to very low equilibrium conversions and to benzene yields of only \( \sim 7\% \) at the low temperatures (950 K) required for selective chain growth. C\textsubscript{2}–C\textsubscript{10} hydrocarbon selectivities as high...
as 80% have been reported at near-equilibrium conversions on Mo/H-ZSM5 (Wang et al., 1996). H2 is formed during methane pyrolysis and it inhibits the forward reaction rates of both catalytic and homogeneous pyrolysis pathways. Hydrogen transport membranes can remove the thermodynamic and kinetic hurdles imposed by the accumulation of H2 non-oxidative methane reactions (Andersen, Dahl, Jens, Rytter, & Slagter, 1989; Woldman & Sokolovskii, 1991; Hamakawa, Hibino, & Iwahara, 1993; Hamakawa, Hibino, & Iwahara, 1994; Langguth, Dittmeyer, Hofmann, & Tomandl, 1997). The coupling of methane conversion reactions with hydrogen removal via selective membrane walls poses significant design, optimization, and fabrication issues. The first two issues and the guidance required for the third can be addressed by simulations using reaction kinetic and thermodynamic data together with rigorous descriptions of membrane transport and reactor hydrodynamics.

A previous report described reaction-transport models for homogeneous methane pyrolysis reactions, including their coupling with a simple surface-catalyzed initiation step leading to methyl radicals (Li, Borry, & Iglesia, 2001). The coupling of these homogeneous pathways (Dean, 1990) with H2 permeation through the reactor walls led to higher CH4 reaction rates, mostly as a result of the removal of thermodynamic constraints in the near-equilibrium region, and to C2–C10 yields of ~90% at intermediate values of the dimensionless ratio of characteristic H2 transport and CH4 reaction rates (δ = 1–10). H2 removal, however, did not influence the slow irreversible initiation steps that initially form radicals or the faster steps in the productive chain transfer region, and lead to impractical residence times and reactor volumes. Here, we use reaction-transport simulations in order to probe the identity of rate-determining steps in homogeneous CH4 pyrolysis and to propose specific catalytic steps required in order to overcome the significant kinetic barriers inherent in these homogeneous pyrolysis pathways, even when initiated by heterogeneous methyl radical generation steps. Specifically, we combine experimental kinetics for shape-selective bifunctional catalysts developed in a parallel experimental effort (Borry et al., 1999; Kim, Borry, & Iglesia, 2000) with homogeneous kinetic models and hydrodynamic descriptions of tubular membrane reactors. The resulting simulations are used to describe the effects of hydrogen removal on hydrocarbon yields and on required residence times and to obtain rigorous criteria for the design of catalyst and membrane materials for the direct conversion of methane to higher hydrocarbons.

2. Kinetics and simulation methods

The rates of homogeneous methane pyrolysis reactions and of hydrogen permeation are described by kinetic and transport equations reported previously (Li et al., 2001) and only a brief description is included here. For complex networks involving n reactions and m components, the rate of reaction for component j is given by

\[ R_j = \sum_{i=1}^{n} \lambda_{ij} k_i(T, p) f_i(K, p), \]

where \( \lambda_{ij} \) is the stoichiometric coefficient for species j in reaction i, T is the reaction temperature, K is the equilibrium constant vector, p is the partial pressure vector of the reaction mixture, and \( k_i \) and \( f_i \) are the rate constant and the dimensionless rate expression for reaction i, respectively. The hydrogen transport flux through the reactor wall is assumed to be proportional to the H2 partial pressure gradient across the membrane:

\[ J_{H2} = P \frac{1}{T} (p_{H2,1} - p_{H2,2}), \]

where P is the permeability of H2 through the membrane, l is the membrane thickness, and \( p_{H2,1} \) and \( p_{H2,2} \) are the H2 partial pressures on the feed and permeate sides of the membrane, respectively. Certain membrane systems may obey modified versions of Eq. (2), but the use of the appropriate equation in such cases will not alter the trends and the concepts described here using Eq. (2) as a specific example.

In a plug-flow tubular reactor with permselective walls, differential mole balances on the reaction and permeation channels give the dimensionless differential equations

\[ \frac{1}{Da} \frac{d \phi_j}{d \xi} = \sum_{i=1}^{n} \lambda_{ij} \beta_i f_i(K, p) - \delta z_j(y_{ji} - y_{js}) \quad \text{(reaction side)}, \]

\[ \frac{1}{Da} \frac{d \beta_i}{d \xi} = \delta z_j(y_{ji} - y_{js}) \quad \text{(permeation side)}. \]

Several dimensionless parameters (Da, δ, \( z_j \) and \( \beta_i \)) arise from the non-dimensionalization of these mole balances. These are defined as

\[ Da = \frac{Lk}{F_{10}} \quad \text{(Damkohler number, reactant conversion rate/reactant inlet rate)}, \]

\[ \delta = \frac{4P_r}{dk} \quad \text{(Rate ratio, permeation rate/reaction rate)}, \]

\[ z_j = \frac{P_j}{P_f}, \]

\[ \beta_i = \frac{k_i}{k_1}. \]

Da is a Damkohler number, which reflects the probability of the reaction as the ratio of the reactor residence time to the characteristic reaction time. The parameter δ accounts for the ability of the reactor to transport H2 and to convert CH4, as the ratio of the characteristic times for reaction and for H2 transport.
The dimensionless parameters, $Da, \delta, \alpha$, and $\beta_1$, are defined in terms of a basis reactant, chosen here as CH$_4$. The consequences of H$_2$ removal are explored by defining the parameter $\delta$ as the ratio of characteristic H$_2$ transport and CH$_4$ conversion molar rates. For homogeneous pyrolysis, methane conversion rates are described by a complex kinetic network, and the rate constant ($k$) required to define $Da$ and $\delta$ is not apparent by inspection. In this case, we use a pseudo-first-order rate constant, $k_{eff}$, obtained by fitting simulated rates using a first-order expression (Li et al., 2001). For catalytic reaction pathways, the reaction rate is expressed per unit catalyst mass, and such rates are converted to a reactor volume basis in the equation for $\delta$ by using the catalyst bed density in the packed bed reactor.

Simulations were carried out using CHEMKIN II and DVODE subroutines (Kee, Rupley, & Miller, 1990). Homogeneous kinetic models and rate constants for each elementary step are identical to those reported previously (Li et al., 2001). The catalytic conversion of methane on Mo/H-ZSM5 was simulated by inserting non-elementary catalytic steps into the kinetic network, as described below. The required rate constants for Mo/H-ZSM5 catalysts were obtained using error minimization techniques from the experimental effects of effective reactor residence time on reaction rates and selectivities (Borry, 1998).

3. Results and discussions

3.1. Effect of catalytic pathways on the conversion of C$_2$H$_4$ to C$_6$H$_6$

Homogeneous methane pyrolysis reactions exhibit three kinetic stages (Fig. 2 in Li et al., 2001):

(i) an induction period ($t \sim 2400$ s, $T = 1038$ K), during which CH$_4$ conversion is limited by slow initiation steps ($CH_4 \rightarrow CH_3 + H$),

(ii) a chain transfer regime reached as CH$_3$ and H radicals accumulate and reach pseudosteady-state and within which most of the CH$_4$ conversion occurs,

(iii) a near-equilibrium stage within which most elementary steps (and the overall reaction) become unproductive as they reach thermodynamic equilibrium.

The coupling of homogeneous pyrolysis with H$_2$ permeation through reactor walls led to higher CH$_4$ reaction rates at high methane conversions (stage (iii)), mostly as a result of the removal of the prevalent thermodynamic constraints near equilibrium. H$_2$ removal, however, did not influence the slow irreversible initiation steps that initially form radicals or the faster steps in the productive chain transfer region, within which most of the chemical conversion occurs; therefore, reactor residence times and volumes remained impractically large.

The introduction of a surface-catalyzed initiation step $CH_4 + \left[ ^* \right] \rightarrow CH_3 + \left[ ^* H \right]$ increased methane conversion rates at low conversions by replacing the homogeneous version of this step with a faster step, which rapidly forms the radicals required to enter the chain transfer regime. The effects of these surface steps can be explored by introducing a dimensionless parameter $\rho = k_{ch}/k_{init}$, which reflects the relative contributions of catalytic ($k_{ch}$) and homogeneous ($k_{init}$) methyl radical generation steps. Induction periods become shorter with increasing $\rho$, but chain transfer rates and near-equilibrium conversion rates are largely unaffected by surface-catalyzed initiation steps. Also, product distributions were essentially unaffected by heterogeneous methyl radical formation processes, because CH$_4$ conversion occurs predominantly in the chain transfer region, within which radical concentrations and reaction rates are controlled by homogeneous chain transfer steps.

The continuous removal of H$_2$ along a tubular reactor increased CH$_4$ reaction rates by removing the molecules required for unproductive reverse reactions as individual steps approach equilibrium. Therefore, methyl radical formation on surfaces cannot increase chain transfer rates, which are required in order to convert radicals into stable reaction products. Surface sites that replace these chain transfer steps are required in order to overcome the intrinsic kinetic barriers imposed by these homogeneous pathways. The attainment of the high C$_2$–C$_{10}$ yields achievable with continuous H$_2$ removal within practical residence times will require catalytic sites that also convert the initial C$_2$ products formed via homogeneous recombination of methyl radicals into more stable aromatics. The predominant CH$_4$ pyrolysis products are ethene, benzene, and naphthalene at 823–1073 K. Thus, we may refer to their inter-conversion using the non-elementary steps in Scheme 1 in order to discuss the behavior of the overall reaction, even when the simulations rigorously include the detailed steps included in the complete kinetic network throughout.

The rigorous monitoring of the approach to equilibrium for homogeneous or catalyst-initiated reaction networks showed that step 1 approaches equilibrium within the chain transfer region and the overall reaction becomes limited by largely irreversible steps that convert ethene to aromatics. The net forward rate of methane conversion reaction and the product distribution in the chain transfer regime, within which most of the conversion occurs, become controlled by the rate of C$_2$H$_4$ conversion to products (via steps 2–4). In the absence of a catalyst for this reaction, these reactions occur only via homogeneous routes.

The quasi-equilibrated nature of the initial CH$_4$ to C$_2$H$_4$ reaction requires that one of the products of this reaction be “scavenged” in order to overcome thermodynamic constraints. One approach involves the removal of the H$_2$ formed using a membrane (Borry, Lu, Kim, & Iglesia, 1998, Li et al., 2001). Another approach would react C$_2$H$_4$ in an
efficient reaction to form aromatic molecules, which are favored by thermodynamics and are present in concentrations well below equilibrium values in the absence of such conversion pathways. Here, we first explore the role of catalytic ethene conversion pathways using a conceptual reaction scheme without H₂ removal. Then, we replace this scheme with one appropriate for available Mo/H-ZSM5 catalysts. Finally, in the last section we couple these realistic catalytic kinetics with continuous H₂ removal in a tubular reactor.

Catalytic C₂H₄ conversion pathways are first described here by introducing the following non-elementary catalytic reaction steps:

\[ 3\text{C}_2\text{H}_4 = \text{C}_6\text{H}_6 + 3\text{H}_2 \]  

The reaction rate is assumed to obey the rate expression

\[ r_2 = k_2 \frac{\text{C}_3\text{H}_3}{\text{C}_2\text{H}_4} (1 - \eta_2) \]  

in which the approach to equilibrium for this step (\( \eta_2 \)) is described by

\[ \eta_2 = \frac{\text{C}_3\text{H}_3}{\text{C}_2\text{H}_4} \frac{1}{K_2} \]  

and \( k_2 \) and \( K_2 \) are the reaction rate constant and equilibrium constant of reaction (6), respectively.

Figs. 1 and 2 show the effects of catalytic ethene conversion rates on CH₄ conversion and on the approach to equilibrium for CH₄ conversion to C₂H₄. The parameter \( \gamma \) is given by the ratio of the first-order rate constants for ethene conversion to benzene \( (k_2 \text{ in Eq. (11)}) \) and for methane conversion \( (k_{\text{eff}}) \). The value of \( \eta_1 \) in Fig. 2 reflects the approach to equilibrium for the CH₄–C₂H₄ reaction (step 1 in Scheme 1) and it is defined as

\[ \eta_1 = \frac{\text{C}_3\text{H}_3}{\text{C}_2\text{H}_4} \frac{1}{K_1} \]  

where \( K_1 \) is the equilibrium constant for the reaction

\[ 2\text{CH}_4 = \text{C}_2\text{H}_4 + 2\text{H}_2 \]  

Fig. 2 shows that step 1 approaches equilibrium quickly in the absence of ethene to benzene conversion catalytic pathways \( (\gamma = 0) \), and \( \eta_1 \) becomes greater than 90% at CH₄ conversions of ~ 10%. The approach to equilibrium is very similar for purely homogeneous and for catalytically initiated homogeneous pyrolysis pathways (Fig. 2), because initiation steps do not contribute to reaction rates in the chain transfer regime, within which the approach to equilibrium occurs. Catalytic initiation pathways decrease the residence time required to reach a given conversion by eliminating the induction period imposed by slow homogeneous initiation processes (Fig. 1). Changes in conversion with residence time become very small as the CH₄ conversion to C₂H₄ reaches equilibrium values, because the higher equilibrium conversions possible as ethene is converted to benzene are
achieved only via slow homogeneous pathways when catalytic sites are not available (γ = 0).

The introduction of catalytic sites (γ=10) decreases the value of η for CH₄ conversion to C₂H₄ by continuously removing the ethene formed in this reaction (Fig. 2). This continuous removal of ethene also eliminates the asymptotic conversion limit reached in the absence of heterogeneous pathways (γ=0; Fig. 1). Such catalytic sites, however, do not influence reaction rates in the chain transfer kinetic regime (Fig. 1), because CH₄ conversion to C₂H₄ is far from equilibrium at low CH₄ conversion. Thus, the residence times required for γ values of 10 are only slightly lower than those for purely homogeneous ethene to benzene conversion pathways. High methane conversions at short contact times will require catalytic sites that increase the rates of ethene formation from methane and of ethene conversion to aromatics.

Many elementary homogeneous steps are involved in the synthesis of C₂H₄ from CH₄. We have carried out a sensitivity analysis of the homogeneous reaction pathways by increasing the rate constants of individual elementary steps in order to identify the rate-determining steps. This allows the selective introduction of specific catalytic sites in order to carry such steps more rapidly and to overcome the kinetic bottlenecks imposed by homogeneous pathways. This sensitivity analysis showed that a catalytic pathway for the synthesis of C₂H₄ from CH₄ is required for practical reactor volumes at the low temperatures suitable for selective pyrolysis pathways. Neither CH₃ radical generation nor ethene to benzene catalytic sites are sufficient for practical reaction rates, because overall methane conversion rates ultimately become limited by homogeneous recombination of CH₃ radicals to form C₂H₆ or by the subsequent dehydrogenation of C₂H₆ to form C₂H₄. Neither one of these steps is sufficiently fast to match the typical rates of the catalytic conversion of ethene to benzene.

Active sites that catalyze methane activation to form CH₃ radicals will also catalyze C₂H₆ dehydrogenation to form C₂H₄. We can include the effects of this reaction as an elementary step for C₂H₆ activation in the heterogeneous kinetic model with a rate constant estimated using a modified Evans–Polanyi correlation (Borry, 1998):

$$C₂H₆ + [*]⁻ → C₂H₅ + [*]H. \quad (15)$$

Fig. 3 gives the methane conversion obtained by considering catalytic activation of CH₄ and C₂H₆ (ρ = 10⁷, and kₛ₂/kₛ₁ = 6) and the catalytic conversion of ethene to benzene (γ = 10). The methane conversion rate is much lower than that experimentally measured on Mo/H-ZSM5 catalysts, and a further increase in the value of ρ did not influence methane conversion rates, which are limited by the recombination of CH₃ to form C₂H₆. This was confirmed by the higher rates obtained by artificially increasing the reaction rate for CH₃ recombination steps (Fig. 3).

Several studies have addressed the reaction pathways for CH₄ conversion to aromatics on Mo/H-ZSM5 (Chen, Lin, Xu, Zhang, 1995; Wang et al., 1996; Solymosi, Cserenyi, Szoke, Bansagi, Oszko, 1997; Borry et al., 1999; Ding, Li, Meitzner, & Iglesia, 2001). Some studies have proposed that ethene forms via homogeneous recombination of CH₃ radicals produced by C–H activation on catalytic sites (Chen et al., 1995), as found earlier for oxidative coupling of methane on oxide catalysts. Our simulations show that purely homogeneous CH₃ recombination pathways cannot account for the observed rate of CH₄ conversion on Mo/H-ZSM5, even for arbitrarily fast heterogeneous CH₃ radical formation steps. Therefore, active sites for both methane conversion to ethene and for ethene cyclodimerization reactions to form aromatics are required in order to reach practical methane conversions in reasonable residence times.

3.2. Simulation of the rate and selectivity of catalytic methane conversion on Mo/H-ZSM5

The requirement for catalysts that:

(i) break C–H bonds in CH₄ (and in any higher alkanes formed) to form CH₃, surface fragments,
(ii) recombine CH₃ groups to form at least C₂ hydrocarbons, and
(iii) oligomerize and cyclize alkenes into thermodynamically favored aromatics

is likely to require metal-like surfaces for steps (i) and (ii) and acid sites for step (iii). Oligomerization and cyclization pathways unconstrained by shape-selective channels, such as those provided by medium-pore pentasil zeolites, however, lead to polynuclear aromatic molecules at the temperatures
required for C–H bond activation in CH₄. Mo/H-ZSM5 catalysts appear to satisfy these requirements. These materials catalyze CH₄ conversion to aromatics via bifunctional pathways, with near-equilibrium yields of benzene and > 80% selectivity to C₂–C₁₀ hydrocarbons at ~ 1000 K (Wang et al., 1993; Solymosi et al., 1995; Wang et al., 1996; Lunsford et al., 1995, Borry et al., 1999).

Our kinetic studies of CH₄ reactions on Mo/H-ZSM5 have confirmed the earlier proposal (Lunsford et al., 1995) that aromatization involves the sequential formation of ethene (and possibly ethane) on MoCₓ clusters (formed from exchanged MoOₓ precursors during reaction). This initial step is followed by the conversion of ethene and ethane to aromatics via bifunctional pathways on acid sites aided by hydrogen desorption from MoCₓ sites. Ethene–ethene equilibrium appears to be maintained throughout the experimental conversion range; therefore, we group both C₂ molecules rigorously into one kinetic lump. These consecutive reactions are similar to those shown previously in Scheme 1, and the rate equations for each reaction are shown in Eqs. (16)–(22) for Mo/H-ZSM5 catalysts.

**Step 1:**

\[ 2\text{CH}_4 = \text{C}_2\text{H}_4 + 2\text{H}_2, \quad (16) \]

\[ r_1 = k_1\text{CH}_4(1 - \eta_1). \quad (17) \]

**Step 2:**

\[ 3\text{C}_2\text{H}_4 = \text{C}_6\text{H}_6 + 3\text{H}_2, \quad (18) \]

\[ r_2 = k_2\text{C}_2\text{H}_4(1 - \eta_2). \quad (19) \]

**Step 3:**

\[ \text{C}_6\text{H}_6 + 2\text{C}_2\text{H}_4 = \text{C}_{10}\text{H}_8 + 3\text{H}_2, \quad (20) \]

\[ r_3 = k_3\text{C}_6\text{H}_6\text{C}_2\text{H}_4(1 - \eta_3), \quad (21) \]

\[ \eta_3 = \frac{C_{10}\text{H}_8}{C_{2}\text{H}_4} \times \frac{C_{2}\text{H}_4}{C_6\text{H}_6} \times \frac{C_6\text{H}_6}{K_3}. \quad (22) \]

The rate constants, \( k_1, k_2 \) and \( k_3 \), in these equations were estimated from experimental residence time effects on rates of formation of individual products. The equilibrium constants, \( K_1, K_2 \) and \( K_3 \) were calculated using literature thermodynamic data (Li et al., 2001). Fig. 4 compares experimental and simulated product selectivities as a function of CH₄ conversion, which was varied by changing the reactor residence time at constant temperature (950 K) and inlet CH₄ partial pressure (0.5 bar) and by allowing the number of sites within the reactor to decrease as deactivation occurs. The values giving the best fit for \( k_1, k_2 \) and \( k_3 \) were 0.04 s⁻¹, 4.2 s⁻¹, and 1.2 \times 10⁷ cm³ mol⁻¹ s⁻¹. This simple, but mechanistically reasonable, set of rate expressions adequately describes CH₄ reaction pathways on Mo/H-ZSM5. H₂ addition experiments have shown inhibition of CH₄ conversion rates consistent with the approach to equilibrium rigorously contained within the kinetic model described above. These experiments, however, also detected kinetic inhibition effects of H₂, which lead to lower pseudo-first order rate constants for each of the steps as H₂ concentrations increase. The kinetic model used here neglects these kinetic inhibition effects; as a result, it will also neglect the additional kinetic benefits of hydrogen removal and underestimate the reaction rate improvements achieved by the continuous removal of H₂ along an actual catalytic reactor.

### 3.3. Effect of hydrogen removal on catalytic CH₄ conversion on Mo/H-ZSM5

The kinetic model for catalytic CH₄ conversion on Mo/H-ZSM5 was coupled with a hydrodynamic model for a tubular reactor with hydrogen-permeable walls (Eqs. (4) and (5)). The catalytic pathways used (Eq. (16)–(22)) can complete the conversion of methane to ethene, benzene, and naphthalene much faster than corresponding homogeneous pathways. Nevertheless, the entire homogeneous kinetic network (Li et al., 2001) was included in the simulations in order to detect any coupling between homogeneous and heterogeneous pathways and to provide a homogeneous path for the formation of polynuclear aromatics via acetylene chain growth steps that occur in the gas phase. Figs. 5–8 show the results of these simulations of heterogeneous and homogeneous reactions in a tubular reactor with continuous H₂ removal. The results are shown for a wide range of the Damkohler number \( (Da = 0−10) \) and of the ratio of characteristic times for reaction and transport \( (\delta = 10⁻³−10²) \). In these simulation results, the rate constant \( k_1 \) for the methane to ethene step (Eq. (16)) is used to define the dimensionless parameters \( Da \) and \( \delta \) after converting the rate constant to a volumetric basis.
For a given value of $Da$, CH$_4$ conversion increases monotonically with increasing $\delta$ values, as a result of the removal of thermodynamic constraints for each one of the heterogeneous steps as H$_2$ is removed. Conversely, the value of $Da$ required to reach a given CH$_4$ conversion decreases with increasing $\delta$, as a result of a higher net forward rate of all three reactions as H$_2$ concentrations decrease. As also found for homogeneous pyrolysis simulations (Li et al., 2001), the effects of H$_2$ removal become detectable for $\delta$ values between 0.1 and 10. Values of $\delta$ larger than 10 lead to negligible H$_2$ concentrations at all residence times. Values of $\delta$ smaller than 0.1 remove negligible amounts of H$_2$ and do not influence local H$_2$ concentrations within the reactor.

In general, the results shown in Figs. 5–8 are similar to those for purely homogeneous pathways (Li et al., 2001). For a given value of $Da$, however, homogeneous and heterogeneous pathways obviously require different reactor residence times, because catalytic pathways provide a much larger first-order kinetic rate constant for the kinetically relevant steps ($k_1 = 4 \times 10^{-2} \text{ s}^{-1}$) than homogeneous pathways ($k_{\text{eff}} = 7 \times 10^{-5} \text{ s}^{-1}$). Catalytic steps that provide a complete path from CH$_4$ to aromatics eliminate the kinetic
barriers that prevent practical methane conversions at short contact times. For example, CH₄ conversions of ~ 90% can be reached for Da values of 4 and δ values of 10. These correspond to residence times of ~ 100 s. As discussed below, the higher reaction rates achievable via these catalytic pathways require correspondingly higher H₂ permeation rates in order to attain the required values of δ.

At low CH₄ conversions and short residence times (Da ≪ 1), H₂ removal increases C₂ yields (Fig. 6), but these yields then decrease at higher contact times (Da), because the continuous removal of H₂ favors also the subsequent conversion of ethene to aromatics. Benzene yields (Fig. 7) show a maximum as the H₂ removal rate increases, because benzene is also ultimately converted to naphthalene (and ultimately to larger aromatics via homogeneous pathways). At high values of δ and Da, the reaction proceeds completely to the final product (naphthalene), which then converts slowly to larger polynuclear aromatics via homogeneous routes. Our heterogeneous kinetic model does not explicitly include coke formation steps. The homogeneous kinetic model includes H-abstraction/C₂H₂-addition steps that lead to the formation of polynuclear aromatic hydrocarbons (PAH). In order to probe the effect of catalytic sites on the potential formation of acetylene via C–H bond activation in ethene, we introduced such pathways with a rate constant chosen based on the C–H bond energy in ethene and the Evans–Polanyi relations described previously (Borry, 1998). The simulations show that ethene conversion to acetylene reaction approaches equilibrium even for purely homogeneous pathways. Thus, catalytic pathways do not increase the effectiveness of homogeneous PAH formation steps or produce acetylene more efficiently than purely homogeneous steps. Homogeneous H-abstraction/C₂H₂-addition reactions are slower compared with catalytic formation rates for benzene and naphthalene; therefore, naphthalene yields approach 100% as H₂ removal rates increase (Fig. 8).

This simplified kinetic model cannot address the effect of H₂ removal on catalytic pathways for coke formation, which is a slow but detectable process on Mo/H-ZSM5 catalysts. The maximum attainable C₂–C₁₀ hydrocarbon yields will ultimately depend on the relative effects of H₂ concentration on the formation of these products and on their subsequent conversion to larger aromatics and coke, a step that appears to be inhibited by the shape-selective environment within zeolite channels. These simulation results (Figs. 5–8) suggest that bifunctional catalysts, such as Mo/H-ZSM5 and continuous H₂ removal can lead to near complete conversions of CH₄. These simulations suggest that very high C₆–C₁₀ yields can be achieved in these catalytic membrane reactors in the absence of significant chain growth beyond naphthalene.

The results described above suggest that δ values between 1 and 10 are required in order to attain high conversions and high C₂–C₁₀ yields. The defining equation for δ (Eq. (6)) shows that for a given reaction rate, δ depends on the membrane permeability P, the membrane thickness l, and the tube reactor diameter d (inversely proportional to its surface-to-volume ratio). The membrane permeability is controlled by the nature of the membrane material. For proton-conducting membranes based on SrCe₀.₅O₃₋ₓ or SrZr₀.₅O₃₋ₓ perovskites, which are well suited for methane pyrolysis applications (Schober, Friedrich, & Condon, 1995; Hamakawa et al., 1993; Hamakawa et al., 1994; Borry et al., 1998), H₂ permeabilities are 10⁻¹³–10⁻¹² mol m⁻¹ s⁻¹ Pa⁻¹ at 1000 K. The rate constant for CH₄ conversion on Mo/H-ZSM5 is k₁ which is 4 × 10⁻² s⁻¹ at 950 K. Thus, for a reactor diameter of 1 cm, the thickness of the membrane walls must be 10–100 µm in order to achieve δ values of 1–10. Recently, we have achieved the synthesis of such membrane films supported on porous substrates for SrZr₀.₉₅Y₀.₀₅O₃₋ₓ (Lu, 1999) and SrCe₀.₉₅Yb₀.₀₅O₃₋ₓ (Hamakawa, Li, Li, & Iglesia, 2002).

4. Conclusions

The nature of rate-determining steps in methane homogeneous pyrolysis sequences was explored in order to identify specific catalytic steps required to overcome the significant kinetic barriers inherent in purely homogeneous pyrolysis pathways. Catalytic sites that increase ethene to benzene conversion lead to higher methane conversion rates by removing the thermodynamic and kinetic inhibition effects caused by the increasing concentration of the H₂ formed in CH₄ reactions. Such sites, however, do not influence reaction rates in the chain transfer regime, within which homogeneous methane conversion pathways to form ethene limit overall reaction rates. Therefore, a catalyst that activates C–H bonds in CH₄ (and in any larger alkanes or alkenes), recombines CH₄ groups to form C₂ hydrocarbons, and oligomerizes and cyclizes alkenes into aromatics is required. Mo/H-ZSM5 catalysts appear to satisfy all of these requirements, but CH₄ conversion and hydrocarbon yields are limited by unfavorable reaction thermodynamics. A simplified consecutive reaction scheme using rate equations measured on Mo/H-ZSM5 were used in order to simulate the effects of H₂ removal on methane conversion rates and product selectivities. Simulation results suggest that bifunctional catalysts, such as Mo/H-ZSM5, with continuous H₂ removal can lead to almost complete CH₄ conversion at practical residence time (~ 100 s) and intermediate values of dimensionless transport rates (δ = 1–10). For currently available membrane materials however, such δ values require 10–100 µm dense ceramic membrane films; the successful synthesis of such films has recently been reported.

Notation

- Cᵢ: Concentration of component i, mol m⁻³
- Da: Damkohler number
- d: inner diameter of reactor, m
- Fₓ0: mole feed flow rate of component j, mol m⁻³ s⁻¹
References


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