

# The effects of CO<sub>2</sub>, CO and H<sub>2</sub> co-reactants on methane reactions catalyzed by Mo/H-ZSM-5

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The effects of CO<sub>2</sub>, CO and H<sub>2</sub> co-reactants on CH<sub>4</sub> pyrolysis reactions catalyzed by Mo/H-ZSM-5 were investigated as a function of reaction temperatures and co-reactant and CH<sub>4</sub> concentrations. Total CH<sub>4</sub> conversion rates were not affected by CO<sub>2</sub> co-reactants, except at high CO<sub>2</sub> pressures, which led to the oxidation of the active MoC<sub>x</sub> species, but CH<sub>x</sub> intermediates formed in rate-determining C–H bond activation steps increasingly formed CO instead of hydrocarbons as CO<sub>2</sub> concentrations increased. CO formation rates increased with increasing CO<sub>2</sub> partial pressure; all entering CO<sub>2</sub> molecules reacted with CH<sub>4</sub> within the catalyst bed to form two CO molecules at 950–1033 K. In contrast, hydrocarbon formation rates decreased linearly with increasing CO<sub>2</sub> partial pressure and reached undetectable levels at CO<sub>2</sub>/CH<sub>4</sub> ratios above 0.075 at 950 K. CO formation continued for a short period of time at these CO<sub>2</sub>/CH<sub>4</sub> molar ratios, but then all catalytic activity ceased, apparently as a result of the conversion of active carbide structures to MoO<sub>x</sub>. The removal of CO<sub>2</sub> from the CH<sub>4</sub> stream led to gradual catalyst reactivation *via* reduction–carburization processes similar to those observed during the initial activation of MoO<sub>x</sub>/H-ZSM-5 precursors in CH<sub>4</sub>. The CO<sub>2</sub>/CH<sub>4</sub> molar ratios required to inhibit hydrocarbon synthesis were independent of CH<sub>4</sub> pressure because of the first-order kinetic dependencies of both CH<sub>4</sub> and CO<sub>2</sub> 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 (CH<sub>4</sub>) than for oxidant (CO<sub>2</sub>) activation, leading to catalyst oxidation at higher relative oxidant concentrations as temperature increases. The scavenging of CH<sub>x</sub> intermediates by CO<sub>2</sub>-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 CH<sub>4</sub> pyrolysis reactions on Mo/H-ZSM-5; therefore, CO formed during reactions of CO<sub>2</sub>/CH<sub>4</sub> mixtures are not responsible for the observed effects of CO<sub>2</sub> on reaction rates and selectivities, or in catalyst deactivation rates during CH<sub>4</sub> reactions. H<sub>2</sub> addition studies showed that H<sub>2</sub> formed during CH<sub>4</sub>/CO<sub>2</sub> reactions near the bed inlet led to inhibited catalyst deactivation in downstream catalyst regions, even after CO<sub>2</sub> co-reactants were depleted.

**KEY WORDS:** CO<sub>2</sub>; CO; H<sub>2</sub> 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 CH<sub>4</sub> 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-ZSM-5 zeolites modified by Mo or W remain the most active catalysts for this reaction. The exchange, reduction and carburization of MoO<sub>x</sub> species during synthesis and catalysis [11–18] and the bifunctional mechanism by which MoC<sub>x</sub> and acid sites catalyze methane conversion [11,14,19] have been previously demonstrated.

CH<sub>4</sub> 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 CH<sub>4</sub> and block both metal carbide and Brønsted acid sites [9, 20]. Co-reactants, such as O<sub>2</sub>, CO and CO<sub>2</sub>, can inhibit deactivation and influence reaction rates and selectivities [20–26]. CO<sub>2</sub> addition to CH<sub>4</sub> 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 CO<sub>2</sub> on catalyst stability but, in contradiction with these previous reports, we find that CO<sub>2</sub> scavenges also CH<sub>4</sub>-derived reaction intermediates and leads to lower pyrolysis rates on Mo/H-ZSM-5. The reported increase in CH<sub>4</sub> pyrolysis rates merely reflects the slower rate of catalyst deactivation when CO<sub>2</sub> co-reactants are present.

In the present study, we examine the details of these CO<sub>2</sub> effects on reaction rate, selectivity, and catalyst stability during CH<sub>4</sub> aromatization on Mo/H-ZSM-5. We show that the kinetic coupling between methane activation and the removal of its CH<sub>x</sub> initial products

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via desorption as hydrocarbons or via reaction with CO<sub>2</sub> 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 H<sub>2</sub> as a result of CO<sub>2</sub> addition (via CO<sub>2</sub> reforming or reverse water gas shift) led us to also examine the kinetic effects of H<sub>2</sub> and CO co-reactants on CH<sub>4</sub> 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 MoO<sub>3</sub> 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 cm<sup>3</sup> s<sup>-1</sup> 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. CH<sub>4</sub> reaction-rate measurements

CH<sub>4</sub> reactions were carried out at 950 K in a quartz tubular reactor (0.11 cm<sup>3</sup> s<sup>-1</sup>, 85 kPa CH<sub>4</sub>, 15 kPa Ar). Mo/H-ZSM-5 (0.50 g) was held on top of a porous quartz frit and treated in 20% O<sub>2</sub>/He (0.82 cm<sup>3</sup> s<sup>-1</sup>, Airgas, UHP) at 950 K for 0.2 h. Samples were flushed with He (0.67 cm<sup>3</sup> s<sup>-1</sup>, UHP) for 0.3 h and the He stream was then replaced with an 85% CH<sub>4</sub>/Ar reactant mixture (0.11 cm<sup>3</sup> s<sup>-1</sup>). 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, CO<sub>2</sub> or H<sub>2</sub>) was added to the CH<sub>4</sub> 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 H<sub>2</sub>, Ar, CO, CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>O, and a methyl silicone capillary column (HP-1 0.32 mm × 50 m, HP) with a flame ionization detector (FID) in order to measure C<sub>1</sub>–H<sub>12</sub> hydrocarbons. CH<sub>4</sub> 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

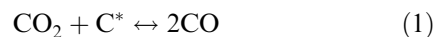
the amount of CH<sub>4</sub> converted to large hydrocarbons or to adsorbed products, neither one of which reaches the gas chromatograph. Selectivities are reported on a carbon basis as the percentage of the converted CH<sub>4</sub> appearing as each detected reaction product. The carbon not present within the measured products is reported as C<sub>12+</sub>, 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 CH<sub>4</sub> was calculated from the CO concentration by assuming it forms via CO<sub>2</sub> reforming (CH<sub>4</sub> + CO<sub>2</sub> = 2CO + 2H<sub>2</sub>) and that equimolar amounts of CO form from CH<sub>4</sub> and CO<sub>2</sub>. This assumption was confirmed by the finding that CO formation rates were always twice the rate of disappearance of CO<sub>2</sub>.

## 3. Results and discussion

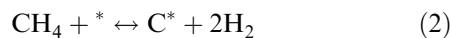
### 3.1. Effects of CO<sub>2</sub> co-reactants on catalytic CH<sub>4</sub> reactions

CO<sub>2</sub> effects on catalytic CH<sub>4</sub> reactions at 950 K were first examined by adding 3 kPa CO<sub>2</sub> to a reactant mixture containing CH<sub>4</sub> (85 kPa) and Ar (12 kPa) (figures 1 and 2). The rate of CH<sub>4</sub> conversion decreased very slightly when CO<sub>2</sub> was added, suggesting a weak kinetic influence of CO<sub>2</sub> on the rate of CH<sub>4</sub> activation steps (figure 3). The rates of benzene and C<sub>12+</sub> formation and of catalyst deactivation, however, were much lower when CO<sub>2</sub> was present (figure 1). The first-order deactivation rate constant (*k<sub>d</sub>*) decreased from 0.04 h<sup>-1</sup> to 0.0027 h<sup>-1</sup> in the presence of 3 kPa CO<sub>2</sub>. In contrast, a previous study [20] reported similar effects of CO<sub>2</sub> on deactivation, but benzene formation rate increased when CO<sub>2</sub> was added to the CH<sub>4</sub> reactants.

CO<sub>2</sub> 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 CO<sub>2</sub> introduction, as expected from the complete reaction of each CO<sub>2</sub> fed with one C\* atom derived from CH<sub>4</sub> activation steps:



This reaction resembles mechanistically the reverse Boudouard reaction and it is one step in the overall catalytic sequence involved in CH<sub>4</sub>–CO<sub>2</sub> reactions to form H<sub>2</sub> and CO. When this step (equation (2)) is coupled kinetically with the step that forms C\* from CH<sub>4</sub>:



the overall stoichiometry becomes that of the CO<sub>2</sub> reforming of CH<sub>4</sub> (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 H<sub>2</sub>O in reaction products and the conversion of CO<sub>2</sub> to form two CO molecules, as

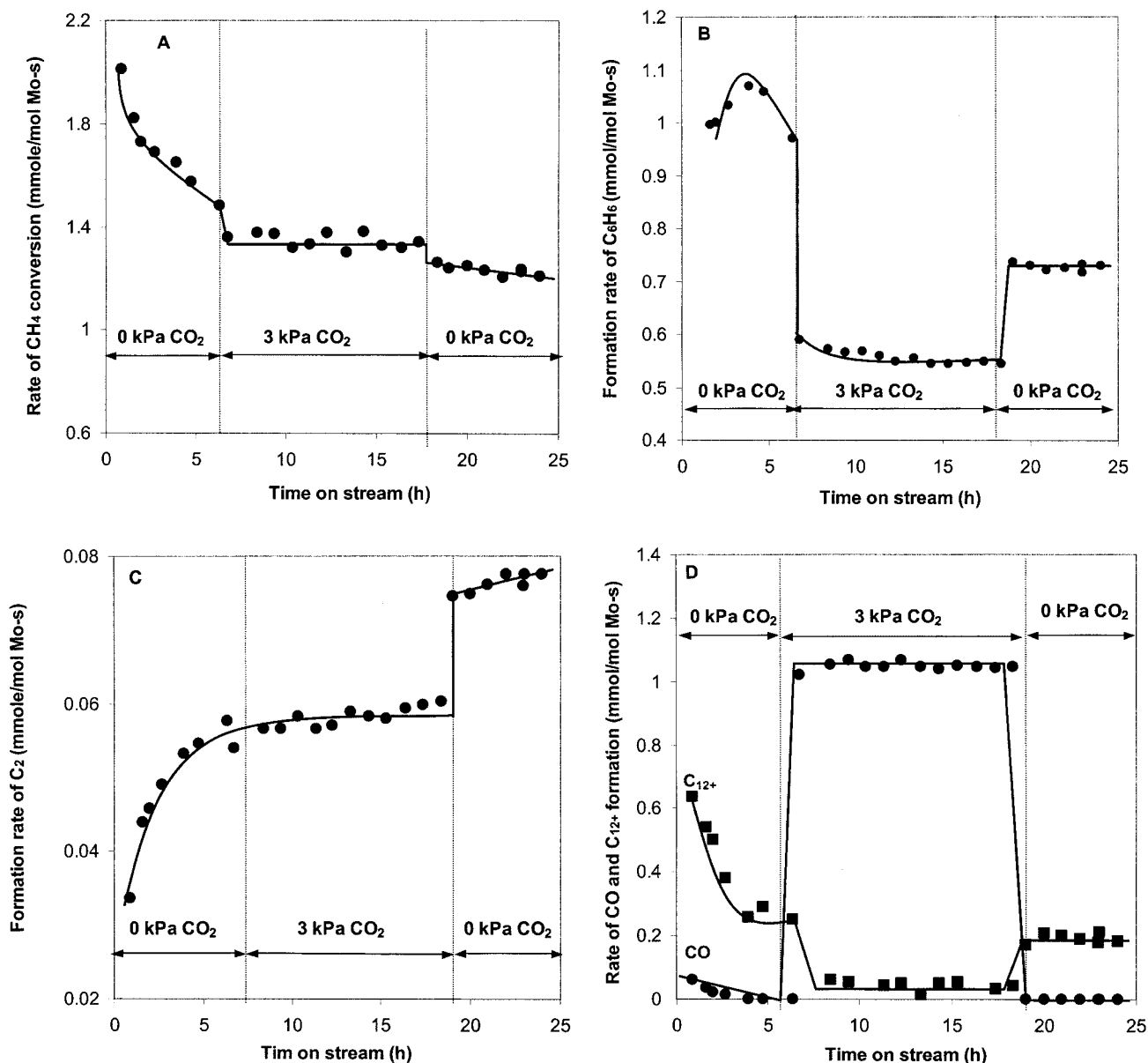


Figure 1. Effects of 3 kPa CO<sub>2</sub> addition on the rates of methane conversion and hydrocarbon formation on 4 wt% Mo/H-ZSM-5 (85 kPa CH<sub>4</sub>/12 kPa Ar/3 kPa CO<sub>2</sub>, 950 K, 780 cm<sup>3</sup>/h/g-cat). (A) CH<sub>4</sub> conversion rate; (B) C<sub>6</sub>H<sub>6</sub> formation rate; (C) C<sub>2</sub> formation rate; (D) CO and C<sub>12+</sub> formation rates.

also shown previously [26], suggest that steam reforming of CH<sub>4</sub> 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 H<sub>2</sub>O partial pressure calculated at the condition of these experiments from literature thermodynamic data [27,28] is only  $3 \times 10^{-3}$  kPa.

In contrast to the weak kinetic effect of CO<sub>2</sub> on CH<sub>4</sub> conversion rates, hydrocarbon formation rates (C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub> and C<sub>12+</sub>) decreased markedly when 3 kPa CO<sub>2</sub> was added to CH<sub>4</sub> reactants (figure 1). These weak effects on CH<sub>4</sub> conversion rates reflect a remarkable compensation between an increase in the number of CH<sub>4</sub>-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 CH<sub>4</sub> reactants) are much lower with 3 kPa CO<sub>2</sub> than with CO<sub>2</sub>-free reactants (figure 2(A)) (62% and 82%, respectively), but this merely reflects the inclusion of the CO formed from CH<sub>4</sub> 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 C<sub>12+</sub> are formed with much higher selectivities when CO<sub>2</sub> (3 kPa) is present (figure 2(B)). Almost no C<sub>12+</sub> formed during CH<sub>4</sub> pyrolysis when CO<sub>2</sub> co-reactants were present. These results clearly show that CO<sub>2</sub> decreases the average molecular weight of CH<sub>4</sub> pyrolysis products; this inhibition of chain growth steps reflects the combined effects of a slightly higher H<sub>2</sub> concentration (as a result of

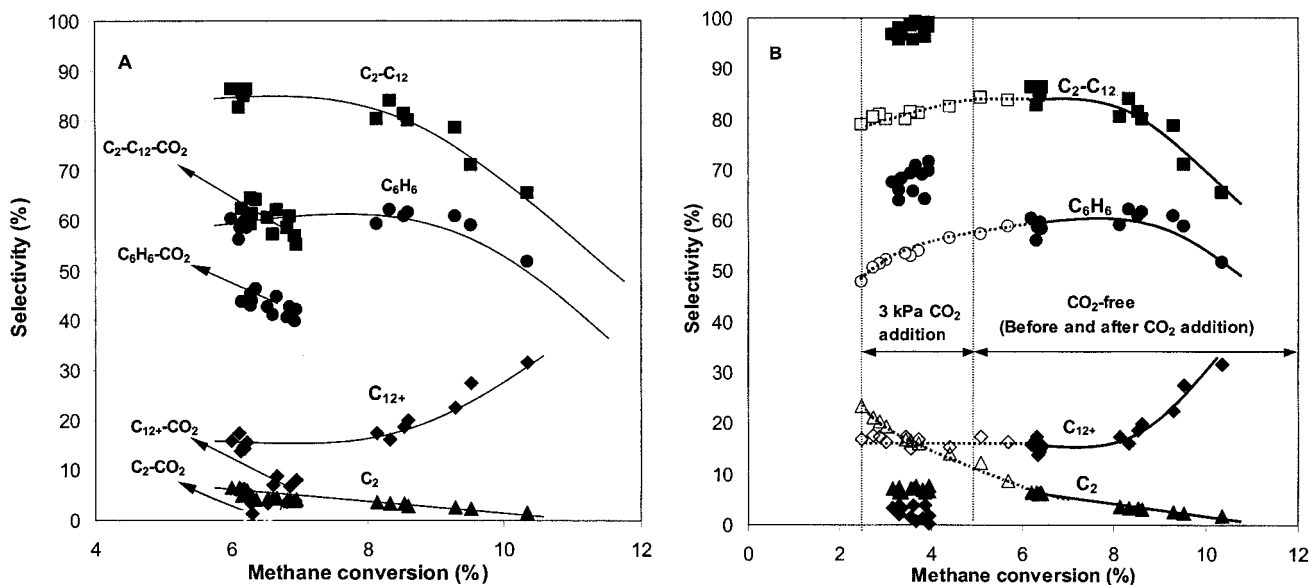


Figure 2. Effects of CO<sub>2</sub> addition on the distribution of hydrocarbon products on 4 wt% Mo/H-ZSM-5 (85 kPa CH<sub>4</sub>/12 kPa Ar/3 kPa CO<sub>2</sub>, 950 K, 780 cm<sup>3</sup>/h/g-cat). (A) Selectivities on basis of overall CH<sub>4</sub> conversions; the groups of data points at 6–7% CH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

CO<sub>2</sub>–CH<sub>4</sub> reactions) and of lower concentrations of CH<sub>x</sub><sup>\*</sup> and C<sup>\*</sup> chain growth intermediates (as a result of their reactions with CO<sub>2</sub> to form CO).

The effects of CO<sub>2</sub> are shown over a wider partial pressure range (0–6 kPa) in table 1 and in figure 3 for CH<sub>4</sub> reactions on Mo/H-ZSM-5 at 950 K. CO<sub>2</sub> pressures between 0 and 3 kPa did not influence steady-state methane conversion rates (1.3–1.4 mmol/mol Mo-s),

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 CH<sub>4</sub> conversion to CO. Deactivation rate constants ( $k_d$ ) decreased monotonically with increasing CO<sub>2</sub> concentration (table 1). CO formation rates increased proportionally with CO<sub>2</sub> partial pressure to a value equal to twice the rate of introduction of CO<sub>2</sub>, as expected from complete CO<sub>2</sub> reforming. At CO<sub>2</sub> pressures of ~6 kPa, the rate of CH<sub>4</sub> 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 CH<sub>4</sub> or CO<sub>2</sub> co-reactants were detected after this time.

After all reactions ceased with these CH<sub>4</sub>–CO<sub>2</sub> mixtures, CO<sub>2</sub> was removed from the reactant stream. This led to the complete recovery of the CH<sub>4</sub> conversion and hydrocarbon formation rates initially observed with pure CH<sub>4</sub> reactants. This reactivation process occurred after an initial induction period (~0.5 h), within which oxygen atoms were removed as CO and H<sub>2</sub>O from the deactivated catalysts. This process is similar in both stoichiometry and dynamics to that initially observed during activation of MoO<sub>x</sub>/H-ZSM-5 precursors in the early stages of CH<sub>4</sub> reactions [10–14,16,21]. These data suggest that the cessation of catalytic reactions at high CO<sub>2</sub> partial pressures is caused by the stoichiometric conversion of active MoC<sub>x</sub> to inactive MoO<sub>x</sub> species when CO<sub>2</sub> levels exceed 6 kPa during CH<sub>4</sub> reactions at

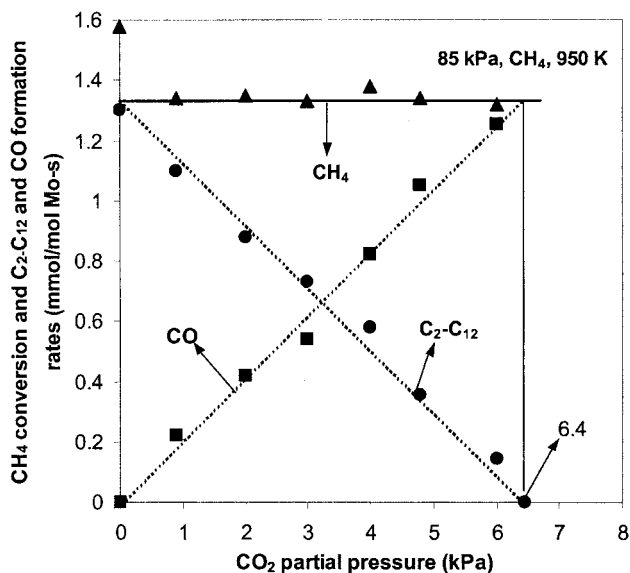


Figure 3. Dependence of rates of CH<sub>4</sub> conversion, and C<sub>2</sub>–C<sub>12</sub> and CO formation on CO<sub>2</sub> pressures on 4 wt% Mo/H-ZSM-5 (85 kPa CH<sub>4</sub>/15 kPa (Ar + CO<sub>2</sub>), 950 K, 780 cm<sup>3</sup>/h/g-cat). Note: CO formation rates reported here are those from the CH<sub>4</sub> reactant only. Reaction rates with pure CH<sub>4</sub> are average values over the first 5 h. Reaction rates for CH<sub>4</sub>/CO<sub>2</sub> experiments are average values over 20 h experiments.

Table 1  
Effects of CO<sub>2</sub> partial pressure and reaction temperature on the CH<sub>4</sub> reaction rates on 4 wt% Mo/H-ZSM-5<sup>a</sup>

T (K)	CO <sub>2</sub> partial pressure (kPa)	Reaction rates (mmol/mol Mo-s)				$k_d^c$ (h <sup>-1</sup> × 10 <sup>-3</sup> )
		CH <sub>4</sub>	C <sub>2</sub> -C <sub>12</sub>	CO	C <sub>12+</sub> × 10 <sup>3</sup>	
950 <sup>b</sup>	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 <sup>d</sup>	1.32	0.14	1.27	–	–
1033 <sup>c</sup>	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

<sup>a</sup> Reaction conditions: 0.5 g cat., 85 kPa CH<sub>4</sub>/15 kPa (Ar + CO<sub>2</sub>), 950 K, 780 ml/h/g-cat. The CO formation rate reported here is that formed from CH<sub>4</sub> only.

<sup>b</sup> Reaction rates without CO<sub>2</sub> are those before the introduction of CO<sub>2</sub>. Reaction rates with CO<sub>2</sub> are average rates at steady state.

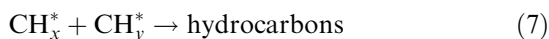
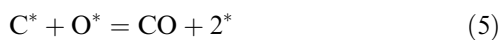
<sup>c</sup> Reaction rates without CO<sub>2</sub> are those before the introduction of CO<sub>2</sub>. Reaction rates with 2 kPa CO<sub>2</sub> are maximum values at initial reaction stage. Reaction rates with 6 and 10 kPa CO<sub>2</sub> are average rates at steady state.

<sup>d</sup> 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.

<sup>e</sup> First-order deactivation rate constant for total methane conversion rates.

950 K. At these CO<sub>2</sub> concentrations, the relative rates at which carbon intermediates (C\*) form *via* CH<sub>4</sub> dissociation and chemisorbed oxygen species (O\*) form *via* CO<sub>2</sub> dissociation cause O\* chemical potentials to reach levels that render MoC<sub>x</sub> species thermodynamically unstable with respect to MoO<sub>x</sub>. The subsequent removal of CO<sub>2</sub> restores catalytic activity *via* reduction and carburization processes identical to those that lead to the initial activation of MoO<sub>x</sub>/H-ZSM-5 precursors during CH<sub>4</sub> reactions at high temperatures [10–14,16, 21].

These oxidation–reduction cycles caused by changes in the relative concentrations of the reductant (CH<sub>4</sub>) and the oxidant (CO<sub>2</sub>) and their catalytic consequences resemble those reported recently reported for bulk Mo carbides during CH<sub>4</sub> reforming reactions [29]. As in our study, dissociative adsorption of CO<sub>2</sub> 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 CH<sub>4</sub> to re-form C\*, or with CO<sub>2</sub> 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 CH<sub>4</sub> show that CO<sub>2</sub> pressures of ~6 kPa lead to O\* chemical potentials required for the conversion of active carbide species, in the form of MoC<sub>x</sub> clusters, into inactive Mo oxides. Clearly, this threshold CO<sub>2</sub> value will depend also on the CH<sub>4</sub> pressure and on the reaction temperature, because both variables will influence the relative rates of O\* formation (from CO<sub>2</sub>; step (3)) and removal (using CH<sub>4</sub> 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 CO<sub>2</sub> partial pressures on CH<sub>4</sub> conversion rates and on the rates of formation of hydrocarbons and CO at 950 K are shown in figure 3. CH<sub>4</sub> conversion rates were not influenced by the presence of CO<sub>2</sub>. The rates of CO formation from CH<sub>4</sub> increased linearly with CO<sub>2</sub> pressure and its value equals the rate at which CO is formed from the CO<sub>2</sub> co-reactant. Hydrocarbon formation rates decreased linearly with increasing CO<sub>2</sub> pressure, reaching undetectable levels at ~6 kPa CO<sub>2</sub>, at which point catalytic activity for reactions of CH<sub>4</sub> with CO<sub>2</sub> becomes undetectable after a short period of time. The total rate of CH<sub>4</sub> activation is unaffected by the presence of CO<sub>2</sub>, suggesting that the number of sites available for C–H bond activation is not influenced by CO<sub>2</sub> pressures below 6 kPa. The fate of CH<sub>x</sub>\* species formed from CH<sub>4</sub>, however, depends on the coupling of these CH<sub>4</sub> activation steps with the removal of CH<sub>x</sub>\* *via* either oligomerization to form the initial C<sub>2</sub> pyrolysis products or *via* reaction with CO<sub>2</sub> to form CO. Thus, as long as the O\* concentration remains below the threshold value required to form Mo oxides, this kinetic

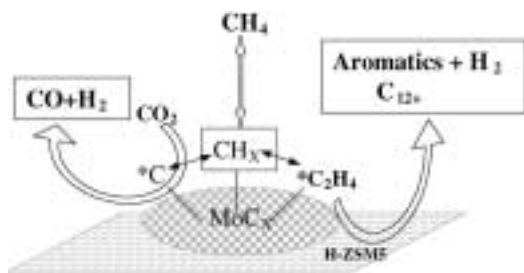


Figure 4. Schematic diagram of CO<sub>2</sub> scavenging pathways during CH<sub>4</sub> reactions on MoC<sub>x</sub>/H-ZSM-5.

coupling merely influences the selectivity of CH<sub>4</sub> 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<sub>2</sub> on deactivation. CO<sub>2</sub> 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<sub>2</sub> is added to the CH<sub>4</sub> reactant stream.

Similar effects were observed when CO<sub>2</sub> co-reactants were added at lower CH<sub>4</sub> pressures (40 kPa) and 950 K (figure 5). Hydrocarbon formation rates are proportional to CH<sub>4</sub> partial pressures for CO<sub>2</sub>-free reactants. CO<sub>2</sub> 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<sub>4</sub> reactant pressures, instead of the value of ~6 kPa required at higher CH<sub>4</sub> 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<sub>4</sub>/CO<sub>2</sub>), consistent with the expected linear dependence of both CH<sub>4</sub> and CO<sub>2</sub> dissociation rates on the partial pressures of the respective reactants at these high temperatures.

Figures 3 and 6 contrast the effects of CO<sub>2</sub> addition to a CH<sub>4</sub> stream (85 kPa) at 950 and 1033 K, respectively, on Mo/H-ZSM-5. The effects of CO<sub>2</sub> are qualitatively similar at these two temperatures. Initial CH<sub>4</sub> conversion rates without CO<sub>2</sub> 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<sub>2</sub> leads to a proportional decrease in hydrocarbon formation rates at both temperatures. The CO<sub>2</sub> 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<sub>2</sub> 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<sub>4</sub> and CO<sub>2</sub> reactions is achieved at lower CH<sub>4</sub>/CO<sub>2</sub> ratios as reaction temperatures increase. This suggests that CH<sub>4</sub> activation proceeds *via* pathways

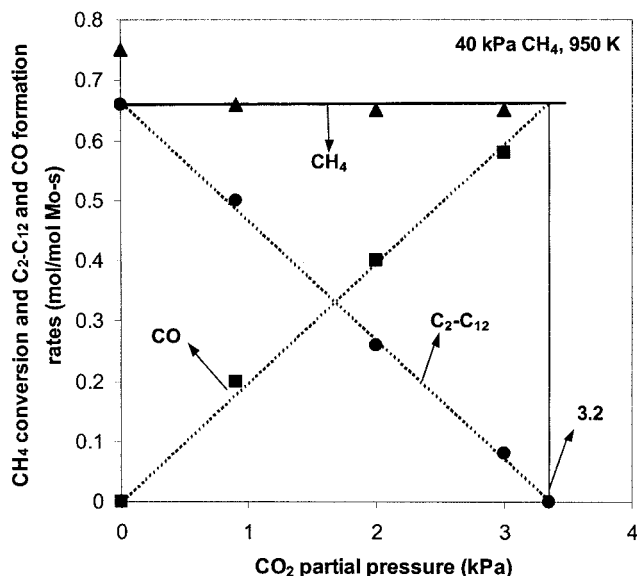


Figure 5. Dependence of rates of CH<sub>4</sub> conversion and C<sub>2</sub>-C<sub>12</sub> and CO formation on CO<sub>2</sub> pressure on 4 wt% Mo/H-ZSM-5 (40 kPa CH<sub>4</sub>/60 kPa (Ar + CO<sub>2</sub>), 950 K, 780 cm<sup>3</sup>/min/g-cat). Note: CO formation rates reported here are those from the CH<sub>4</sub> reactant only. Reaction rates with pure CH<sub>4</sub> are average values over the first 5 h. Reaction rates for CH<sub>4</sub>/CO<sub>2</sub> experiments are average values over 20 h experiments.

with higher activation energy than corresponding CO<sub>2</sub> dissociation steps.

Table 1 shows first-order deactivation rate constants during reactions of CH<sub>4</sub> (85 kPa) at 950 and 1033 K in the presence of CO<sub>2</sub> at various partial pressures. Deactivation rate constants and the CO<sub>2</sub> partial pressure required in order to inhibit deactivation are both

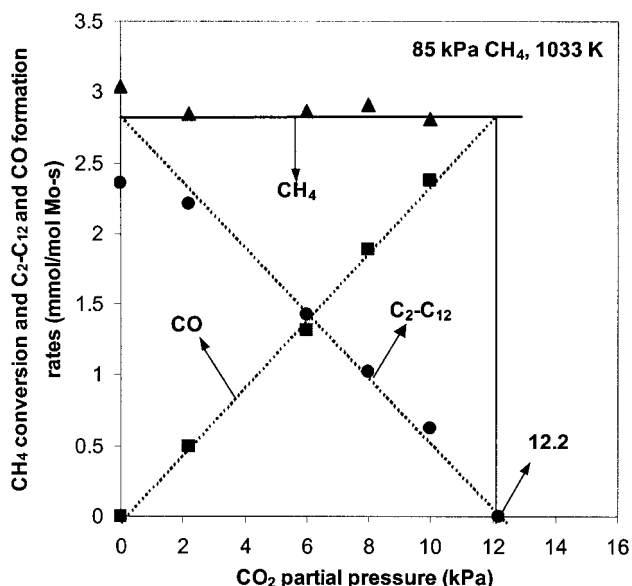


Figure 6. Dependence of rates of CH<sub>4</sub> conversion and C<sub>2</sub>-C<sub>12</sub> and CO formation on CO<sub>2</sub> pressure on 4 wt% Mo/H-ZSM-5 (85 kPa CH<sub>4</sub>/15 kPa (Ar + CO<sub>2</sub>), 1033 K, 780 cm<sup>3</sup>/h/g-cat). Note: CO formation rates reported here are those from the CH<sub>4</sub> reactant only. Reaction rates with pure CH<sub>4</sub> are average values over the first 5 h. Reaction rates for CH<sub>4</sub>/CO<sub>2</sub> 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 CH<sub>4</sub>) relative to that for CO<sub>2</sub> activation steps, which leads in turn to higher C\* concentrations for a given CH<sub>4</sub>/CO<sub>2</sub> ratio as temperature increases. As a result, the CO<sub>2</sub> 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 CH<sub>4</sub> conversion rate enhancements with CO<sub>2</sub> 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 CO<sub>2</sub> is present in the reactant mixture.

Figure 7 shows CH<sub>4</sub> conversion rates and hydrocarbon and CO (from CH<sub>4</sub>) formation rates as a function of reaction temperature using CH<sub>4</sub>-CO<sub>2</sub> mixtures (85 kPa CH<sub>4</sub>, 6 kPa CO<sub>2</sub>). CH<sub>4</sub> 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 CO<sub>2</sub> co-reactant, which is entirely consumed within the catalyst bed at each reaction temperature. Near the bed inlet, the predominant reaction uses CO<sub>2</sub> to remove the CH<sub>x</sub> fragments of CH<sub>4</sub> activation steps (figure 4), while CH<sub>x</sub> species condense into desorbable hydrocarbons as CO<sub>2</sub> concentrations decrease along the catalyst bed. At higher CO<sub>2</sub> pressures, CO<sub>2</sub> is depleted nearer the end of the bed than at lower CO<sub>2</sub> pressures and the fraction of the catalyst bed involved in hydrocarbon formation becomes smaller; this leads to the observed decrease in CH<sub>4</sub> pyrolysis rates with increasing CO<sub>2</sub> pressures (figures 3, 5 and 6). At

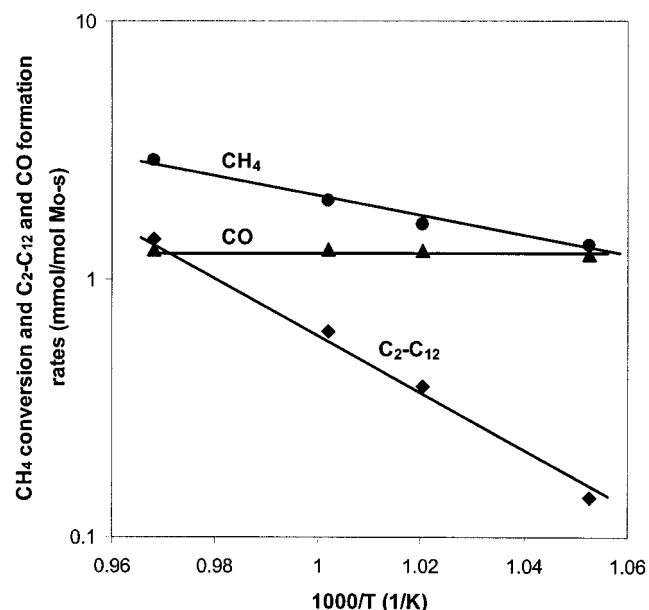


Figure 7. Dependence of rates of CH<sub>4</sub> conversion, and C<sub>2</sub>-C<sub>12</sub> and CO formation on reaction temperature on 4wt% Mo/H-ZSM-5 (85 kPa CH<sub>4</sub>/9 kPa Ar/6 kPa CO<sub>2</sub>, 780 cm<sup>3</sup>/h/g-cat). Note: CO formation rates reported here are those from the CH<sub>4</sub> reactant only. Reaction rates for CH<sub>4</sub>/CO<sub>2</sub> experiments are average values over 20 h experiments.

950 K, only CO<sub>2</sub> reforming occurs as CO<sub>2</sub> pressures reach values of ~6 kPa (figure 3); at higher temperatures, higher CO<sub>2</sub> pressures are required in order to maintain nonzero CO<sub>2</sub> concentrations at the bed exit and to inhibit pyrolysis reactions.

Even though the catalyst bed regions near the exit do not contain any remaining CO<sub>2</sub>, deactivation is inhibited even from those regions, which form exclusively hydrocarbons. This leads to very low deactivation rates in the presence of CO<sub>2</sub> co-reactants. These effects and the inhibition of pyrolysis reaction rates with CO<sub>2</sub> addition suggest that the H<sub>2</sub> or CO products formed near the bed inlet by the complete reaction of CO<sub>2</sub> with CH<sub>4</sub> 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 H<sub>2</sub> and CO co-reactants on the rate and selectivity of CH<sub>4</sub> reactions on Mo/H-ZSM-5.

### 3.2. Effects of CO and H<sub>2</sub> co-reactants on catalytic CH<sub>4</sub> reactions on Mo/H-ZSM-5

Figure 8 shows the effect of CO (1 kPa) on CH<sub>4</sub> conversion and on C<sub>2</sub>, C<sub>6</sub>H<sub>6</sub> and C<sub>12+</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> reactants to re-form CO and H<sub>2</sub>. These results are not consistent

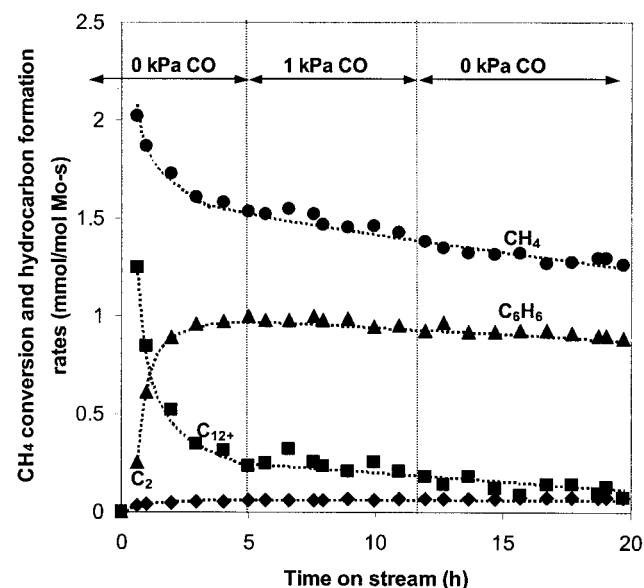


Figure 8. Effects of 1 kPa CO addition on CH<sub>4</sub> aromatization on 4wt% Mo/H-ZSM-5 (85 kPa CH<sub>4</sub>/14 kPa Ar/1 kPa CO, 950 K, 780 cm<sup>3</sup>/h/g-cat).

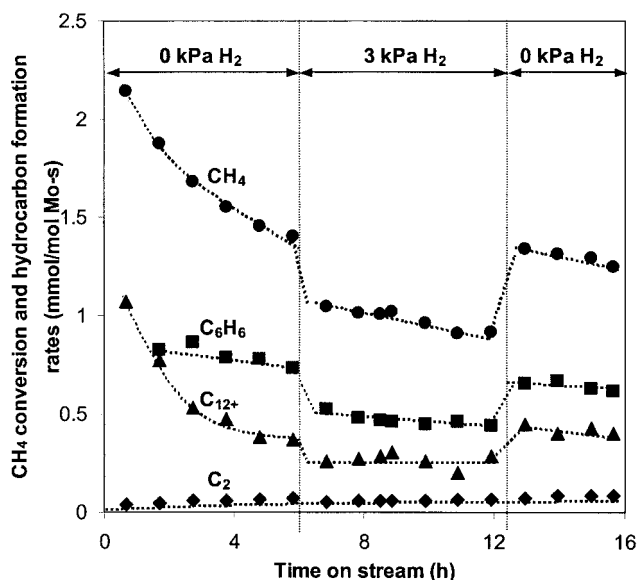


Figure 9. Effects of 3 kPa H<sub>2</sub> addition on CH<sub>4</sub> aromatization on 4 wt% Mo/H-ZSM-5 (85 kPa CH<sub>4</sub>/12 kPa Ar/3 kPa H<sub>2</sub>, 950 K, 780 cm<sup>3</sup>/h/g-cat).

with a recent report of CO effects on methane pyrolysis reactions [20]. In this report, the addition of 1.8–12% CO to CH<sub>4</sub> on 3 wt% Mo/H-ZSM-5 at 973 K led to a marked increase in the rates of both CH<sub>4</sub> 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 CH<sub>4</sub>-derived carbonaceous deposits.

Figure 9 shows the rates of CH<sub>4</sub> conversion and of C<sub>2</sub>, C<sub>6</sub>H<sub>6</sub> and C<sub>12+</sub> formation for reactions of CH<sub>4</sub> at 950 K in the presence of H<sub>2</sub>. CH<sub>4</sub> conversion decreased from 1.44 to 1.06 mmol/mol Mo-s and C<sub>6</sub>H<sub>6</sub> formation rates decreased from 0.82 to 0.57 mmol/mol Mo-s, when 3 kPa H<sub>2</sub> was added to a stream containing 85 kPa CH<sub>4</sub>. C<sub>12+</sub> formation rates were also lower when H<sub>2</sub> was added. All reaction rates returned to values near those before H<sub>2</sub> addition when H<sub>2</sub> was removed from the CH<sub>4</sub> reactant stream. First-order deactivation rate constants ( $k_d$ ) were slightly lower when H<sub>2</sub> was present (0.031 h<sup>-1</sup> versus 0.039 h<sup>-1</sup>). The product selectivity was not strongly influenced by H<sub>2</sub>, once the differences in CH<sub>4</sub> conversion shown in figure 10 were taken into account. These weak effects of H<sub>2</sub> on methane conversion rates and selectivities and on catalyst stability suggest that the effects of CO<sub>2</sub> reported above reflect for the most part the scavenging effects of CO<sub>2</sub> on CH<sub>4</sub>-derived CH<sub>x</sub><sup>\*</sup> intermediates involved in chain growth.

The inhibition of CH<sub>4</sub> pyrolysis and C<sub>6</sub>H<sub>6</sub> formation rate by H<sub>2</sub> is consistent with the expected effects of reverse reactions calculated from thermodynamic data

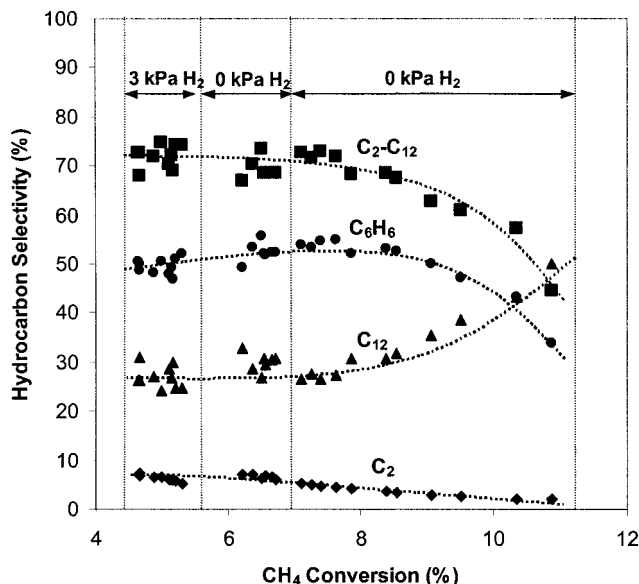
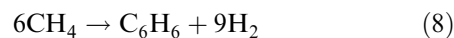


Figure 10. Effects of 3 kPa H<sub>2</sub> addition on hydrocarbon selectivity on 4 wt% Mo/H-ZSM-5 (85 kPa CH<sub>4</sub>/12 kPa Ar/3 kPa H<sub>2</sub>, 959 K, 780 cm<sup>3</sup>/h/g-cat).

[30]. As reaction (8) approaches equilibrium



the net rate of CH<sub>4</sub> 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  $\eta$

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

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

In equation (9),  $r_{\text{net}}$  is the measured rate of benzene formation and  $r_f$  is the forward reaction rate, measurable only far away from equilibrium. The equilibrium constant  $K_{\text{eq}}$  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 H<sub>2</sub>, we obtain a value of  $\eta$  of 0.86, while the value after H<sub>2</sub> 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 H<sub>2</sub> to 0.45–0.52 mmol/mol Mo-s after H<sub>2</sub> addition, suggesting that the addition of H<sub>2</sub> merely decreases the thermodynamic driving force for methane conversion to aromatics.

Thus, we conclude that CO<sub>2</sub> decreases CH<sub>4</sub> pyrolysis rates by depleting CH<sub>4</sub> derived predominantly near the bed inlet, while the H<sub>2</sub> formed inhibits the formation of higher-molecular-weight hydrocarbons and of deactivating deposits in the latter stages of the bed, where CO<sub>2</sub> may no longer be present and CH<sub>4</sub> pyrolysis is the predominant reaction.



#### 4. Conclusions

CO<sub>2</sub> co-reactants increased catalyst stability and decreased product molecular weight during reactions of CH<sub>4</sub> on Mo/H-ZSM-5 by scavenging of CH<sub>x</sub> species formed in CH<sub>4</sub> activation steps and by forming H<sub>2</sub>, which inhibits deactivation and hydrocarbon synthesis rates. Total CH<sub>4</sub> conversion rates were not affected by CO<sub>2</sub> co-reactants, which did not influence the rate of CH<sub>4</sub> activation, but only the fate of the CH<sub>x</sub> intermediates formed in this reaction. The linear decrease in hydrocarbon synthesis rates with increasing CO<sub>2</sub> pressure was balanced exactly by a concurrent increase in the rate of CH<sub>4</sub> conversion to CO, *via* reactions with CO<sub>2</sub>. As CO<sub>2</sub> is depleted, pyrolysis reactions increasingly occur, in a gradual shift in the CH<sub>x</sub> removal pathways, from reactions with CO<sub>2</sub> to form CO, to chain growth steps that form desorbable hydrocarbons. The amount of CO<sub>2</sub> required to inhibit pyrolysis reaction increases with increasing temperature, because of the faster depletion of CO<sub>2</sub> reactants as temperature increases. The H<sub>2</sub> 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 CO<sub>2</sub> reforming near the bed inlet does not influence CH<sub>4</sub> conversion to hydrocarbons. The relative rates of reforming and pyrolysis reactions and the tendency of active MoC<sub>x</sub> species to form inactive MoO<sub>y</sub> structures depend only on the CO<sub>2</sub>/CH<sub>4</sub> molar ratio, because of the first order of both CO<sub>2</sub> and CH<sub>4</sub> activation reactions, but the CH<sub>4</sub> activation steps proceed with a higher activation energy than corresponding CO<sub>2</sub> activation reactions; as a result a higher CO<sub>2</sub>/CH<sub>4</sub> ratio is required for the inhibition of pyrolysis reactions and for the conversion of active carbide structures to MoO<sub>x</sub> as the reaction temperature increases.

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