

Catalytic pyrolysis of methane on Mo/H-ZSM5 with continuous hydrogen removal by permeation through dense oxide films

Zheng Liu¹, Lin Li², and Enrique Iglesia*

Materials Sciences Division, E. O. Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720, USA

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A dense $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ thin film ($\sim 2\ \mu\text{m}$) was used to remove H_2 during non-oxidative conversion of methane to higher hydrocarbons on Mo/H-ZSM5 in order to overcome kinetic and thermodynamic constraints. At 950 K, these films removed only a small fraction of the H_2 produced and hydrocarbon synthesis rates were unaffected by H_2 removal. Higher temperatures led to a modest increase in CH_4 conversion rates, but also to slightly lower $\text{C}_2\text{--C}_{12}$ hydrocarbon selectivities and to higher catalyst deactivation rates. These undesired effects were eliminated by the addition of small amounts of CO_2 to the CH_4 reactants. The combination of dense $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ thin films, chain-limiting catalytic pyrolysis reactions on Mo/H-ZSM5, and CO_2 co-reactants led to stable catalyst performance and modestly higher hydrocarbon synthesis rates than in conventional reactors. The improvements achieved by continuous H_2 removal are in agreement with predictions of kinetic-transport model simulations in tubular reactors with permeable walls.

KEY WORDS: methane pyrolysis; membrane reactors; Mo/H-ZSM5.

1. Introduction

Recent studies of methane pyrolysis on Mo/H-ZSM5 and W/H-ZSM5 have addressed the structure of these catalytic materials [1–10] and the bifunctional pathways by which Mo carbide and Brønsted acid sites contribute to the predominant formation of benzene and naphthalene [1–3,6,11]. MoC_x clusters within spatially constrained zeolite channels containing Brønsted acid sites lead to limited chain growth and to high C_{11-} hydrocarbon selectivities. Methane conversion to higher hydrocarbons is highly endothermic and equilibrium conversions and product yields are typically low (e.g. $\sim 12\%$ benzene at 923 K and 100 kPa CH_4) [12]. Catalytic sites within shape-selective channels can minimize the formation of polynuclear aromatics, typical of homogeneous pyrolysis pathways, but they cannot influence the position of chemical equilibrium. Recent reaction-transport simulations suggest that continuous removal of H_2 can alleviate thermodynamic and kinetic constraints when H_2 permeation rates approach the rates of H_2 formation in CH_4 pyrolysis reactions [14,15]. The presence of H_2 addition decreases both the forward methane conversion rates and the methane conversion levels attainable at equilibrium [13,16].

Dense membranes with perovskite structure selectively transport hydrogen as protons at high temperatures

($\sim 800\text{--}1000\ \text{K}$) [17]; their use has been suggested for catalytic CH_4 pyrolysis on Mo/H-ZSM5 [18]. The reported proton conductivities in these materials require that they be used as thin films in order to achieve the H_2 permeation rates needed in order to influence H_2 concentrations and equilibrium conversions and yields [14,15]. Dense thin films with $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ composition and $\sim 2\ \mu\text{m}$ thickness have recently been prepared using controlled sintering of porous substrates and of thin perovskite coatings [19,20]. Here, we use these thin films in reactors containing Mo/H-ZSM5 catalysts for CH_4 conversion with continuous H_2 removal. A modest increase of CH_4 conversion and hydrocarbon yields over their equilibrium levels was achieved and the observed deleterious effects of H_2 removal on catalyst stability were eliminated by the use of CO_2 co-reactants.

2. Experimental methods

2.1. Catalyst synthesis methods

Mo/H-ZSM5 (4 wt% Mo) was prepared by thermal treatment of physical mixtures of H-ZSM5 (Zeolyst International, Si/Al = 15) and MoO_3 powders (Johnson Matthey Electronics, 99.95%), as reported previously [1,2]. The samples were pressed into wafers and crushed and sieved in order to retain agglomerates with 0.25–0.5 mm diameter. These synthesis procedures led to the exchange of MoO_x as $(\text{Mo}_2\text{O}_5)^{2+}$ dimers; subsequent exposure to CH_4 during reaction at 950–1000 K caused the carburization of these dimers to form MoC_x clusters active in CH_4 activation reactions [1,21].

*To whom correspondence should be addressed.

E-mail: iglesias@cchem.berkeley.edu

¹Current address: Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA.

²Current address: UOP LLC, 25 East Algonquin Rd., Des Plaines, IL 60017, USA.

2.2. Methane reaction rate and selectivity measurements

Methane reactions were carried out at 950–1000 K using a quartz tubular reactor ($0.11 \text{ cm}^3 \text{ s}^{-1}$, 85 kPa CH_4 , 15 kPa Ar). Exchanged $\text{MoO}_x/\text{H-ZSM5}$ samples (0.50 g) were held on a porous quartz frit and treated in 20% O_2/He ($0.82 \text{ cm}^3 \text{ s}^{-1}$, Airgas, UHP) at 950 K for 0.2 h. Samples were flushed with He ($0.67 \text{ cm}^3 \text{ s}^{-1}$, UHP) for 0.3 h and the He stream was then replaced with the reactant mixture (85% CH_4/Ar ; $0.11 \text{ cm}^3 \text{ s}^{-1}$). CH_4 initially reacts with exchanged species MoO_x to remove O atoms as CO_x and H_2O and to form MoC_x clusters [22–24]. After this initial induction period (~ 3 h), hydrocarbon formation rates reached relatively constant values, and the temperature was then increased to the desired reaction temperature. In some experiments, CO_2 was added to the CH_4/Ar stream. All reactants were $>99.9\%$ purity (Praxair and Matheson); they were passed over a 13X molecular sieve trap held at ambient temperature before entering the reactor. Gas flows were metered using electronic mass flow controllers (Porter Instruments).

The reactor effluent was analyzed on-line by gas chromatography (Hewlett-Packard HP6890) using a Carboxen 1000 packed column ($3.2 \text{ mm} \times 2 \text{ m}$, Supelco) and a thermal conductivity detector (TCD) to detect H_2 , Ar, CH_4 , CO and CO_2 , and a methyl silicone capillary column (HP-1 $0.32 \text{ mm} \times 50 \text{ m}$) with a flame ionization detector (FID) to measure C_1 – C_{12} hydrocarbons. CH_4 conversions were measured using Ar as an inert internal standard and reported as the percentage of CH_4 in the inlet stream that disappears as the reactant stream passes through the reactor. Selectivities for all detected products are reported on a carbon basis as the percentage of the converted CH_4 appearing as each detected reaction product. The carbon atoms not detected within the observed products are reported as C_{12+} ; this product lumps all hydrocarbons retained in the catalyst or in transfer lines kept at $\sim 423 \text{ K}$.

2.3. Thin-film membranes and the reactor module

The influence of H_2 removal on CH_4 conversion rates and selectivities was examined using the membrane reactor module shown in figure 1. Two glass seals are used to hold each side of a $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ membrane against the two alumina tubes. These glass seals soften at $\sim 903 \text{ K}$ and lead to a gastight seal at temperatures up to $\sim 1073 \text{ K}$. The membrane consists of a porous substrate of 1 mm thickness with one of its surfaces covered by a dense film of similar composition and a thickness of $\sim 2 \mu\text{m}$. These film–substrate composites were prepared using previously reported procedures and their structure and H_2 permeation behavior have been extensively characterized [15,19,20].

$\text{Mo}/\text{H-ZSM5}$ samples (0.5 g, 0.25–0.5 mm) were placed on the top surface of the membrane as a 5 mm

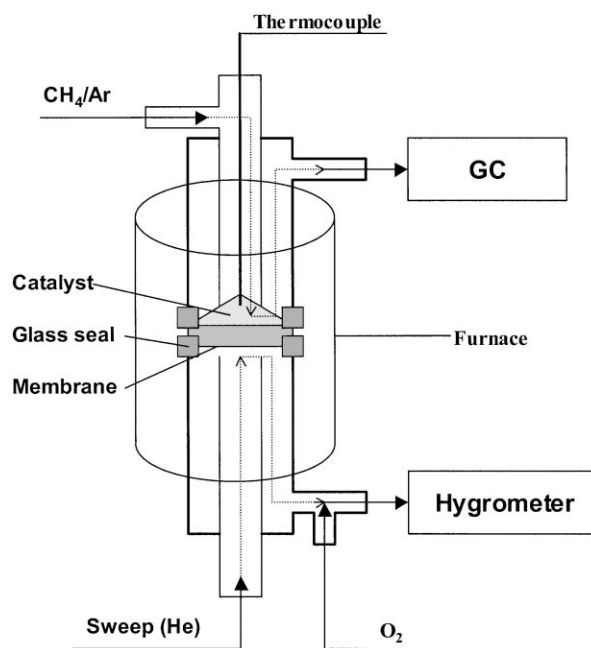


Figure 1. Reactor module for catalytic methane pyrolysis with continuous hydrogen removal.

layer. The reactant flow was introduced through the inner tube in the top section of the module and it exited through the outer annular region. Reactant and product concentrations were measured using the chromatographic protocols described above. The opposite side of the membrane was exposed to He (Airgas, 99.99%). No reactants or products, except H_2 , were detected on the permeate side, but H_2 can be detected during CH_4 pyrolysis reactions. The H_2 flux was determined by reacting the permeated H_2 molecules with a stream of O_2 (5 kPa O_2) on a Pt mesh placed after the reactor and measuring the water formed using an HMI 38 humidity meter (Vaisala).

3. Results and discussion

3.1. Effects of H_2 removal on catalytic CH_4 pyrolysis on $\text{Mo}/\text{H-ZSM5}$

Figure 2 shows that CH_4 conversion and hydrocarbon synthesis (C_2 – C_{12} , C_6H_6 , and C_2) rates are very similar with and without H_2 removal on 4 wt% $\text{Mo}/\text{H-ZSM5}$ at 950 K. Only a slight increase ($\sim 6\%$) in the initial CH_4 conversion rate was detected in the membrane reactor (relative to the conventional reactor) without any detectable change in product distribution. The average H_2 permeation rate measured during the experiment at 950 K was $64 \mu\text{mol/h}$, which is much lower than the average H_2 formation rate in pyrolysis reactions ($960 \mu\text{mol/h}$). H_2 removal efficiencies (ϵ) (defined as the ratio of H_2 removal to H_2 formation rates) are shown as curve A in figure 3 for this experiment. Less than

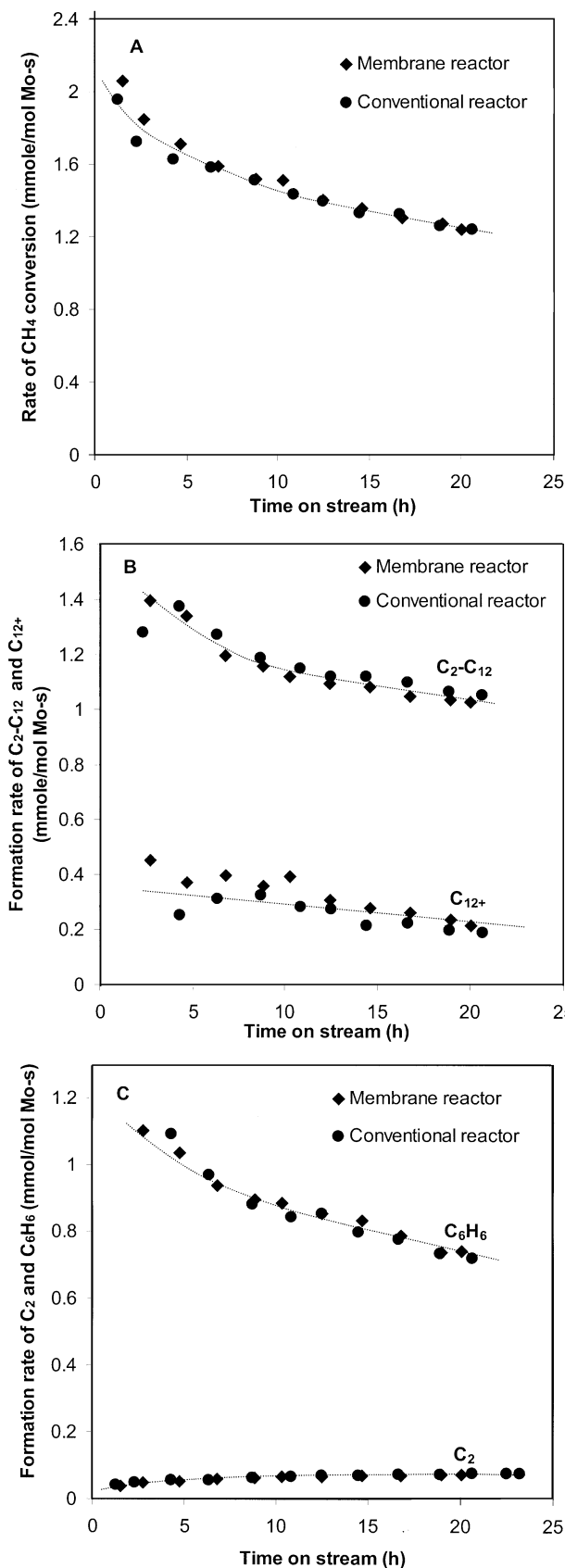


Figure 2. Effects of continuous hydrogen removal on the rates of methane conversion and hydrocarbon formation on 4 wt% Mo/H-ZSM5 at 950 K (85 kPa CH₄; 15 kPa Ar; 780 cm³/g-h). (A) CH₄ conversion rate; (B) C₂-C₁₂ and C₁₂+ formation rates; (C) C₆H₆ and C₂ formation rates.

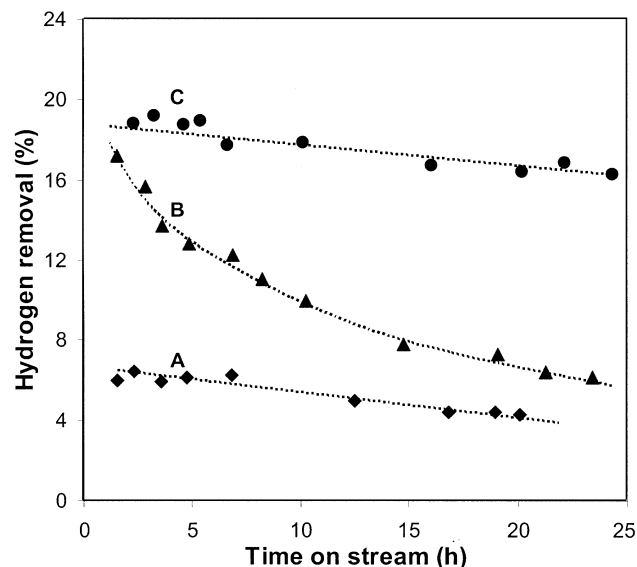


Figure 3. The dependence of hydrogen removal efficiency (ϵ) during CH₄ pyrolysis reaction on the time on steam on 4 wt% Mo/H-ZSM5 (85 kPa CH₄; 15 kPa (Ar + CO₂); 780 cm³/g-h). (A) 0 kPa CO₂, 950 K; (B) 0 kPa CO₂, 993 K; (C) 2 kPa CO₂, 993 K.

7% of the H₂ formed was removed; therefore, the effect of H₂ removal was not clearly detectable at 950 K.

A higher membrane reactor temperature would increase H₂ permeation rates because H₂ permeation is an activated process ($E \approx 60$ kJ/mol [26]) and because equilibrium H₂ pressures for endothermic pyrolysis reactions increase with increasing temperature. Thus, both the hydrogen mobility and its permeation driving force increase with temperature. This was confirmed by the higher hydrogen removal efficiency measured at 993 K (6.1–17.0%, curve B, figure 3) compared with that at 950 K (4.2–6.4%, curve A, figure 3). At both temperatures, but especially at the higher temperature, the fraction of the hydrogen removed decreased with time on stream, a process that reflects a gradual decrease in the catalytic activity of Mo/H-ZSM5. This apparently reflects a decrease in the H₂ permeability due to the gradual and slight reduction of the stoichiometric perovskite. This process can be minimized by the use of an oxidizing stream in the permeate side during reaction.

Curve B in figure 3 indicates that the effects of H₂ removal on CH₄ pyrolysis at 993 K should be stronger, at least during the initial stages of contact with CH₄ reactants, than at 950 K. Figure 4 shows that H₂ removal leads to a modest increase in CH₄ conversion rates on 4 wt% Mo/H-ZSM5 at 993 K. Benzene and C₂-C₁₂ hydrocarbon formation rates, however, were unaffected by H₂ removal, and the higher CH₄ conversion rates reflect almost entirely a proportional increase in the rate of formation of C₁₂+ hydrocarbons (figure 4(B)). The product distribution shows that H₂ removal favors the formation of higher molecular weight aromatics (table 1). The deactivation rate constant (k_d) constant at 993 K increased from a value of 0.044 h⁻¹ without

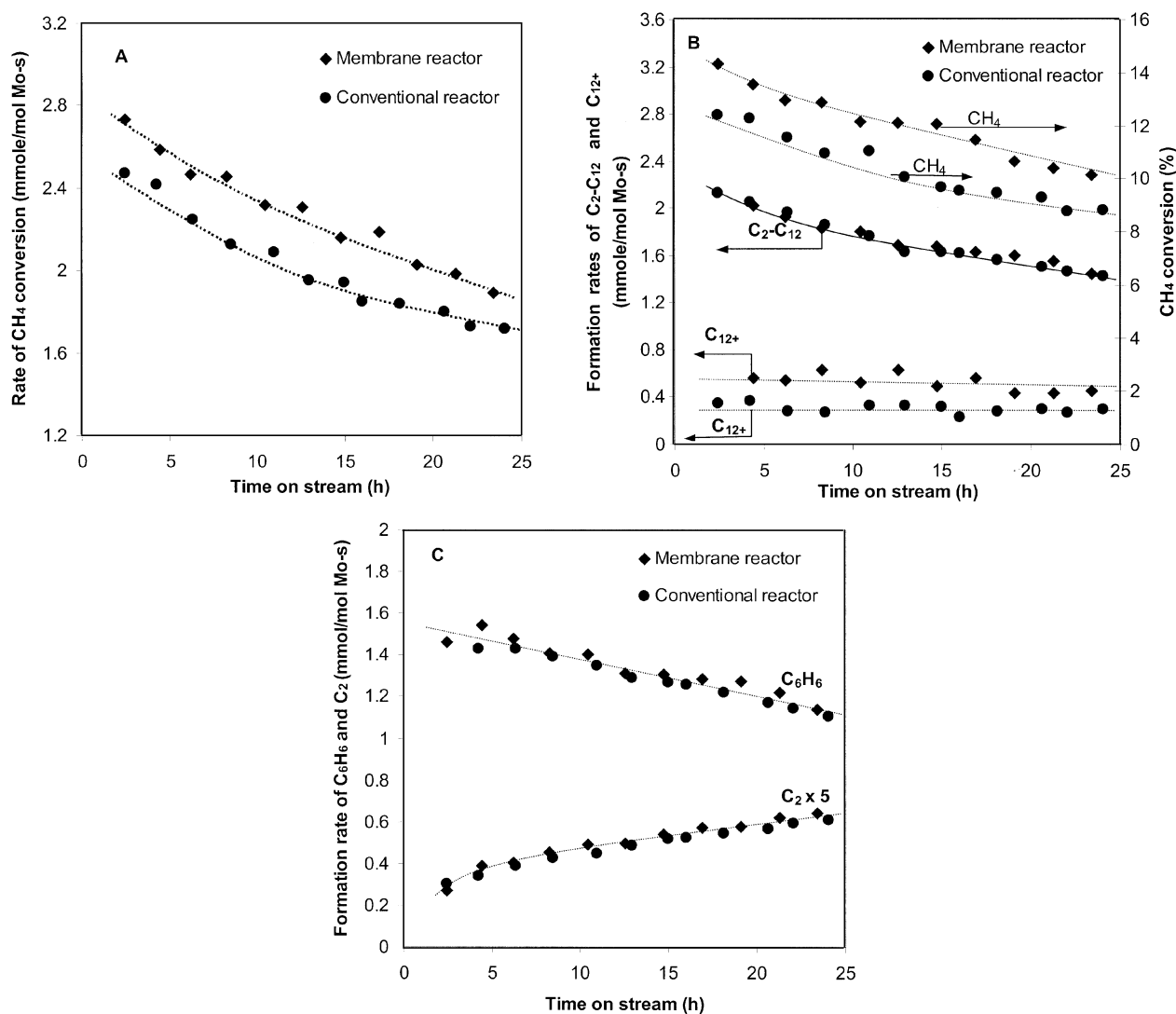


Figure 4. Effects of continuous hydrogen removal on the rates of methane conversion and hydrocarbon formation on 4 wt% Mo/H-ZSM5 at 993 K (85 kPa CH₄; 15 kPa Ar; 780 cm³/g-h). (A) CH₄ conversion rate; (B) CH₄ conversion, and C₂-C₁₂ and C₁₂⁺ formation rates; (C) C₆H₆ and C₂ formation rates.

Table 1
Effects of continuous hydrogen removal on reaction rates and hydrocarbon selectivities during catalytic CH₄ pyrolysis on 4 wt% Mo/H-ZSM5^a

Temperature (K)	Methane conversion (%)	Average selectivities (%)			k_d (deactivation rate constant) (h ⁻¹)
		C ₂ -C ₅	C ₆ -C ₁₂	C ₁₂ ⁺	
950 ^b					
Membrane	6.5–8.5	6.5	72	18	0.034
Non-membrane	6.4–8.7	6.2	75	16	0.035
993 ^b					
Membrane	10.2–13.5	7.0	60	33	0.059
Non-membrane	9.3–11.5	7.0	65	26	0.044
993 (2 kPa CO ₂ as co-reactant) ^b					
Membrane	12.6–13.3	3.3	70	6	0.0045
Non-membrane	11.5–12.0	4.1	73	2	0.0032

^a Reaction conditions: 0.5 g cat., 85 kPa CH₄/15 kPa (Ar + CO₂), 950 K, 780 cm³/g-h.

^b Data were taken during reaction period of 5–20 h. Selectivities are average values over their small changes in the initial 5–20 h on stream.

H₂ removal to 0.059 h⁻¹ for the membrane reactor (figure 4, table 1), suggesting that H₂ decreases the rate of deposition of hydrogen-deficient large organic residues, perhaps by decreasing their extent of unsaturation and allowing them to desorb as stable aromatic products [16].

3.2. Stabilizing effects of CO₂ co-reactants during CH₄ conversion in membrane reactors

The addition of CO₂ to CH₄ reactants improves the stability of Mo/H-ZSM5 catalysts in conventional flow reactors [16,27]. Therefore, a CO₂/CH₄/Ar (2 kPa/85 kPa/13 kPa) reactant stream was used instead of CH₄/Ar in the membrane reactor at 993 K, in an effort to achieve more stable CH₄ conversion rates. Figure 3 (curve C) shows that the presence of CO₂ does not influence the initial H₂ removal efficiency, but preserves the high initial values for longer times on stream, apparently by minimizing the deactivation of both the catalyst and the membrane. Figure 5 shows CH₄ conversion and hydrocarbon formation rates with CH₄/CO₂ reactant mixtures at 993 K in the membrane reactor and also in a conventional flow reactor. These results clearly show that the presence of small amounts of CO₂ lead to lower deactivation rate constants in both types of reactor (table 1). The presence of CO₂ decreases the concentration of unreactive organic residues or their precursors, apparently *via* reactions with such species to form CO [16,27].

With CO₂/CH₄ mixtures, modestly higher CH₄ conversion rates and hydrocarbon yields can be achieved by removing a fraction of the H₂ formed, without consequent negative effects on catalyst stability. H₂ removal leads to slightly higher yields of undesired C₁₂₊ hydrocarbons for both pure CH₄ and CO₂/CH₄ reactants, but these effects are less marked with CO₂/CH₄ reactant mixtures. The removal of some H₂ produced in pyrolysis reactions can minimize kinetic inhibition effects by H₂ and also shift equilibrium CH₄ conversion levels and hydrocarbon yields. The relative importance of these two effects cannot be rigorously inferred from the data presented here, but the importance of the thermodynamic effects is clear from the near-equilibrium CH₄ conversion and hydrocarbon yield values achieved in conventional flow reactors in this study.

These preliminary studies illustrate the need to understand the kinetic effects of H₂ on the chain growth pathways involved in pyrolysis reactions catalyzed by Mo/H-ZSM5 in order to balance the beneficial effects of H₂ removal on reaction rates with their concomitant effects on chain growth selectivity. This study indicates that additional increases in H₂ permeation rates are required in order to achieve H₂ removal efficiencies higher than those shown in figure 3 and consequently stronger effects on CH₄ conversion and hydrocarbon formation rates. These higher hydrogen permeation

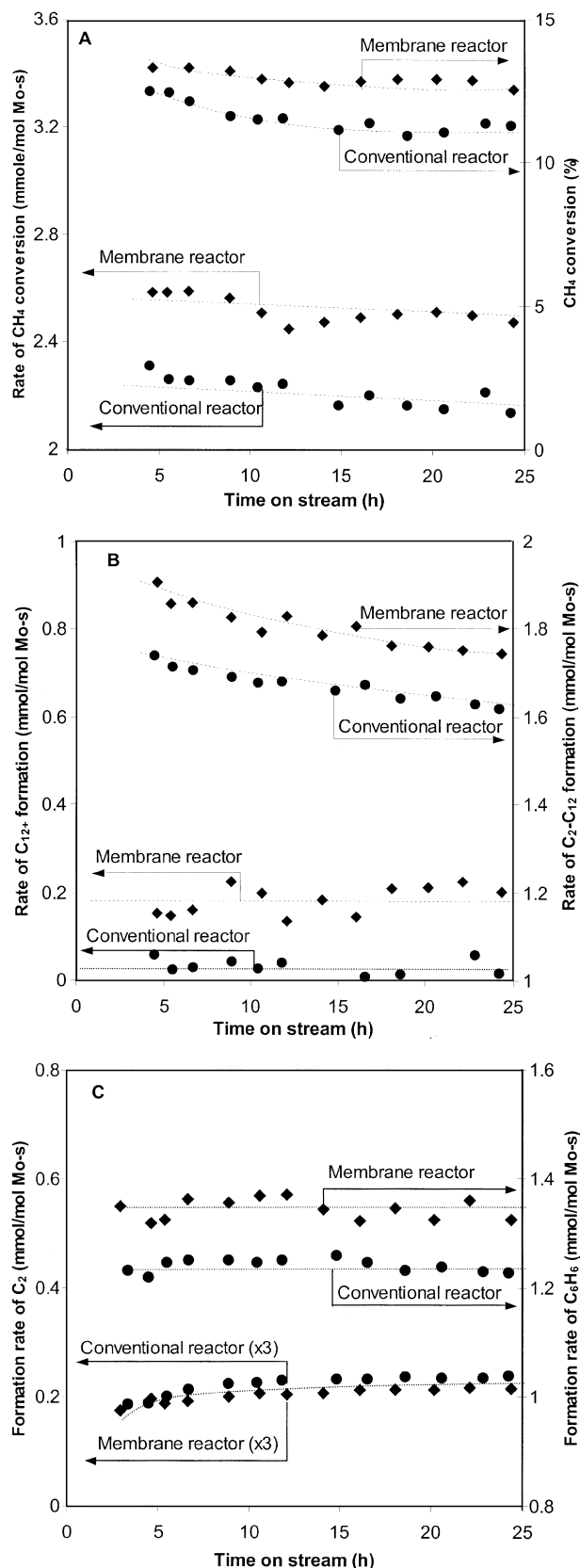


Figure 5. Effects of continuous hydrogen removal on catalytic CH₄ pyrolysis on 4 wt% Mo/H-ZSM5 at 993 K in the presence of 2 kPa CO₂ (85 kPa CH₄; 13 kPa Ar; 780 cm³/g-h). (A) CH₄ conversion rates and CH₄ conversions; (B) C₂–C₁₂ and C₁₂₊ formation rates; (C) C₆H₆ and C₂ formation rates.

rates will require, in turn, new ceramic compositions, more selective microporous membranes, or Pd-based systems with lower cost and higher stability at high temperatures. These requirements have been recently described in detail using kinetic-transport models and simulations [14,15].

4. Conclusions

Mo/H-ZSM5 catalysts and selective H₂ membranes based on supported SrCe_{0.95}Yb_{0.05}O_{3-α} films (~2 μm) were used in order to probe the effects of H₂ removal on the rate and selectivity of CH₄ pyrolysis reactions. Hydrogen removal efficiencies at 950 K were very low (<7%) and CH₄ pyrolysis reaction rates and hydrocarbon selectivities were similar in conventional and membrane reactors. At 993 K, H₂ removal efficiencies were higher (~16%) than at 950 K, as a result of an increase in the mobility of protons within the dense SrCe_{0.95}Yb_{0.05}O_{3-α} films and in the equilibrium H₂ concentrations with increasing temperature. Modest increases in CH₄ conversion rates were observed, but they reflected predominantly an increase in the rate of formation of C₁₂₊ hydrocarbons. H₂ removal also led to slightly higher catalyst deactivation rates. The addition of small amounts of CO₂ to CH₄ reactants markedly decreased deactivation rates in both membrane and conventional reactors and led to a modest increase in CH₄ conversion rates and in the rate of formation of C₂–C₁₂ hydrocarbons in membrane reactors compared with conventional reactors. This study shows that removal of thermodynamic constraints and kinetic inhibition effects can be used to increase CH₄ conversion and hydrocarbon yields in CH₄ pyrolysis reactions. These results also illustrate the need to rigorously describe the effects of H₂ concentration on deactivating side reactions and to develop faster proton conductors in order to render these membrane reactors attractive for commercial practice.

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