

The effects of CO₂, CO and H₂ co-reactants on methane reactions catalyzed by Mo/H-ZSM-5

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The effects of CO₂, CO and H₂ co-reactants on CH₄ pyrolysis reactions catalyzed by Mo/H-ZSM-5 were investigated as a function of reaction temperatures and co-reactant and CH₄ concentrations. Total CH₄ conversion rates were not affected by CO₂ co-reactants, except at high CO₂ pressures, which led to the oxidation of the active MoC_x species, but CH_x intermediates formed in rate-determining C–H bond activation steps increasingly formed CO instead of hydrocarbons as CO₂ concentrations increased. CO formation rates increased with increasing CO₂ partial pressure; all entering CO₂ molecules reacted with CH₄ within the catalyst bed to form two CO molecules at 950–1033 K. In contrast, hydrocarbon formation rates decreased linearly with increasing CO₂ partial pressure and reached undetectable levels at CO₂/CH₄ ratios above 0.075 at 950 K. CO formation continued for a short period of time at these CO₂/CH₄ molar ratios, but then all catalytic activity ceased, apparently as a result of the conversion of active carbide structures to MoO_x. The removal of CO₂ from the CH₄ stream led to gradual catalyst reactivation *via* reduction–carburization processes similar to those observed during the initial activation of MoO_x/H-ZSM-5 precursors in CH₄. The CO₂/CH₄ molar ratios required to inhibit hydrocarbon synthesis were independent of CH₄ pressure because of the first-order kinetic dependencies of both CH₄ and CO₂ activation steps. These ratios increased from 0.075 to 0.143 as reaction temperatures increased from 950 to 1033 K. This temperature dependence reflects higher activation energies for reductant (CH₄) than for oxidant (CO₂) activation, leading to catalyst oxidation at higher relative oxidant concentrations as temperature increases. The scavenging of CH_x intermediates by CO₂-derived species leads also to lower chain growth probabilities and to a significant inhibition of catalyst deactivation *via* oligomerization pathways responsible for the formation of highly unsaturated unreactive deposits. CO co-reactants did not influence the rate or selectivity of CH₄ pyrolysis reactions on Mo/H-ZSM-5; therefore, CO formed during reactions of CO₂/CH₄ mixtures are not responsible for the observed effects of CO₂ on reaction rates and selectivities, or in catalyst deactivation rates during CH₄ reactions. H₂ addition studies showed that H₂ formed during CH₄/CO₂ reactions near the bed inlet led to inhibited catalyst deactivation in downstream catalyst regions, even after CO₂ co-reactants were depleted.

KEY WORDS: CO₂; CO; H₂ co-reactants; methane reactions; Mo/H-ZSM-5 catalyst.

1. Introduction

The direct conversion of natural gas to hydrocarbons, oxygenates or synthesis gas has been widely studied, but only conversion to synthesis gas *via* partial oxidation and autothermal or steam reforming is currently practiced [1–4]. Catalytic pyrolysis of methane using shape-selective microporous materials containing active carbide clusters leads to CH₄ conversions to benzene near those predicted by thermodynamics at relatively low temperatures (800–900 K) [5]. Initial reports using Mo/H-ZSM-5 catalysts were followed by studies on H-ZSM-5 and other zeolites modified by transition metal ions (*e.g.*, Mo, W, V, Fe and Cr) [6–10]. H-SM-5 zeolites modified by Mo or W remain the most active catalysts for this reaction. The exchange, reduction and carburization of MoO_x species during synthesis and catalysis [11–18] and the bifunctional mechanism by which MoC_x and acid sites catalyze methane conversion [11,14,19] have been previously demonstrated.

CH₄ reaction rates, however, decrease with time on stream because strongly adsorbed carbonaceous deposits, such as large unsaturated hydrocarbon residues caused by unrestricted chain growth, form during reactions of CH₄ and block both metal carbide and Brønsted acid sites [9, 20]. Co-reactants, such as O₂, CO and CO₂, can inhibit deactivation and influence reaction rates and selectivities [20–26]. CO₂ addition to CH₄ reactants decreased deactivation rates on Mo/H-ZSM-5 and led to an apparent increase in benzene formation rates after some time on stream [20,23,26]. Our initial studies confirmed these effects of CO₂ on catalyst stability but, in contradiction with these previous reports, we find that CO₂ scavenges also CH₄-derived reaction intermediates and leads to lower pyrolysis rates on Mo/H-ZSM-5. The reported increase in CH₄ pyrolysis rates merely reflects the slower rate of catalyst deactivation when CO₂ co-reactants are present.

In the present study, we examine the details of these CO₂ effects on reaction rate, selectivity, and catalyst stability during CH₄ aromatization on Mo/H-ZSM-5. We show that the kinetic coupling between methane activation and the removal of its CH_x initial products

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via desorption as hydrocarbons or via reaction with CO₂ control the concentration of adsorbed intermediates and the selectivity towards the formation of hydrocarbons, of CO, and of unreactive deposits leading to deactivation. The concurrent formation of CO and of additional H₂ as a result of CO₂ addition (via CO₂ reforming or reverse water gas shift) led us to also examine the kinetic effects of H₂ and CO co-reactants on CH₄ pyrolysis reactions.

2. Experimental methods

2.1. Catalyst synthesis procedures

Mo/H-ZSM-5 (4 wt% Mo) was prepared by thermal treatment of physical mixtures of H-ZSM-5 (Zeolyst International, Si/Al = 15) and MoO₃ powders (Johnson Matthey Electronics, 99.95%) ground together for ~0.1 h using an alumina mortar and pestle [10,11]. This mixture was then placed in a quartz boat held within a resistively heated furnace and the temperature was increased rapidly to 673 K and held for 10 h, and then to 973 K for 0.5 h in 1.67 cm³ s⁻¹ dry air (Praxair, Ultra-high-purity). The samples were then pressed into pellets and crushed to retain agglomerates with 0.25–0.5 mm diameter.

2.2. CH₄ reaction-rate measurements

CH₄ reactions were carried out at 950 K in a quartz tubular reactor (0.11 cm³ s⁻¹, 85 kPa CH₄, 15 kPa Ar). Mo/H-ZSM-5 (0.50 g) was held on top of a porous quartz frit and treated in 20% O₂/He (0.82 cm³ s⁻¹, Airgas, UHP) at 950 K for 0.2 h. Samples were flushed with He (0.67 cm³ s⁻¹, UHP) for 0.3 h and the He stream was then replaced with an 85% CH₄/Ar reactant mixture (0.11 cm³ s⁻¹). After reduction and carburization were complete and the rate of hydrocarbon formation reached a relatively constant value (~3 h), the temperature was increased to the desired value and a co-reactant (CO, CO₂ or H₂) was added to the CH₄ stream. All co-reactants were >99.9% purity (Praxair or Matheson); they were purified further using 13× molecular sieve traps held at ambient temperature. All gases 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 mm × 2 m, Supelco) with a thermal conductivity detector (TCD) to detect H₂, Ar, CO, CH₄, CO₂ and H₂O, and a methyl silicone capillary column (HP-1 0.32 mm × 50 m, HP) with a flame ionization detector (FID) in order to measure C₁–H₁₂ hydrocarbons. CH₄ conversion is reported as the percentage of the entering methane that disappears, calculated using Ar as an unreactive internal standard. This internal standard is required in order to measure

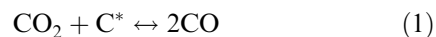
the amount of CH₄ converted to large hydrocarbons or to adsorbed products, neither one of which reaches the gas chromatograph. Selectivities are reported on a carbon basis as the percentage of the converted CH₄ appearing as each detected reaction product. The carbon not present within the measured products is reported as C₁₂₊, and it includes all carbon deposits retained on the catalyst or in the transfer lines (kept at ~423 K). The rate of CO formation from CH₄ was calculated from the CO concentration by assuming it forms via CO₂ reforming (CH₄ + CO₂ = 2CO + 2H₂) and that equimolar amounts of CO form from CH₄ and CO₂. This assumption was confirmed by the finding that CO formation rates were always twice the rate of disappearance of CO₂.

3. Results and discussion

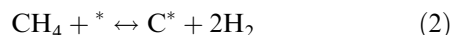
3.1. Effects of CO₂ co-reactants on catalytic CH₄ reactions

CO₂ effects on catalytic CH₄ reactions at 950 K were first examined by adding 3 kPa CO₂ to a reactant mixture containing CH₄ (85 kPa) and Ar (12 kPa) (figures 1 and 2). The rate of CH₄ conversion decreased very slightly when CO₂ was added, suggesting a weak kinetic influence of CO₂ on the rate of CH₄ activation steps (figure 3). The rates of benzene and C₁₂₊ formation and of catalyst deactivation, however, were much lower when CO₂ was present (figure 1). The first-order deactivation rate constant (*k_d*) decreased from 0.04 h⁻¹ to 0.0027 h⁻¹ in the presence of 3 kPa CO₂. In contrast, a previous study [20] reported similar effects of CO₂ on deactivation, but benzene formation rate increased when CO₂ was added to the CH₄ reactants.

CO₂ was not detected in the reactor effluent, indicating its complete conversion to CO within the catalyst bed. CO was formed at about twice the rate of CO₂ introduction, as expected from the complete reaction of each CO₂ fed with one C* atom derived from CH₄ activation steps:



This reaction resembles mechanistically the reverse Boudouard reaction and it is one step in the overall catalytic sequence involved in CH₄–CO₂ reactions to form H₂ and CO. When this step (equation (2)) is coupled kinetically with the step that forms C* from CH₄:



the overall stoichiometry becomes that of the CO₂ reforming of CH₄ (equation (1)). These steps merely denote stoichiometric reactions, without any implications that the elementary steps required to satisfy the stated stoichiometry occur as written above. The substantial absence of H₂O in reaction products and the conversion of CO₂ to form two CO molecules, as

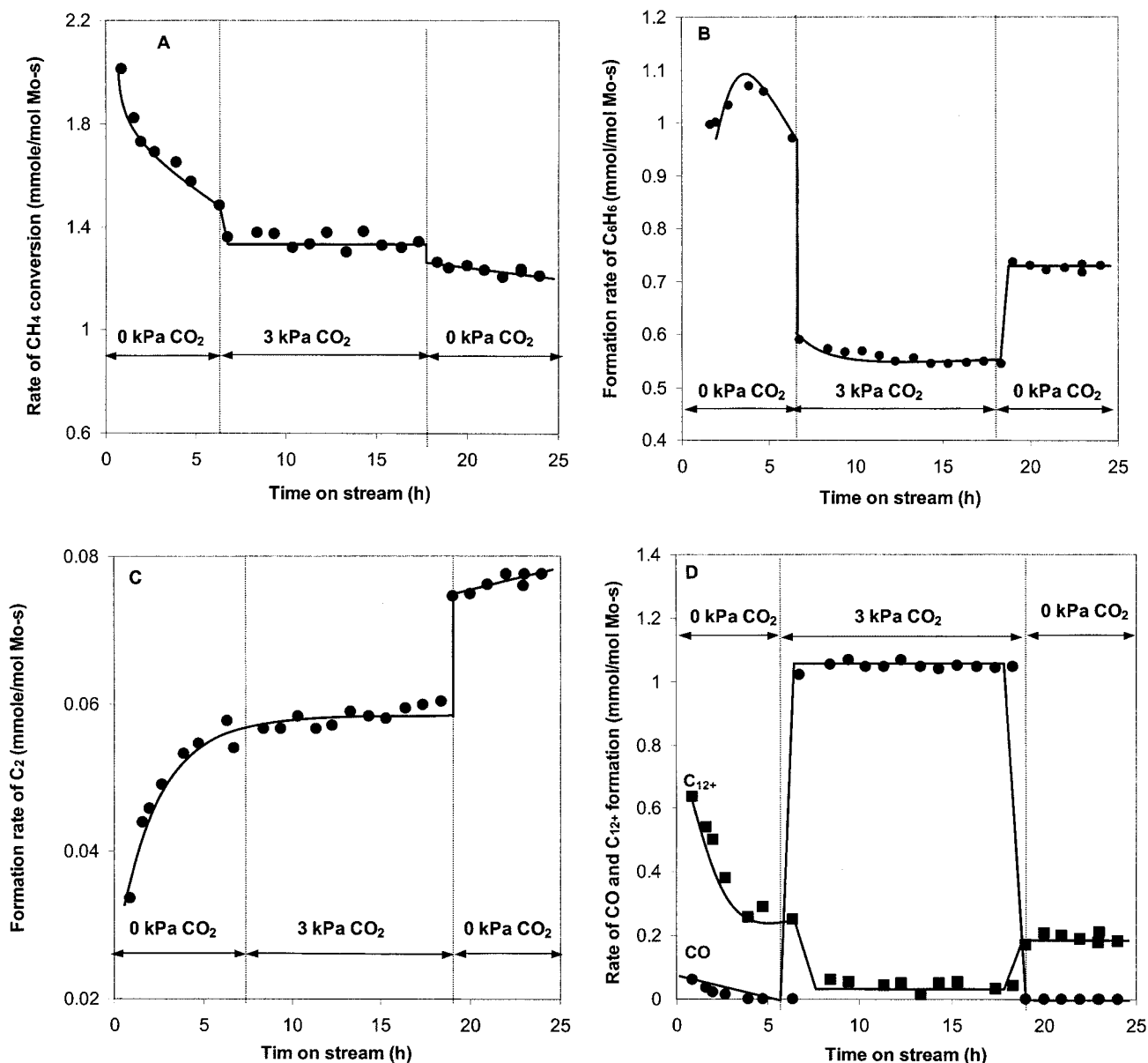


Figure 1. Effects of 3 kPa CO₂ addition on the rates of methane conversion and hydrocarbon formation on 4 wt% Mo/H-ZSM-5 (85 kPa CH₄/12 kPa Ar/3 kPa CO₂, 950 K, 780 cm³/h/g-cat). (A) CH₄ conversion rate; (B) C₆H₆ formation rate; (C) C₂ formation rate; (D) CO and C₁₂₊ formation rates.

also shown previously [26], suggest that steam reforming of CH₄ and reverse water–gas shift reactions do not contribute significantly to the observed products. These findings are consistent with thermodynamic equilibria at the conditions of these experiments. For example, the equilibrium H₂O partial pressure calculated at the condition of these experiments from literature thermodynamic data [27,28] is only 3×10^{-3} kPa.

In contrast to the weak kinetic effect of CO₂ on CH₄ conversion rates, hydrocarbon formation rates (C₆H₆, C₂ and C₁₂₊) decreased markedly when 3 kPa CO₂ was added to CH₄ reactants (figure 1). These weak effects on CH₄ conversion rates reflect a remarkable compensation between an increase in the number of CH₄-derived C* intermediates that appear as CO and a parallel decrease in the number of C* that ultimately

appears within pyrolysis products. The benzene (~43%) and total hydrocarbon (~60%) selectivities (based on CH₄ reactants) are much lower with 3 kPa CO₂ than with CO₂-free reactants (figure 2(A)) (62% and 82%, respectively), but this merely reflects the inclusion of the CO formed from CH₄ in this carbon-based selectivity. When CO is excluded from the methane-derived products and selectivities are reported on a CO-free basis, all hydrocarbons except C₁₂₊ are formed with much higher selectivities when CO₂ (3 kPa) is present (figure 2(B)). Almost no C₁₂₊ formed during CH₄ pyrolysis when CO₂ co-reactants were present. These results clearly show that CO₂ decreases the average molecular weight of CH₄ pyrolysis products; this inhibition of chain growth steps reflects the combined effects of a slightly higher H₂ concentration (as a result of

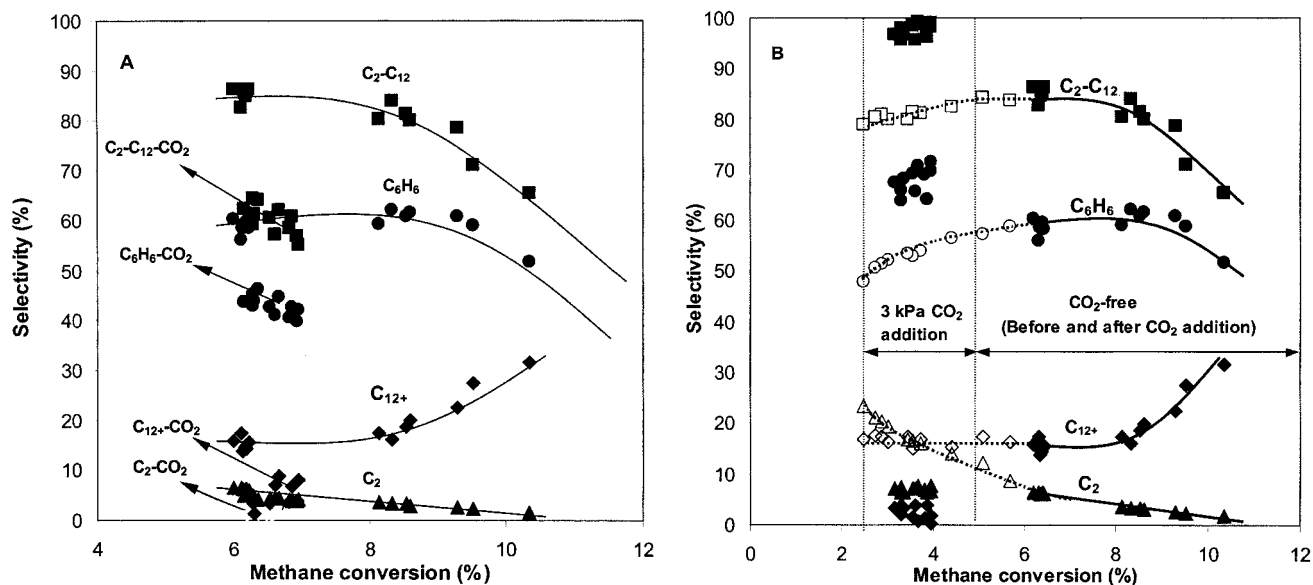


Figure 2. Effects of CO₂ addition on the distribution of hydrocarbon products on 4 wt% Mo/H-ZSM-5 (85 kPa CH₄/12 kPa Ar/3 kPa CO₂, 950 K, 780 cm³/h/g-cat). (A) Selectivities on basis of overall CH₄ conversions; the groups of data points at 6–7% CH₄ with the arrows as labels correspond to the CH₄/CO₂ reactants. The remaining data correspond to pure CH₄ feeds. (B) The selectivities and CH₄ conversions excluding the methane conversion to CO. The open symbols correspond to CO₂-free feeds in a separate low-conversion experiment. The grouped data between 3–4% CH₄ conversion correspond to CH₄/CO₂ feeds.

CO₂–CH₄ reactions) and of lower concentrations of CH_x^{*} and C^{*} chain growth intermediates (as a result of their reactions with CO₂ to form CO).

The effects of CO₂ are shown over a wider partial pressure range (0–6 kPa) in table 1 and in figure 3 for CH₄ reactions on Mo/H-ZSM-5 at 950 K. CO₂ pressures between 0 and 3 kPa did not influence steady-state methane conversion rates (1.3–1.4 mmol/mol Mo-s),

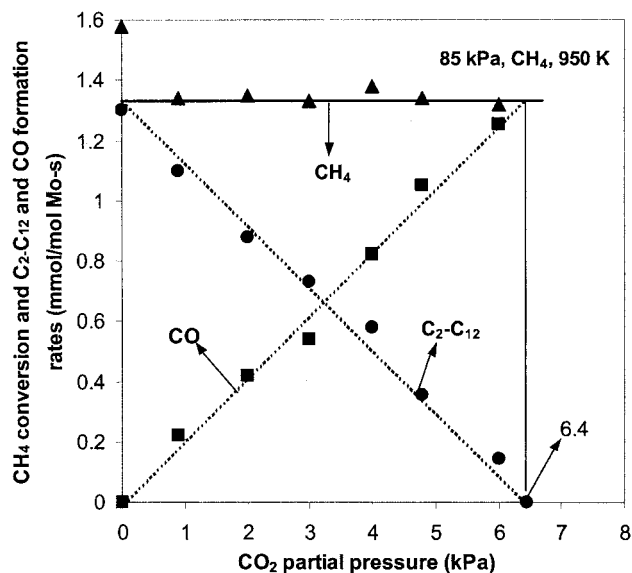


Figure 3. Dependence of rates of CH₄ conversion, and C₂-C₁₂ and CO formation on CO₂ pressures on 4 wt% Mo/H-ZSM-5 (85 kPa CH₄/15 kPa Ar + CO₂), 950 K, 780 cm³/h/g-cat). Note: CO formation rates reported here are those from the CH₄ reactant only. Reaction rates with pure CH₄ are average values over the first 5 h. Reaction rates for CH₄/CO₂ experiments are average values over 20 h experiments.

but all hydrocarbon formation rates decreased markedly. In every case, this decrease in pyrolysis rates was compensated exactly by a parallel increase in the rate of CH₄ conversion to CO. Deactivation rate constants (k_d) decreased monotonically with increasing CO₂ concentration (table 1). CO formation rates increased proportionally with CO₂ partial pressure to a value equal to twice the rate of introduction of CO₂, as expected from complete CO₂ conversion with the stoichiometry of CO₂ reforming. At CO₂ pressures of ~6 kPa, the rate of CH₄ pyrolysis became almost undetectable (table 1 and figure 3). At these conditions, the rate of methane conversion (1.32 mmol/mol Mo-s) remained initially at about one-half the rate of CO formation (2.53 mmol/mol Mo-s). These initial reaction rates, however, decreased sharply within ~1 h and no formation of CO or hydrocarbons or depletion of the CH₄ or CO₂ co-reactants were detected after this time.

After all reactions ceased with these CH₄–CO₂ mixtures, CO₂ was removed from the reactant stream. This led to the complete recovery of the CH₄ conversion and hydrocarbon formation rates initially observed with pure CH₄ reactants. This reactivation process occurred after an initial induction period (~0.5 h), within which oxygen atoms were removed as CO and H₂O from the deactivated catalysts. This process is similar in both stoichiometry and dynamics to that initially observed during activation of MoO_x/H-ZSM-5 precursors in the early stages of CH₄ reactions [10–14,16,21]. These data suggest that the cessation of catalytic reactions at high CO₂ partial pressures is caused by the stoichiometric conversion of active MoC_x to inactive MoO_x species when CO₂ levels exceed 6 kPa during CH₄ reactions at

Table 1
Effects of CO₂ partial pressure and reaction temperature on the CH₄ reaction rates on 4 wt% Mo/H-ZSM-5^a

T (K)	CO ₂ partial pressure (kPa)	Reaction rates (mmol/mol Mo-s)				k_d^c (h ⁻¹ × 10 ⁻³)
		CH ₄	C ₂ -C ₁₂	CO	C ₁₂₊ × 10 ³	
950 ^b	0	1.58	1.41	0	23	35
	1	1.34	1.10	0.22	9.5	4.7
	3	1.33	0.73	0.54	2.4	2.2
	6 ^d	1.32	0.14	1.27	—	—
1033 ^c	0	3.00	2.36	0	64	69
	2	2.85	2.21	0.46	18	42
	6	2.85	1.43	1.31	10	3.5
	10	2.84	0.63	2.38	2.0	2.6

^a Reaction conditions: 0.5 g cat., 85 kPa CH₄/15 kPa (Ar + CO₂), 950 K, 780 ml/h/g-cat. The CO formation rate reported here is that formed from CH₄ only.

^b Reaction rates without CO₂ are those before the introduction of CO₂. Reaction rates with CO₂ are average rates at steady state.

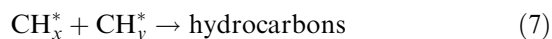
^c Reaction rates without CO₂ are those before the introduction of CO₂. Reaction rates with 2 kPa CO₂ are maximum values at initial reaction stage. Reaction rates with 6 and 10 kPa CO₂ are average rates at steady state.

^d Data were taken at the initial stage (~2 h) after 6 kPa addition and after that the catalytic activation decreased rapidly to zero. —: Not detectable.

^e First-order deactivation rate constant for total methane conversion rates.

950 K. At these CO₂ concentrations, the relative rates at which carbon intermediates (C*) form *via* CH₄ dissociation and chemisorbed oxygen species (O*) form *via* CO₂ dissociation cause O* chemical potentials to reach levels that render MoC_x species thermodynamically unstable with respect to MoO_x. The subsequent removal of CO₂ restores catalytic activity *via* reduction and carburization processes identical to those that lead to the initial activation of MoO_x/H-ZSM-5 precursors during CH₄ reactions at high temperatures [10–14,16, 21].

These oxidation–reduction cycles caused by changes in the relative concentrations of the reductant (CH₄) and the oxidant (CO₂) and their catalytic consequences resemble those reported recently reported for bulk Mo carbides during CH₄ reforming reactions [29]. As in our study, dissociative adsorption of CO₂ led to O* species that react with lattice or surface C*, leaving behind a vacancy (*) in a stoichiometric carbide. These vacancies can then react with CH₄ to re-form C*, or with CO₂ to form O*. The relative rates of these two reactions will establish the stoichiometry of near-surface regions and the respective chemical potentials of *, C* and O*. These, in turn, will determine the identity of the thermodynamically stable bulk phase (oxide, carbide or metal). The stoichiometry of these reactions can be described by steps (3)–(7) below:



Our rate measurements on Mo/H-ZSM-5 at 950 K and 85 kPa CH₄ show that CO₂ pressures of ~6 kPa lead to O* chemical potentials required for the conversion of active carbide species, in the form of MoC_x clusters, into inactive Mo oxides. Clearly, this threshold CO₂ value will depend also on the CH₄ pressure and on the reaction temperature, because both variables will influence the relative rates of O* formation (from CO₂; step (3)) and removal (using CH₄ in steps (4) and (5)). We note that H* can also be used for the net removal of O*, but the prevalent thermodynamics leads to the ultimate reversal of this reaction and to very low rates of water formation at the conditions of our experiments.

The effects of CO₂ partial pressures on CH₄ conversion rates and on the rates of formation of hydrocarbons and CO at 950 K are shown in figure 3. CH₄ conversion rates were not influenced by the presence of CO₂. The rates of CO formation from CH₄ increased linearly with CO₂ pressure and its value equals the rate at which CO is formed from the CO₂ co-reactant. Hydrocarbon formation rates decreased linearly with increasing CO₂ pressure, reaching undetectable levels at ~6 kPa CO₂, at which point catalytic activity for reactions of CH₄ with CO₂ becomes undetectable after a short period of time. The total rate of CH₄ activation is unaffected by the presence of CO₂, suggesting that the number of sites available for C–H bond activation is not influenced by CO₂ pressures below 6 kPa. The fate of CH_x* species formed from CH₄, however, depends on the coupling of these CH₄ activation steps with the removal of CH_x* *via* either oligomerization to form the initial C₂ pyrolysis products or *via* reaction with CO₂ to form CO. Thus, as long as the O* concentration remains below the threshold value required to form Mo oxides, this kinetic

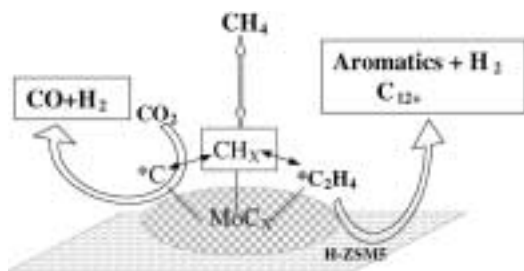


Figure 4. Schematic diagram of CO_2 scavenging pathways during CH_4 reactions on $\text{MoC}_x/\text{H-ZSM-5}$.

coupling merely influences the selectivity of CH_4 conversion reactions, and not their rate, on Mo carbides. This kinetic coupling is depicted schematically in figure 4. This proposal is also consistent with the observed effect of CO_2 on deactivation. CO_2 reacts with surface carbon species so as to decrease their steady-state concentration and the probability that they will oligomerize to form unreactive forms of polymeric carbon species. These lower surface concentrations of these chain growth species lead also to the lower average product molecular weight observed when CO_2 is added to the CH_4 reactant stream.

Similar effects were observed when CO_2 co-reactants were added at lower CH_4 pressures (40 kPa) and 950 K (figure 5). Hydrocarbon formation rates are proportional to CH_4 partial pressures for CO_2 -free reactants. CO_2 partial pressures required to suppress hydrocarbon formation and to cause catalyst oxidation and loss of all catalytic activity are ~ 3.2 kPa for 40 kPa CH_4 reactant pressures, instead of the value of ~ 6 kPa required at higher CH_4 pressures (85 kPa). Thus, it appears that the relevant variable in determining the state of the Mo species, and thus their catalytic properties, is the reductant to oxidant ratio (CH_4/CO_2), consistent with the expected linear dependence of both CH_4 and CO_2 dissociation rates on the partial pressures of the respective reactants at these high temperatures.

Figures 3 and 6 contrast the effects of CO_2 addition to a CH_4 stream (85 kPa) at 950 and 1033 K, respectively, on Mo/H-ZSM-5. The effects of CO_2 are qualitatively similar at these two temperatures. Initial CH_4 conversion rates without CO_2 addition are significantly higher at 1033 K (3.0 mmol/mol Mo-s) than at 950 K (1.58 mmol/mol Mo-s) and the presence of CO_2 leads to a proportional decrease in hydrocarbon formation rates at both temperatures. The CO_2 partial pressure required to suppress hydrocarbon formation at 1033 K, however, was significantly higher than at 950 K. Stable catalytic rates were obtained at CO_2 partial pressures (6 kPa) that led to undetectable hydrocarbon or CO formation rates at 950 K (table 1). Thus, it appears that the balance between CH_4 and CO_2 reactions is achieved at lower CH_4/CO_2 ratios as reaction temperatures increase. This suggests that CH_4 activation proceeds *via* pathways

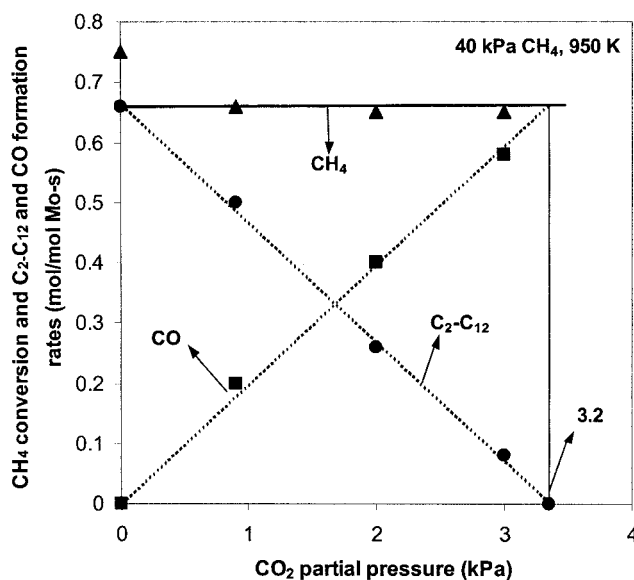


Figure 5. Dependence of rates of CH_4 conversion and $\text{C}_2\text{-C}_{12}$ and CO formation on CO_2 pressure on 4 wt% Mo/H-ZSM-5 (40 kPa CH_4 /60 kPa ($\text{Ar} + \text{CO}_2$), 950 K, 780 $\text{cm}^3/\text{min/g-cat}$). Note: CO formation rates reported here are those from the CH_4 reactant only. Reaction rates with pure CH_4 are average values over the first 5 h. Reaction rates for CH_4/CO_2 experiments are average values over 20 h experiments.

with higher activation energy than corresponding CO_2 dissociation steps.

Table 1 shows first-order deactivation rate constants during reactions of CH_4 (85 kPa) at 950 and 1033 K in the presence of CO_2 at various partial pressures. Deactivation rate constants and the CO_2 partial pressure required in order to inhibit deactivation are both

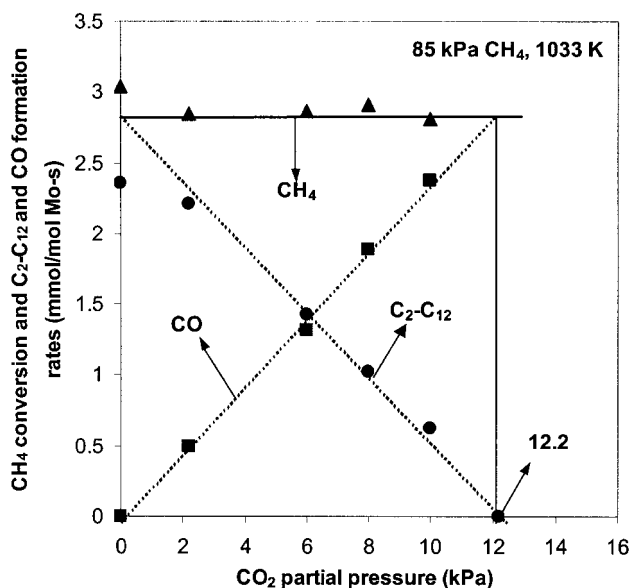


Figure 6. Dependence of rates of CH_4 conversion and $\text{C}_2\text{-C}_{12}$ and CO formation on CO_2 pressure on 4 wt% Mo/H-ZSM-5 (85 kPa CH_4 /15 kPa ($\text{Ar} + \text{CO}_2$), 1033 K, 780 $\text{cm}^3/\text{min/g-cat}$). Note: CO formation rates reported here are those from the CH_4 reactant only. Reaction rates with pure CH_4 are average values over the first 5 h. Reaction rates for CH_4/CO_2 experiments are average values over 20 h experiments.

higher at 1033 K than at 950 K. This appears to reflect the stronger temperature dependence of the C* formation rates (from CH₄) relative to that for CO₂ activation steps, which leads in turn to higher C* concentrations for a given CH₄/CO₂ ratio as temperature increases. As a result, the CO₂ pressures required to reach a given O* concentration increase with increasing temperature. These reaction and deactivation rate data at higher temperatures confirm that previous reports of CH₄ conversion rate enhancements with CO₂ co-reactants [20] are not kinetic in nature, but arise instead from the inhibition of deactivation pathways caused by the lower C* concentrations prevalent when CO₂ is present in the reactant mixture.

Figure 7 shows CH₄ conversion rates and hydrocarbon and CO (from CH₄) formation rates as a function of reaction temperature using CH₄-CO₂ mixtures (85 kPa CH₄, 6 kPa CO₂). CH₄ conversion and hydrocarbon formation rates increased with temperature, but CO formation rates were unaffected, because CO formation is limited by the inlet molar rate of the CO₂ co-reactant, which is entirely consumed within the catalyst bed at each reaction temperature. Near the bed inlet, the predominant reaction uses CO₂ to remove the CH_x fragments of CH₄ activation steps (figure 4), while CH_x species condense into desorbable hydrocarbons as CO₂ concentrations decrease along the catalyst bed. At higher CO₂ pressures, CO₂ is depleted nearer the end of the bed than at lower CO₂ pressures and the fraction of the catalyst bed involved in hydrocarbon formation becomes smaller; this leads to the observed decrease in CH₄ pyrolysis rates with increasing CO₂ pressures (figures 3, 5 and 6). At

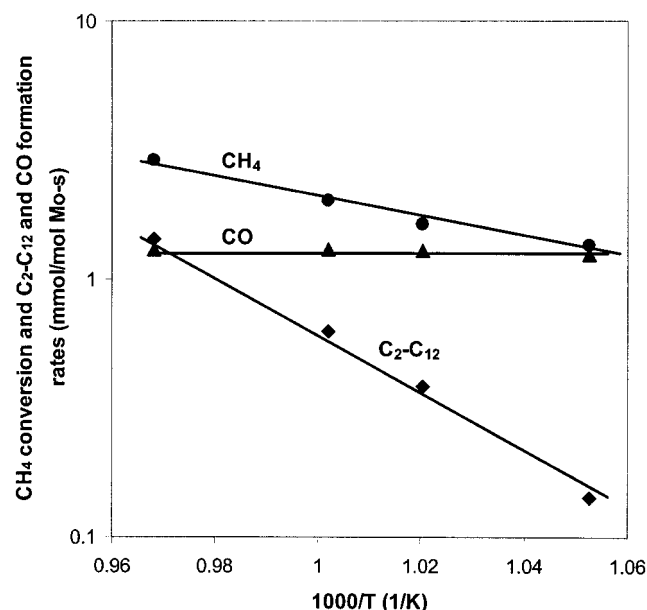


Figure 7. Dependence of rates of CH₄ conversion, and C₂-C₁₂ and CO formation on reaction temperature on 4 wt% Mo/H-ZSM-5 (85 kPa CH₄/9 kPa Ar/6 kPa CO₂, 780 cm³/h/g-cat). Note: CO formation rates reported here are those from the CH₄ reactant only. Reaction rates for CH₄/CO₂ experiments are average values over 20 h experiments.

950 K, only CO₂ reforming occurs as CO₂ pressures reach values of ~6 kPa (figure 3); at higher temperatures, higher CO₂ pressures are required in order to maintain nonzero CO₂ concentrations at the bed exit and to inhibit pyrolysis reactions.

Even though the catalyst bed regions near the exit do not contain any remaining CO₂, deactivation is inhibited even from those regions, which form exclusively hydrocarbons. This leads to very low deactivation rates in the presence of CO₂ co-reactants. These effects and the inhibition of pyrolysis reaction rates with CO₂ addition suggest that the H₂ or CO products formed near the bed inlet by the complete reaction of CO₂ with CH₄ can also influence reaction and carbon deposition rates during methane pyrolysis on Mo/H-ZSM-5. Therefore, we examine in the next section the effects of H₂ and CO co-reactants on the rate and selectivity of CH₄ reactions on Mo/H-ZSM-5.

3.2. Effects of CO and H₂ co-reactants on catalytic CH₄ reactions on Mo/H-ZSM-5

Figure 8 shows the effect of CO (1 kPa) on CH₄ conversion and on C₂, C₆H₆ and C₁₂₊ formation rates. CO did not influence any of these rates or the rate of catalyst deactivation rates and no conversion of CO was detected. Higher CO pressures (3 kPa) led to identical results. Thus, CO acts essentially as an inert during CH₄ reactions on Mo/H-ZSM-5 at 950 K. This is not unexpected, because oxygen atoms in CO can only be used to produce another CO molecule or to form water; the latter pathways are thermodynamically unfavored at these reaction conditions and any water formed would react with the predominant CH₄ reactants to re-form CO and H₂. These results are not consistent

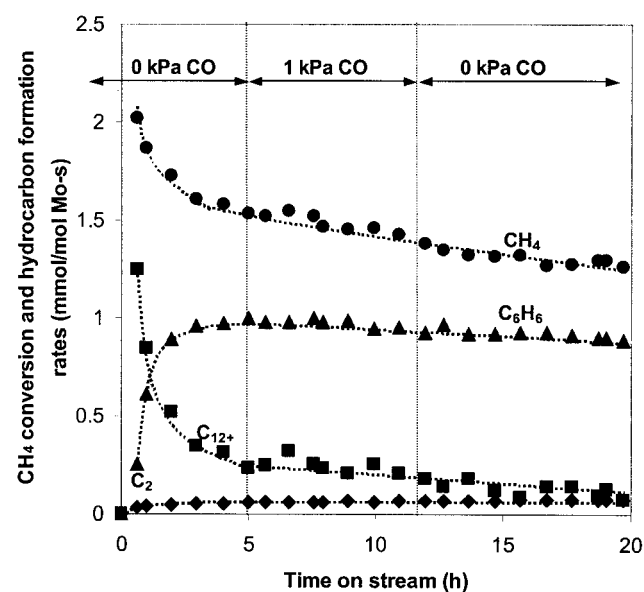


Figure 8. Effects of 1 kPa CO addition on CH₄ aromatization on 4 wt% Mo/H-ZSM-5 (85 kPa CH₄/14 kPa Ar/1 kPa CO, 950 K, 780 cm³/h/g-cat).

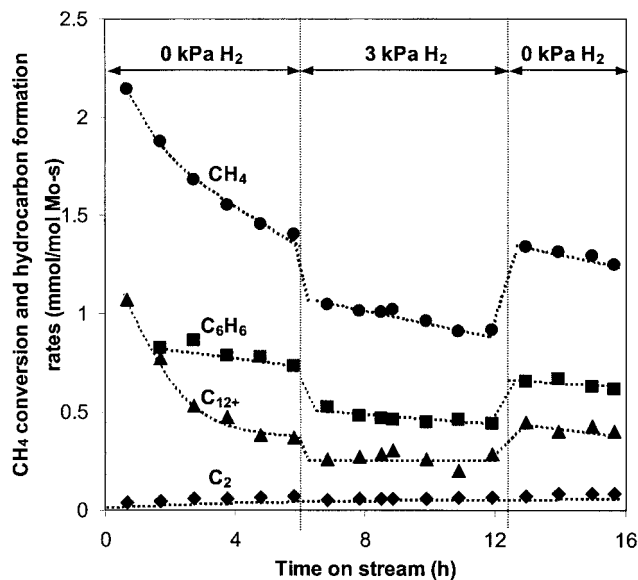


Figure 9. Effects of 3 kPa H₂ addition on CH₄ aromatization on 4 wt% Mo/H-ZSM-5 (85 kPa CH₄/12 kPa Ar/3 kPa H₂, 950 K, 780 cm³/h/g-cat).

with a recent report of CO effects on methane pyrolysis reactions [20]. In this report, the addition of 1.8–12% CO to CH₄ on 3 wt% Mo/H-ZSM-5 at 973 K led to a marked increase in the rates of both CH₄ conversion and of hydrocarbon formation and to significant inhibition of catalyst deactivation. The reasons for these differences are not clear at this time. We find, however, no reasonable mechanism or even reaction stoichiometry for the reported effects of CO on methane rates or catalyst stability or any feasible pathways for the participation of CO in hydrocarbon formation or in the removal of any CH₄-derived carbonaceous deposits.

Figure 9 shows the rates of CH₄ conversion and of C₂, C₆H₆ and C₁₂₊ formation for reactions of CH₄ at 950 K in the presence of H₂. CH₄ conversion decreased from 1.44 to 1.06 mmol/mol Mo-s and C₆H₆ formation rates decreased from 0.82 to 0.57 mmol/mol Mo-s, when 3 kPa H₂ was added to a stream containing 85 kPa CH₄. C₁₂₊ formation rates were also lower when H₂ was added. All reaction rates returned to values near those before H₂ addition when H₂ was removed from the CH₄ reactant stream. First-order deactivation rate constants (k_d) were slightly lower when H₂ was present (0.031 h⁻¹ versus 0.039 h⁻¹). The product selectivity was not strongly influenced by H₂, once the differences in CH₄ conversion shown in figure 10 were taken into account. These weak effects of H₂ on methane conversion rates and selectivities and on catalyst stability suggest that the effects of CO₂ reported above reflect for the most part the scavenging effects of CO₂ on CH₄-derived CH_x^{*} intermediates involved in chain growth.

The inhibition of CH₄ pyrolysis and C₆H₆ formation rate by H₂ is consistent with the expected effects of reverse reactions calculated from thermodynamic data

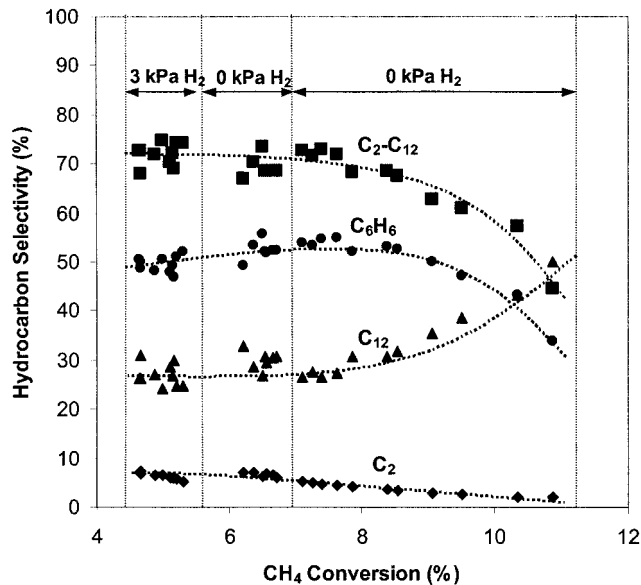
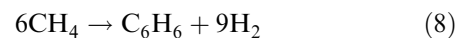


Figure 10. Effects of 3 kPa H₂ addition on hydrocarbon selectivity on 4 wt% Mo/H-ZSM-5 (85 kPa CH₄/12 kPa Ar/3 kPa H₂, 959 K, 780 cm³/h/g-cat).

[30]. As reaction (8) approaches equilibrium



the net rate of CH₄ pyrolysis reactions is given by

$$r_{\text{net}} = k_f C_{\text{CH}_4} (1 - \eta) = r_f (1 - \eta) \quad (9)$$

where the approach to equilibrium is rigorously taken into account by η

$$\eta = \frac{[\text{C}_6\text{H}_6] \cdot [\text{H}_2]^9}{[\text{CH}_4]^6} \frac{1}{K_{\text{eq}}} \quad (10)$$

which approaches zero values far away from equilibrium and the value of unity at equilibrium.

In equation (9), r_{net} is the measured rate of benzene formation and r_f is the forward reaction rate, measurable only far away from equilibrium. The equilibrium constant K_{eq} for this reaction is $4.8 \times 10^{-10} \text{ atm}^4$ at 950 K [28]. Using the exit concentration of reactants and products in the absence of added H₂, we obtain a value of η of 0.86, while the value after H₂ addition (3 kPa) is nearly 0.90. These values are in qualitative agreement with the observed decrease in the rate of benzene formation from 0.65–0.85 mmol/mol Mo-s before the addition of 3 kPa H₂ to 0.45–0.52 mmol/mol Mo-s after H₂ addition, suggesting that the addition of H₂ merely decreases the thermodynamic driving force for methane conversion to aromatics.

Thus, we conclude that CO₂ decreases CH₄ pyrolysis rates by depleting CH₄ derived predominantly near the bed inlet, while the H₂ formed inhibits the formation of higher-molecular-weight hydrocarbons and of deactivating deposits in the latter stages of the bed, where CO₂ may no longer be present and CH₄ pyrolysis is the predominant reaction.

4. Conclusions

CO₂ co-reactants increased catalyst stability and decreased product molecular weight during reactions of CH₄ on Mo/H-ZSM-5 by scavenging of CH_x species formed in CH₄ activation steps and by forming H₂, which inhibits deactivation and hydrocarbon synthesis rates. Total CH₄ conversion rates were not affected by CO₂ co-reactants, which did not influence the rate of CH₄ activation, but only the fate of the CH_x intermediates formed in this reaction. The linear decrease in hydrocarbon synthesis rates with increasing CO₂ pressure was balanced exactly by a concurrent increase in the rate of CH₄ conversion to CO, *via* reactions with CO₂. As CO₂ is depleted, pyrolysis reactions increasingly occur, in a gradual shift in the CH_x removal pathways, from reactions with CO₂ to form CO, to chain growth steps that form desorbable hydrocarbons. The amount of CO₂ required to inhibit pyrolysis reaction increases with increasing temperature, because of the faster depletion of CO₂ reactants as temperature increases. The H₂ formed near the bed inlet is responsible in part for the lower deactivation and pyrolysis rates in the rest of the catalyst bed. The CO concurrently formed by CO₂ reforming near the bed inlet does not influence CH₄ conversion to hydrocarbons. The relative rates of reforming and pyrolysis reactions and the tendency of active MoC_x species to form inactive MoO_y structures depend only on the CO₂/CH₄ molar ratio, because of the first order of both CO₂ and CH₄ activation reactions, but the CH₄ activation steps proceed with a higher activation energy than corresponding CO₂ activation reactions; as a result a higher CO₂/CH₄ ratio is required for the inhibition of pyrolysis reactions and for the conversion of active carbide structures to MoO_x as the reaction temperature increases.

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