Stability, structure, and oxidation state of Mo/H-ZSM-5 catalysts during reactions of CH₄ and CH₄–CO₂ mixtures

Howard S. Lacheen, Enrique Iglesia*

Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720, USA

Received 1 October 2004; revised 25 November 2004; accepted 29 November 2004

Abstract

Mo₂O₅²⁺-ZSM-5 (Mo/Alᵣ = 0.4, Si/Alᵣ = 20) samples prepared by sublimation of MoO₃ were carburized in CH₄ to form MoCx clusters active in CH₄ pyrolysis and then exposed to different CO₂/CH₄ mixtures. CO₂/CH₄ reactant ratios between 0 and 0.1 increased catalyst stability but decreased pyrolysis rates, and ratios above 0.1 led to a sudden loss of activity that was reversed after removal of CO₂. Below CO₂/CH₄ ratios of 0.1, the catalyst bed can be described as a CO₂-reforming and pyrolysis reactor in series. In the first segment of the bed, where CO₂ is present, pyrolysis is completely suppressed by reverse Boudouard reactions; pyrolysis reactions begin after CO₂ is completely consumed. CO₂ cannot directly influence rates or deactivation for pyrolysis reactions. Rather, the greater stability observed with CO₂-containing reactants arises solely from the presence of H₂, formed in the CO₂-reforming section, in the pyrolysis regions within the catalyst bed. The evolution of catalyst structure and composition in CO₂/CH₄ reactants was also probed by mass spectrometric analysis of effluent streams and by in situ X-ray absorption spectroscopy to determine the underlying processes responsible for reversible deactivation at CO₂/CH₄ ratios greater than 0.1. MoCx-ZSM-5 samples exposed to CO₂/CH₄ streams with 0.022 and 0.055 ratios at 950 K acquire 0.3±0.01 and 1.75±0.03 O-atoms/Mo, respectively. X-ray absorption edge energies in MoCx-ZSM-5 increased from 0.2 to 1.9 eV (relative to Mo⁰) after contact with 0.025 CO₂/CH₄ mixtures at 950 K for 1 h, indicating that oxidation of some Mo centers occurs. These spectral changes occurred concurrently with the detection of pre-edge features typical of MoOₓ structures. Radial structure functions resemble those for samples exposed to pure CH₄, which consist of 0.6-nm MoCx clusters, but show an additional Mo–O coordination shell also detected in bulk β-Mo₂C exposed to ambient air. These data suggest that the inhibition and ultimate suppression of catalytic pyrolysis reactions with CO₂ addition reflect the oxidation of active MoCx structures, the extent of which increases with increasing CO₂/CH₄ reactant ratios. CO₂/CH₄ reactant ratios above 0.1 lead to conversion of MoCx to MoOₓ structures, which are inactive for both reforming and pyrolysis reactions of CH₄, but which reform active MoCx after an induction period when exposed to pure CH₄ reactants at reaction conditions.

Keywords: Molybdenum; Carbides; ZSM-5; MFI; CO₂; CH₄; Reforming; Pyrolysis; EXAFS; XANES; Aromatization

1. Introduction

Medium-pore zeolites with MFI structure and modified by transition metal cations catalyze oligomerization, cyclization, and dehydrogenation reactions required to convert small alkanes to alkenes and arenes [1–14]. Wang et al. [15] first reported that MFI modification by contact with aqueous Mo⁶⁺ salts leads to near-equilibrium yields of ethene, ethane, and benzene during nonoxidative CH₄ reactions with low selectivities for larger unsaturated products, apparently because of steric constraints imposed by MFI channels. MoO₃ precursors were shown to form carbide clusters during initial contact with CH₄ at 950 K [16]; these clusters provide the catalytic surfaces required for activation of C–H bonds in CH₄ and for removal of H-atoms as H₂ during both CH₄ conversion to C₂ molecules and sequential conversion of these primary C₂ products to arenes [17]. The exchange of acidic protons with D₂ [18], together with Raman spectroscopy and multiple-scattering simulations of the extended...
fine structure in X-ray absorption spectra [19], provided direct evidence that Mo(VI)-oxo dimers form at exchange sites during sublimation of MoO3/H-ZSM-5 physical mixtures. These Mo-oxo dimers subsequently convert to active MoCx structures during CH4 reactions.

Mo-ZSM-5 catalysts deactivate during nonoxidative CH4 reactions [20–22] via carbon deposition processes, which become slower as external acid sites on zeolite crystals are selectively titrated by bulky organosilanes [23]. CO2/CH4 mixtures lead to slower deactivation than pure CH4 reactants [24,25], an observation attributed to continuous carbon removal via

$$\text{CO}_2 + C^* \rightarrow 2\text{CO} + *.\quad (1)$$

A sudden loss of catalytic activity above a threshold CO2/CH4 reactant ratio (∼0.06), reversed upon removal of CO2 from the CH4 reactant stream, has also been reported [26]. This sudden but reversible deactivation in CO2/CH4 feeds appears to reflect the oxidation of MoCx instead of carbon deposition processes prevalent with pure CH4 reactants [27]. At CO2/CH4 ratios below these threshold values, CH4 conversion rates were lower but more stable than those obtained with pure CH4 reactants. These lower rates reflect, at least in part, kinetic and thermodynamic inhibition by H2 formed in CH4–CO2 reforming reactions; H2 can also inhibit the formation of large organic residues. Lower pyrolysis rates may also reflect the continuous removal of reactive carbon, required for C–C bond formation, as CO, with the use of CO2 as a reactant. Green et al. [28] examined CO2 reforming on bulk Mo2C and WC and proposed that CO2 dissociates at carbon vacancies to form a steady-state concentration of chemisorbed oxygen (O*) at carbide surfaces. High O* thermodynamic activities, prevalent at high CO2/CH4 ratios, can lead to Mo2C oxidation to less reactive MoOx species.

Here we probe CH4 pyrolysis catalysis and deactivation pathways on carburized Mo2O52+-ZSM-5 at low CO2 concentrations by rigorously isolating and examining the kinetic and thermodynamic effects of CO2 on measured reaction rates. Kinetic factors contributing to decreased hydrocarbon formation rates such as C* scavenging by CO2 and H2 and oxidative deactivation of carbide active sites are examined independently with varying feed composition and concentration. In contrast to previous studies, we report true forward rates by accounting for reactions of products and using thermodynamic equations that account for the equilibrium approach inherent in measured rates. Moreover, we report new evidence suggesting that the enhanced stability of Mo-ZSM-5 in CO2/CH4 mixtures is due to H2 alone and not, as previously proposed, CO2 [24]. Finally, in situ time-resolved mass spectrometry and X-ray absorption spectroscopy were used to measure the oxidation state, local coordination, and structure of Mo-ZSM-5 in CH4 reactants with low CO2 concentrations and to identify processes leading to the observed effects of CO2 on the catalytic rates, selectivity, and ultimate reversible deactivation of active Mo-based structures at high CO2 concentration.

2. Experimental

2.1. Catalyst synthesis

We prepared H-ZSM-5 from Na-ZSM-5 (Si/Al = 20, Zeochem; Alf = framework Al) by heating Na-ZSM-5 (2 g) to 823 K at 0.083 K s−1 in He (2.5 cm3 s−1 g−1 Airgas, UHP) and holding at 823 K for 2 h in dry air (2.5 cm3 s−1 g−1 Airgas, zero grade), a process that removes the organic templates used in ZSM-5 synthesis without a detectable loss of crystallinity. The resulting template-free Na-ZSM-5 (10 g) was converted to NH4-ZSM-5 by ion-exchange with 1 L of NH4NO3,aq (1 M, Fisher, Cert. ACS) at 353 K for 12 h, followed by washing with 2 L of deionized H2O. This exchange procedure was carried out three times with fresh solutions; samples were then dried for 12 h at 400 K in ambient air. NH4-ZSM-5 (5 g) was converted to H-ZSM-5 by heating in 0.5 cm3 s−1 g−1 dry air to 773 K at 0.167 K s−1 and holding for 24 h. H-ZSM-5 and MoO3 (Johnson Matthey, 99.5%) were then ground in an agate mortar and pestle for 0.2 h to form intimate mixtures containing a Mo/Al ratio of 0.41. This mixture was heated to 623 K at 0.167 K s−1 and then held at 623 K for 24 h in 20% O2/He to remove water and to spread MoO3 on external zeolite surfaces [17,19]; finally, the mixture was heated to 973 K at 0.167 K s−1 and held at 973 K for 2 h to form exchanged Mo2O52+-ZSM-5 [19]. The catalysts were formed into pellets with 0.12–0.25-mm diameter for use in structural characterization and catalytic studies.

2.2. Catalytic reactions of CH4 and CH4–CO2 mixtures

Steady-state catalytic rates were measured at 950 K with 1-g catalyst samples held within a quartz reactor (12 mm i.d.). Reactants were 90% CH4/Ar (Matheson, UHP, purified with a Matheson MTRP-0019-XX oxygen-moisture trap; 1 bar total pressure, 0.208 cm3 s−1) mixed with 50% CO2/He (Matheson, UHP) or H2 (Airgas, UHP). We held CH4 partial pressures constant (91 kPa) when using CO2 or H2 coreactants by increasing the total reactor pressure. The reactor effluent was directly transferred via heated lines (423 K) into a gas chromatograph (Agilent model 6890). Hydrocarbons were separated with a capillary column (Agilent HP-1, 50 m × 0.32 mm × 1.05 µm) and their concentrations were measured by flame ionization. CH4, Ar, CO, CO2, and H2 were separated with a packed column (Agilent Porapak Q, 4.5 m) connected to a thermal conductivity detector. CH4 conversion rates were measured with Ar as an internal standard to ensure rigorous mass balances. Product selectivities are reported on a carbon basis as the percentage of converted CH4 molecules appearing as each product. Unreactive residues or nonvolatile products remaining on catalysts or transfer lines were determined by difference and reported as C12+. CO selectivities are reported as the percentage of the CH4 converted and appearing as CO (using half the total CO formed, i.e., excluding CO formed in Eq. (1)); in this way,
the sum of all reported carbon selectivities, including CO, equals unity. Yields are reported as the product of each selectivity and the fractional CH4 conversion.

Measurements of O-atoms removed from or added to the catalyst with sudden changes in reactant composition required product analyses at short time intervals (<1 s). Product evolution rates in these experiments were measured by mass spectrometry (MKS Minilab with electron multiplier; detection limit ~1 × 10⁻⁴ kPa for fixed gases), with the use of a heated capillary for continuous sampling of condensable species. All transient experiments were conducted at 950 K and ambient total pressure. During reduction/carburization of MoO2O5²⁺-ZSM-5, the reactor feed was rapidly changed from pure He at 1 cm³ s⁻¹ to a mixture containing 54 kPa CH4, 6 kPa Ar, and the balance in He at a total flow rate of 1 cm³ s⁻¹. During oxidation of reduced/carburized Mo-ZSM-5, the feed was switched from the latter composition to one containing 54 kPa CH4, 6 kPa Ar, 1–3 kPa CO2, and He as a balancing gas to maintain a constant flow of 1 cm³ s⁻¹. CH4 pyrolysis and reforming products with overlapping mass fragments were measured with the use of matrix deconvolution methods adapted from earlier studies [18,29].

Measured net product formation rates are lower than the true kinetic forward rates when the product formed is in-detectable, samples were exposed to one of two reaction mixtures. Some samples were exposed to pure CH4 for 1 h, and then extended X-ray absorption fine spectra (EXAFS) were recorded with method 1. The remaining samples were exposed to a reaction mixture with a 0.025 CO2/CH4 molar ratio and the XANES region was monitored with acquisition method 2 until no further spectral changes were detected, at which time a detailed spectrum, including the details of the fine structure, was acquired with method 1. MoO3 (Johnson Matthey, 99.5%), MoO2-Al2O3 (Aldrich, 99.9%), \( \beta \)-Mo2O7 (prepared by temperature-programmed reduction of MoO3 in 20% H2/CH4 at 973 K [33], MgMo2O7 (preparation as in [34]), and (NH4)2Mo2O7 (Strem Chemicals, 99.98%) were diluted with boron nitride and sealed with Kapton tape before we acquired X-ray absorption spectra for these materials with known structures. The \( \beta \)-Mo2O7 sample was passivated before exposure to ambient air; the near-surface regions of the sample contained oxygen. These compounds provide structural and oxidation state standards for the assessment of unknown structures as they evolve during catalysis in various reactant mixtures.

Spectra were analyzed with the use of WinXAS Version 2.1 [35]. Pre-edge and post-edge baselines were subtracted with the use of first- and third-order polynomials, respectively, and the near-edge region was analyzed between 2.6 and 13.0 Å⁻¹. The spectra were then corrected for phase shifts and fitted in R-space between 0.5 and 4 Å with the use of the Hanning window and FEFFIT [36] to determine interatomic...
distances and coordination numbers. Backscattering amplitudes and phase shifts of theoretical standards were generated with the use of FEFF8.0 [37] algorithms, and ATOMS [38] was used to generate the required input files from previously reported atomic coordinates. We determined the amplitude reduction factor, $S_0^2$, by fitting experimental Mo foil spectra. Factor analysis was used to identify the principal components in the samples from near-edge spectra recorded during transient experiments. WinXAS software contains a built-in factor analysis code that uses the Malinowski indicator function [39] to estimate the number of pure components, and a target transformation module to identify the pure components [40]. The target transformation algorithm generates an absorption vector of a known reference compound by interpolating its spectra onto the same energy grid as the unknown experimental spectra. A least-squares fitting procedure is then used to determine a transformation vector that will be identical to the absorption vector of the reference compound within experimental error if the reference is indeed a principal component. A goodness-of-fit parameter, or residual, less than 1% is generally considered acceptable [40].

3. Results and discussion

3.1. Steady-state catalytic studies

Steady-state catalytic rates and selectivities were first measured on Mo$_2$O$_5^{2+}$-ZSM-5 (Mo/Al$_f$ = 0.41) at 950 K with the use of pure CH$_4$ reactants (91 kPa). This catalyst composition led to maximum CH$_4$ pyrolysis rates by balancing the number of MoC$_x$ species required for CH$_4$ activation and the residual Bronsted acid sites required for alkene oligomerization and cyclization, while avoiding dealumination of the zeolite framework via formation of Al molybdate species at higher Mo loadings [17].

Table 1 shows forward rates for product formation at 950 K and 91 kPa CH$_4$ after 8.6 and 30.1 ks of contact with reactants. Ethane and ethene $\eta$ values are almost identical, indicating that their interconversion is equilibrated. The approach to equilibrium for arene synthesis was substantial but decreased with time because of catalyst deactivation by deposition of unreactive residues, which form on active sites within channels, restrict reactant access to such sites, and decrease CH$_4$ conversion levels [27]. The sequential nature of arene formation pathways (via C$_2$ initial products) led to stronger time-on-stream effects on arene formation rates than on C$_2$ formation rates. Therefore, the selectivity shifts to primary C$_2$ products as deactivation occurs.

CH$_4$ was added to CH$_4$ reactants to probe the effects of CO$_2$ concentration on CH$_4$ reaction rates and catalyst stability. Steady-state CH$_4$ conversion and CO and hydrocarbon yields are shown in Fig. 1 for CO$_2$/CH$_4$ molar ratios less than 0.1. Samples were first activated by reduction and carbonization with pure CH$_4$ reactants until hydrocarbon yields reached maximum values ($\sim$ 2 h); CO$_2$ was then added. CH$_4$ conversion remained constant at $\sim$ 7% for CO$_2$/CH$_4$ ratios below 0.064; CO$_2$ was not detected in the effluent with these reactant mixtures. At slightly higher CO$_2$/CH$_4$ ratios, CH$_4$ conversion increased proportionally with CO$_2$ concentration. Methane conversions were very similar to the sum of hydrocarbons and CO (from CH$_4$, defined in the Experimental section) yields; no detectable C$_{12+}$ products were formed at these moderate CO$_2$ concentrations. Fig. 2 shows CH$_4$ conversion and hydrocarbon and CO yields for reactant mixtures with CO$_2$/CH$_4$ ratios of 0, 0.05, and 0.1 after activation in pure CH$_4$ for 2 h. Hydrocarbon yields were 2.1% at a 0.05 CO$_2$/CH$_4$ ratio and did not decrease even

| Time on stream (ks) | CH$_4$ conversion (%) | Distance to equilibrium ($\eta$, %)$^a$
<table>
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<tr>
<td>8.6</td>
<td>7.0</td>
<td>70</td>
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<tr>
<td>30.1</td>
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Table 1: CH$_4$ pyrolysis over Mo/H-ZSM-5 (1 g, Mo/Al$_f$ = 0.41, 950 K, 0.19 cm$^3$ s$^{-1}$ CH$_4$; 101.1 kPa, CH$_4$–Ar = 9:1)

<table>
<thead>
<tr>
<th>Distance to equilibrium for each product defined in Eqs. (2)–(5) (Section 2.2).</th>
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<tbody>
<tr>
<td>C$_2$H$_4$</td>
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<tr>
<td>C$_2$H$_6$</td>
</tr>
<tr>
<td>C$_4$H$_8$</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
</tr>
<tr>
<td>C$_{10}$H$_8$ (naphthalene)</td>
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Forward rates (10$^{-3}$ mol/(g-atom Mo-s))

| C$_2$ | 2.04 | 1.17 |
| C$_4$H$_8$ | 2.55 | 1.16 |
| C$_7$H$_8$ | 0.14 | 0.09 |
| C$_{10}$H$_8$ | 0.47 | 0.15 |

Selectivity (% carbon)

| C$_2$H$_4$ | 3 | 7 |
| C$_2$H$_6$ | 2 | 3 |
| C$_4$H$_8$ | 54 | 59 |
| C$_7$H$_8$ | 3 | 5 |
| C$_{10}$H$_8$ | 14 | 9 |

$^a$ $\eta$: Distance to equilibrium for each product defined in Eqs. (2)–(5) (Section 2.2).
after 15 ks; only traces of C_{12+} hydrocarbons were formed. At a CO_{2}/CH_{4} ratio of 0.1, the initial CH_{4} conversion was ~10%, CO_{2} was completely consumed within the catalyst bed, and hydrocarbons were virtually undetected at less than two orders of magnitude of their yields in CO_{2} free feeds (Fig. 2, right panel). With this reactant mixture, CH_{4} conversion decreased abruptly to undetectable levels after ~1 h. Removal of CO_{2} from the reactant stream led to the recovery of catalytic rates, after an activation period of 3 ks, during which CO was formed and hydrocarbons increased to maximum rates (Fig. 2, right panel).

The lower hydrocarbon yields obtained with CO_{2} coreactants may reflect thermodynamic or kinetic effects. H_{2} formed via CH_{4}–CO_{2} reforming would decrease equilibrium CH_{4} conversion levels and increase rates for the reverse of the dehydrogenation steps required to form alkenes and arenes. Adsorbed organic species may be removed continuously by CO_{2}, thus inhibiting chain growth processes requiring C–C bond formation, but ultimately replacing carbide carbon in MoC_x with O-atoms until CO_{2} is depleted along the catalyst bed. CO products of CH_{4}–CO_{2} mixtures may also form unreactive carbon species via Boudouard reactions that impede access to active sites. We consider each of these possible effects below.

Net rates were corrected for approach to equilibrium to assess the role of H_{2} formed in CH_{4}–CO_{2} reactions on pyrolysis forward rates. The resulting (forward) arene synthesis rates decreased with increasing CO_{2} concentration (Fig. 3). Equilibrium calculations for combined pyrolysis and CO_{2} reforming reactions, made with thermodynamic data [41,42], showed that net hydrocarbon yields decreased with increasing CO_{2} feed concentration because of the H_{2} formed in CO_{2} reforming reactions. If H_{2} were solely responsible, however, for the observed effects of CO_{2} on hydrocarbon synthesis rates, forward arene synthesis rates would be independent of CO_{2} concentration, in contradiction to the data shown in Fig. 3.

We next consider the effect of H_{2} on pyrolysis rates independently of CO_{2} with H_{2}/CH_{4} reactants. H_{2} can decrease net arene synthesis rates because of thermodynamic effects, which are accounted for through our use of forward rates, or via scavenging of reactive carbon and suppression of C–C bond formation pathways. Fig. 4a shows benzene forward rates as a function of average H_{2} pressure (defined as the mean of its inlet and outlet values) with both H_{2}/CH_{4} and CO_{2}/CH_{4} reactants (at 950 K and 91 kPa CH_{4}). We calculated inlet H_{2} pressures for CO_{2}/CH_{4} mixtures by assuming that CO_{2} is depleted near the bed inlet and H_{2} forms with the stoichiometry of CH_{4}–CO_{2} reactions. Forward rates of benzene synthesis decreased with increasing H_{2} pressure in H_{2}/CH_{4} feeds, indicating that H_{2} kinetically inhibits CH_{4}
pyrolysis reactions, because we take thermodynamic effects into account by using Eqs. (2)–(5) to calculate forward rates. Benzene synthesis forward rates were always higher with \( \text{H}_2/\text{CH}_4 \) than with \( \text{CO}_2/\text{CH}_4 \) reactants for any given average \( \text{H}_2 \) pressure. Therefore, the lower benzene forward rates observed with \( \text{CO}_2/\text{CH}_4 \) mixtures are not caused only by inhibition by the \( \text{H}_2 \) formed (in \( \text{CH}_4–\text{CO}_2 \) reforming reactions) near the bed inlet.

The data in Fig. 2 show that at \( \text{CO}_2 \) conversions below 100%, hydrocarbon yields decrease by two orders of magnitude compared with those with \( \text{CO}_2 \)-free feeds. \( \text{CO}_2 \) scavenges \( \text{C}^* \) before \( \text{C}–\text{C} \) bond formation can occur, thus preventing pyrolysis reactions at any reactor position that contains unreacted \( \text{CO}_2 \). Thus, the fraction of the catalyst bed that remains available for \( \text{CH}_4 \) pyrolysis reactions decreases with increasing \( \text{CO}_2 \) concentration. \( \text{CO}_2 \) reforming rates on Ni and noble metal catalysts have been shown to be independent of \( \text{CO}_2 \) and proportional to \( \text{CH}_4 \) concentrations [43,44]; therefore, the fraction of the catalyst exposed to \( \text{CH}_4 \) pyrolysis reactions decreases with increasing \( \text{CO}_2 \) concentration. \( \text{CO}_2 \) reforming rates on \( \text{Ni} \) and noble metal catalysts have been shown to be independent of \( \text{CO}_2 \) and proportional to \( \text{CH}_4 \) concentrations [43,44]; therefore, the fraction of the catalyst exposed to \( \text{CO}_2 \) should be proportional to the inlet \( \text{CO}_2 \) concentration, \( \text{C}_{\text{in}} \), and assuming that for feeds with \( \text{CO}_2 \) inlet concentration, \( \text{C}_i \), the \( \text{CO}_2 \) is completely consumed at a bed length, \( L_i \), equal to

\[
L_i = \frac{(L \cdot C_i)}{C_{\text{max}}},
\]

where \( L \) is the length of the fixed-bed reactor. Forward rates corrected for effective bed length are then equal to

\[
r_{\text{forward,eff}} = \frac{r_{\text{forward}}}{1 - L_i/L}.
\]

The \( r_{\text{forward,eff}} \) vs average \( \text{H}_2 \) partial pressure is plotted in Fig. 4b. Benzene forward rates for \( \text{H}_2/\text{CH}_4 \) and \( \text{CO}_2/\text{CH}_4 \) feeds collapse onto a single line, confirming our new model for the complete suppression of pyrolysis reactions by \( \text{CO}_2 \).

Naphthalene synthesis rates for \( \text{CO}_2/\text{CH}_4 \) and \( \text{H}_2/\text{CH}_4 \) feeds also lie along the same line.

The effective forward rates in Fig. 4 suggest that the lower pyrolysis yields with \( \text{CO}_2/\text{CH}_4 \) mixtures occur as a result of a shorter active catalyst bed available for pyrolysis as a result of \( \text{CO}_2 \) scavenging of active \( \text{C}^* \) near the bed inlet. Yet we observe, as have others [24], that pyrolysis rates are much more stable with time on stream when \( \text{CO}_2 \) is present in \( \text{CH}_4 \) feeds, even though pyrolysis occurs only in those regions of the bed where \( \text{CO}_2 \) is no longer present. Such regions of the bed can detect the presence of \( \text{CO}_2 \) in the inlet stream only through the presence of the \( \text{H}_2 \) and \( \text{CO} \) products formed in \( \text{CH}_4–\text{CO}_2 \) reactions. First-order deactivation constants for hydrocarbon synthesis were 0.011 and 0.0008 ks\(^{-1} \), with \( \text{CH}_4 \) (5 kPa average \( \text{H}_2 \) pressure) and 0.06 \( \text{CO}_2/\text{CH}_4 \) (12.5 kPa \( \langle \text{H}_2 \rangle \)) feeds, respectively, as shown in Table 2. For a \( \text{H}_2/\text{CH}_4 \) feed with an average \( \text{H}_2 \) pressure (12 kPa \( \langle \text{H}_2 \rangle \)) similar to that prevalent after \( \text{CO}_2 \) depletion with 0.06 \( \text{CO}_2/\text{CH}_4 \) reactants, the deactivation constant was 0.001 ks\(^{-1} \), a value very similar to that obtained with \( \text{CO}_2 \) reactants (0.0008 ks\(^{-1} \)). The similar deactivation constants for feeds with similar average \( \text{H}_2 \) pressures (12–12.5 kPa) but different inlet compositions confirm that the sole effect of \( \text{CO}_2 \) coreactants on deactivation is to form \( \text{H}_2 \), which acts as the deactivation inhibitor in downstream pyrolysis reactions of the catalyst bed, within which \( \text{CO}_2 \) could not have any more direct effects because it is no longer available. This exclusive role of \( \text{H}_2 \) in inhibiting deactivation processes contrasts with previous claims attributing it
directly to CO₂ scavenging of C* via reverse Boudouard reactions [24].

Forward rates measured as a function of inlet composition indicate that the catalyst bed can be described as two discrete sections, catalyzing reforming and pyrolysis reactions, at low CO₂/CH₄ ratios. Pyrolysis does not occur while CO₂ is available because it effectively scavenges C* intermediates required for chain growth. The downstream pyrolysis section acts as a catalyst bed with an inlet stream containing CH₄ and equimolar amounts of H₂ and CO. The shorter effective bed for pyrolysis and the thermodynamic effects of H₂ formed in the reforming section lead to lower hydrocarbon yields than with pure CH₄ inlet streams, but also to lower deactivation rates as a result of the role of H₂ in preventing the formation of unreactive residues, probably large polynuclear aromatics requiring sequential dehydrogenation steps reversed by H₂.

The active Mo phase within pyrolysis sections of the bed consists of small carbide clusters similar to Mo₂C [16,45], but the structure and oxidation state of the section of the bed exposed to CO₂ remain unclear. In the sections that follow, we explore the structural and catalytic consequences of CO₂/CH₄ mixtures by mass spectrometric analysis of the bed effluent during compositional transients and in situ X-ray absorption spectroscopy to provide evidence that oxidation of Mo carbides at high CO₂ concentrations forms a Mo phase that is inactive for C–H bond breaking and therefore for catalytic pyrolysis of CH₄.

3.2. Transient evolution of products during contact with CO₂/CH₄ reactant mixtures

The removal of C* by CO₂ to form CO and the potential replacement of the C* species in MoCₓ by oxygen to form MoO₂⁺ species inactive in pyrolysis and even reforming reactions may account for the deactivation of Mo-ZSM-5 observed at high CO₂ concentrations (Fig. 2). The resulting depletion of reactive C* (or CH₄*) monomers would prevent C–C bond formation within regions in the reactor containing CO₂. We examined these effects by measuring changes in effluent composition, as inlet CO₂ concentrations were abruptly changed in an effort to measure the number of O atoms added to or removed from working catalysts in environments containing different CO₂ concentrations.

Fig. 5a shows the CO, H₂O, H₂, C₂H₄, and C₆H₆ formation rates and CH₄ conversion during initial contact of Mo₂O₂²⁺-ZSM-5 with CH₄ at 950 K. H₂, H₂O, and CO were initially detected as a result of the reduction and carbonization of trace amounts of unexchanged MoO₃ [29]; these products inhibit the reduction and carbonization of less reducible exchanged Mo-oxo dimers. As these dimers ultimately converted to MoCₓ clusters, H₂O concentrations decreased and H₂ and CO formation rates increased sharply until all of the O atoms in Mo₂O₂⁺ were removed and catalysts reached maximum CH₄ pyrolysis rates. Initial exposure of Mo₂O₂²⁺-ZSM-5 to CH₄ (CO₂/CH₄ = 0; Fig. 5a) removed 2.5 ± 0.05 O atoms per Mo atom (Fig. 6, left panel), measured from the concentration of oxygen-containing products (CO, CO₂ (x2), H₂O), indicating that all nonzeolithic O atoms in exchanged MoO₂⁺ were removed, as shown previously [18]. Benzene, a representative pyrolysis product, was first detected at ~500 s (Fig. 5a) and reached maximum synthesis rates (5 × 10⁻⁴ mol/(g-atom Mo-s)) before decreasing gradually as deactivation occurred.

Next we consider the transient behavior of Mo₂O₂²⁺-ZSM-5 samples first carburized in pure CH₄ (for 1 h) and then exposed to reactants with a CO₂/CH₄ molar ratio of 0.022 (Fig. 5b). During initial carburization and catalytic CH₄ pyrolysis, CH₄ conversion decreased to ~1% after 1 h before CO₂ was introduced into the pure CH₄ stream. CO₂ was completely converted and CH₄ conversion increased immediately to ~3% upon the introduction of CO₂. The CH₄ conversion oscillations in Fig. 5b reflect pumping fluctuations in the mass spectrometer; they occurred in this experiment also before CO₂ addition and do not reflect oscillations in catalytic rates. Measured net benzene synthesis rates decreased from 2 × 10⁻⁴ to 5 × 10⁻⁵ mol/(g-atom Mo-s) during CO₂ addition.

We measured the amount of oxygen introduced into this sample during contact with this CO₂-containing reactant mixture by subtracting the CO formed from the amount of CO required for CO₂ reforming of CH₄, H₂O, which forms in concurrent water–gas-shift reactions, was below the detection limit, as expected from water–gas shift equilibrium calculations under these reaction conditions (~10⁻⁹ kPa). CO₂/CH₄ inlet ratios of 0.022 and 0.055 led to the introduction of 0.28 ± 0.01 and 1.8 ± 0.03 O atoms per Mo atom (Fig. 6, middle panel), respectively, into MoCₓ clusters formed during initial contact with pure CH₄ reactants. This suggests that some C* in MoCₓ is replaced with O* at the beginning of the bed where CO₂ was present, but the catalyst bed remains active for CO₂ reforming and CH₄ pyrolysis.
Fig. 5. Transient product formation rates and CH₄ conversion during reactions of CO₂/CH₄ mixtures on Mo/H-ZSM-5 (1 g, Mo/Al = 0.41, 950 K, 1 cm³ s⁻¹, 54 kPa CH₄): (a) CO₂/CH₄ = 0, (b) 0.022 CO₂/CH₄, and (c) CO₂/CH₄ = 0 after (b).

at these CO₂ concentrations. Fig. 5c shows product evolution profiles after a 0.022 CO₂/CH₄ stream was replaced with pure CH₄ reactants. CH₄ conversion increased sharply to 7%, and then benzene synthesis rates gradually returned to the values measured during initial contact with pure CH₄ reactants (∼ 2×10⁻⁴ mol/(g-atom Mo-s)) in ∼ 1 ks. The number of O atoms removed during exposure to pure CH₄ reactants was measured from the number of CO molecules formed during contact with pure CH₄ reactants (only traces of H₂O and CO₂ formed) (Fig. 6, right panel). This procedure yielded 0.31 ± 0.01 and 1.7 ± 0.03 O atoms removed per Mo atom for CO₂/CH₄ ratios of 0.022 and 0.055, respectively (Table 3). These values are consistent with the amounts of oxygen deposited on active oxygen-free MoCₓ structures during contact with each of these CO₂-containing streams (0.28 and 1.8 O/Mo, respectively).

After CO₂ was removed from the inlet stream, benzene synthesis rates returned to values measured before CO₂ introduction, but not to those measured after initial activation of fresh exchanged samples in pure CH₄ streams. The formation of carbon deposits on acid sites and external surfaces has been examined by X-ray photoelectron spectroscopy and reactivity studies [27,46]; unreactive carbon residues restrict channel entrances, and their formation is essentially irreversible, except by treatment in O₂ at high temperatures [17]. Oxidation of MoCₓ-ZSM-5 in O₂ at 973 K restores more than 90% of initial pyrolysis rates [17] by converting deactivated MoCₓ clusters to MoO₃ and redispersing it as Mo₂O₅²⁺ dimers above 623 K. In contrast, MoCₓ oxidation in CO₂/CH₄ reactant mixtures does not remove unreactive carbon deposits formed during pyrolysis at other locations, even though these mixtures led to significant conversion of
Table 3
O-atom addition/removal from Mo$_2$O$_5^{2+}$-ZSM-5 (1 g, Mo/Al$_f$ = 0.41, 950 K, 1 cm$^3$ s$^{-1}$; 54 kPa CH$_4$, 6 kPa Ar, balance He with 101.3 kPa total)

<table>
<thead>
<tr>
<th>CO$_2$/CH$_4$</th>
<th>(O-atoms) removed/Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>During initial contact</td>
</tr>
<tr>
<td>0.022</td>
<td>+2.6</td>
</tr>
<tr>
<td>0.055</td>
<td>+2.5</td>
</tr>
</tbody>
</table>

MoC$_x$ species to the corresponding suboxides. The formation of these unreactive deposits appears to be inhibited in CO$_2$-containing feeds, as shown by the low deactivation rates observed for reactant mixtures with CO$_2$/CH$_4$ ratios below 0.1, which reflect the presence of H$_2$ formed via CO$_2$ reforming near the bed inlet. CO$_2$ addition did lead to the ultimate replacement of chemisorbed carbon with oxygen as illustrated in Fig. 7. Fig. 7 depicts a Mo$_2$C particle formed during activation processes in CH$_4$ described above and suddenly exposed to a CO$_2$/CH$_4$ reactant mixture. CO$_2$ can react directly with a vacancy to form CO and O*, or it can react with a surface C* to form two CO molecules and a vacancy (as in Eq. (1)). Similar oxidative deactivation pathways on bulk and supported Mo$_2$C and WC during CO$_2$ reforming of CH$_4$ were proposed by Green et al. [28]. O atoms, generated by dissociation of CO$_2$, react with carbon in carbide structures to form a carbon vacancy that can then be filled with additional O atoms from CO$_2$, leading to the ultimate oxidation of MoC$_x$ structures. Such vacancies can react also with C* formed via CH$_4$ dissociation to reform a stoichiometric carbide; these processes are in a state of dynamic balance during steady catalysis, as depicted in Fig. 7.

These conclusions about reduction–carburization–oxidation cycles are based on rigorous chemical balancing of inlet and outlet streams; they do not, however, provide direct evidence for structural changes in Mo centers during contact with reactant streams with different CO$_2$/CH$_4$ ratios. In the following section, we describe catalyst structure and electronic properties with the use of near-edge (XANES) and extended fine structure (EXAFS) analysis of X-ray absorption spectra during catalytic reactions of CH$_4$–CO$_2$ mixtures.

3.3. In situ near-edge and fine structure X-ray absorption spectra at the Mo K-edge

Near-edge X-ray absorption spectra are shown in Fig. 8 for exchanged Mo$_2$O$_5^{2+}$-ZSM-5 prepared from MoO$_3$/HZSM-5 physical mixtures and for reference Mo compounds with known structure. The spectra for the initial physical mixtures resembled that for crystalline MoO$_3$, within which Mo atoms reside in distorted octahedral coordination. Thermal treatment to 950 K in 20% O$_2$/He led to gradual changes in the near-edge spectra of these mixtures. The spectra ul-
ultimately resemble that for MgMoO$_2$Y, which contains di-tetrahedral Mo centers, indicating the presence of MoO$_2$ZSM-5 structures anchored at vicinal exchange sites [19].

MoO$_2$ZSM-5 structures have been identified as principal components at 0.025 CO$_2$/CH$_4$ addition. The identities of pure components in CO$_2$/CH$_4$ feed transients were established with the use of a target transformation algorithm in WinXAS 2.1 (see details in the Experimental section). MoO$_2$ZSM-5 treated in CH$_4$ for 1–6 h in CH$_4$ at 950 K was shown to exist as 0.5–0.6 nm MoC$_x$ clusters from multiple-scattering simulations of the absorption fine structure [19,45]. MoC$_x$ was identified as a principal component with a residual of 0.26% in carburized Mo-ZSM-5 in this study; residuals lower than 1% indicate an unequivocal identification of a principal component [40]. The fresh exchanged MoO$_2$ZSM-5 sample gave a residual of 5%, a relatively poor fit compared with the carburized Mo-ZSM-5 structural standard. Bulk MoO$_3$ gave a residual of 2.6%, considerably better than MoO$_2$ZSM-5, but still high. Oxycarbides, as depicted in Fig. 7, are most likely the dominant species at 0.025 CO$_2$/CH$_4$, and therefore neither one of the reference compounds accurately describes the experimental transient spectra. In lieu of suitable standards, the oxidation of active Mo carbides by CO$_2$/CH$_4$ mixtures can be described by two principal com-

Factors analysis was used to identify principal components from near-edge spectra. This method has been used previously to identify pure components contributing to X-ray absorption spectra [40,49,51,52]. First, factor analysis was used to determine that two principal components contributed to the 11 near-edge spectra acquired during transient CO$_2$/CH$_4$ = 0.025 addition. The identities of pure components in CO$_2$/CH$_4$ feed transients were established with the use of a target transformation algorithm in WinXAS 2.1 (see details in the Experimental section). MoO$_2$ZSM-5 treated in CH$_4$ for 1–6 h in CH$_4$ at 950 K was shown to exist as 0.5–0.6 nm MoC$_x$ clusters from multiple-scattering simulations of the absorption fine structure [19,45]. MoC$_x$ was identified as a principal component with a residual of 0.26% in carburized Mo-ZSM-5 in this study; residuals lower than 1% indicate an unequivocal identification of a principal component [40]. The fresh exchanged MoO$_2$ZSM-5 sample gave a residual of 5%, a relatively poor fit compared with the carburized Mo-ZSM-5 structural standard. Bulk MoO$_3$ gave a residual of 2.6%, considerably better than MoO$_2$ZSM-5, but still high. Oxycarbides, as depicted in Fig. 7, are most likely the dominant species at 0.025 CO$_2$/CH$_4$, and therefore neither one of the reference compounds accurately describes the experimental transient spectra. In lieu of suitable standards, the oxidation of active Mo carbides by CO$_2$/CH$_4$ mixtures can be described by two principal com-

Changes in the absorption edge energy were also detected during catalytic reactions with other CO$_2$/CH$_4$ reactant mixtures (Table 4). The edge energy was taken as the first inflection point in the absorption edge (or the first inflection after the pre-edge feature, if present). Fresh exchanged MoO$_2$ZSM-5 showed an edge energy (relative to Mo$^0$) at 4.90 eV, similar to that of MoO$_3$ (4.8 eV) and corresponding to that of Mo$^{6+}$. After exposure to CH$_4$, the edge shifts to 0.2 eV and then back to 1.9 eV after contact with a 0.025 CO$_2$/CH$_4$ mixture at 950 K for 1 h. These data show that reduction and carburization occur during activation in pure CH$_4$ and that these processes are reversed, to some extent, as CO$_2$ is introduced along with CH$_4$ reactants. As CO$_2$ is depleted along the plug-flow reactor cell, the composition of the gas phase changes, leading to a mixture of Mo structures and oxidation states, all of which are sampled by the X-ray beam during these absorption measurements.

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Figure 8. Mo K-edge near-edge spectra for β-Mo$_2$C exposed to air, MoO$_2$, MgMgO$_2$, Y, MoO$_3$ and physical mixtures of MoO$_2$/H-ZSM-5 (Mo/Al = 0.41) during treatment in 20% O$_2$/He at 298 and 950 K, CH$_4$ at 950 K and CO$_2$/CH$_4$ = 0.025 at 950 K.

Table 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔE$_{0}$ (eV)</th>
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<tr>
<td>MoO$_3$</td>
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</tr>
<tr>
<td>β-Mo$_2$C</td>
<td>0.2</td>
</tr>
<tr>
<td>(NH$_4$)$_2$Mo$_2$O$_7$</td>
<td>4.4</td>
</tr>
<tr>
<td>MoO$_2$/H-ZSM-5</td>
<td>4.3</td>
</tr>
<tr>
<td>MoO$_2$ZSM-5</td>
<td>4.9</td>
</tr>
<tr>
<td>MoO$_2$ZSM-5 after treatment in CH$_4$ at 950 K for 1 h</td>
<td>0.2</td>
</tr>
<tr>
<td>MoO$_2$ZSM-5 after treatment in CH$_4$ at 950 K for 1 h then in CO$_2$/CH$_4$ = 0.025 at 950 K for 1 h</td>
<td>1.9</td>
</tr>
</tbody>
</table>
components, one of which is Mo$_2$C, but the identification of the other principal components remains ambiguous at this time.

A Fourier transform of the fine structure region gives a radial structure function around Mo absorbers (e.g., Fig. 9 for Mo$_2$O$_5^{2-}$-ZSM-5). The intensity of the features is related to the number of scatterers at a given distance from Mo atoms, which is corrected in structural fits by thermal and static disorder and by the scattering cross section of the neighboring atoms. Fig. 10 shows experimental and fitted $k^2$-weighted EXAFS and radial scattering functions for Mo$_2$O$_5^{2-}$-ZSM-5; the parameters arising from structural refinement procedures are shown in Table 5. These fine structure spectra for exchanged Mo$_2$O$_5^{2+}$-ZSM-5 in 20% O$_2$/He were described via multiple scattering simulations with MgMo$_2$O$_7$ standards as the starting point. The resulting simulated structures confirmed that each Mo atom has four oxygen neighbors in a tetrahedral arrangement at a distance of 0.16–0.18 nm. Scattering from next-nearest neighboring Mo or Al was not detected in the experiments or in simulated radial structure functions because of a $\pi$ phase shift in multiple scattering paths, which leads to destructive interference of scattered electrons [19].

Several features emerged in the radial structure function of Mo$_2$O$_5^{2+}$-ZSM-5 upon exposure to CH$_4$ at 950 K for 1 h (Fig. 10). These features can be described with the use of a cluster with three Mo–C shells and a total coordination of 3.4 together with a weak contribution from a Mo–Mo shell at 0.29 nm with a coordination number of 0.3. A new feature near 0.12 nm appeared in the radial structure function after exposure to CO$_2$/CH$_4$ mixtures at 950 K for 1 h (Fig. 10), but the sample otherwise retained the features present in the sample during contact with pure CH$_4$ reactants. The feature at 0.12 nm and the rest of the radial structure function resemble those in bulk Mo$_2$C containing some oxygen coordination as a result of exposure to ambient air (Fig. 9). The new feature at 0.12 nm was fitted with a Mo–O shell at 0.17 nm with a coordination number of 0.2. Only two Mo–C shells were needed to describe the structure; this gave an overall Mo–C coordination of 3.4. The Mo-ZSM-5 catalysts in CH$_4$ and CO$_2$–CH$_4$ lack scattering centers at longer distances, which is typical of the bulk carbide (Fig. 9), sug-
Refined structural parameters for Mo/H-ZSM-5 with different treatments

<table>
<thead>
<tr>
<th>Mo/H-ZSM-5 treatment</th>
<th>Shell</th>
<th>Coordination number&lt;sup&gt;a&lt;/sup&gt;, this study</th>
<th>Interatomic distance (nm), this study</th>
<th>Coordination number&lt;sup&gt;b&lt;/sup&gt;, Ref. [19]</th>
<th>Interatomic distance (nm), Ref. [19]</th>
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</thead>
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<tr>
<td>20% O&lt;sub&gt;2&lt;/sub&gt;/He</td>
<td>Mo–O</td>
<td>1.0</td>
<td>0.17</td>
<td>1.0</td>
<td>0.169</td>
</tr>
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<td></td>
<td>Mo–O</td>
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<td>0.17</td>
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<td>0.169</td>
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<tr>
<td></td>
<td>Mo–O</td>
<td>1.0</td>
<td>0.18</td>
<td>1.0</td>
<td>0.178</td>
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<tr>
<td></td>
<td>Mo–O</td>
<td>1.0</td>
<td>0.18</td>
<td>1.0</td>
<td>0.184</td>
</tr>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Mo–C</td>
<td>1.7</td>
<td>0.20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Mo–C</td>
<td>1.5</td>
<td>0.23</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Mo–C</td>
<td>0.2</td>
<td>0.24</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Mo–Mo</td>
<td>0.3</td>
<td>0.29</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;/CH&lt;sub&gt;4&lt;/sub&gt; = 0.025</td>
<td>Mo–O</td>
<td>0.2</td>
<td>0.17</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Mo–C</td>
<td>1.9</td>
<td>0.21</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Mo–C</td>
<td>1.5</td>
<td>0.23</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Mo–Mo</td>
<td>0.2</td>
<td>0.28</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

<sup>a</sup> $S_0^2 = 0.77$, Debye–Waller factor fixed at zero, fit using $k^2$-weighted EXAFS.

<sup>b</sup> $S_0^2 = 0.63$, Debye–Waller factor fixed at zero, fit using $k^1$-weighted EXAFS.

Fig. 11. Mo phase fraction as a function of time on Mo<sub>2</sub>O<sub>5</sub><sup>2+</sup>-ZSM-5 (Mo/Al<sub>f</sub> = 0.41). The Mo phase fraction (denoted with symbols connected by broken lines) was determined using a least square’s fit of MgMo<sub>2</sub>O<sub>7</sub> and Mo<sub>2</sub>C near-edge reference spectra to Mo<sub>2</sub>O<sub>5</sub><sup>2+</sup>-ZSM-5 catalysts in different oxidizing environments: 50 kPa CH<sub>4</sub> with 0 kPa (left) and 1.3 kPa (right) CO<sub>2</sub> at 950 K, 5.8 cm<sup>3</sup> s<sup>−1</sup> g<sup>−1</sup> cat<sup>−1</sup>. Solid lines indicate O/Mo ratios in the catalyst measured using on-line mass spectrometry (1 g, Mo/Al<sub>f</sub> = 0.41, 950 K, 5.8 cm<sup>3</sup> s<sup>−1</sup> g<sup>−1</sup> cat<sup>−1</sup>, 54 kPa CH<sub>4</sub>) with 0 kPa (left) and 1.2 kPa (right) CO<sub>2</sub>.

the sample containing high enough CO<sub>2</sub> concentrations because MoO<sub>2</sub> has no pre-edge feature. These MoO<sub>3</sub> species would then redisperse to form the Mo-oxo dimers present in the starting material while the rest of the catalyst continues to function as fully carburized clusters active in CH<sub>4</sub> pyrolysis reactions.

4. Conclusions

The improvement in the stability of Mo<sub>C</sub><sub>x</sub>-ZSM-5 catalysts resulting from the addition of an oxidant such as CO<sub>2</sub> at low concentrations to CH<sub>4</sub> feeds is a result of the H<sub>2</sub> formed by CO<sub>2</sub>–CH<sub>4</sub> reactions. CH<sub>4</sub> reacts with CO<sub>2</sub> exclusively at the beginning of the bed; this reaction occurs via scavenging of surface C<sup>+</sup> and inhibits C–C bond formation. After CO<sub>2</sub> is completely consumed, pyrolysis products are formed at

gesting the presence of small clusters of a size similar to that found with those samples exposed to pure CH<sub>4</sub> reactants.

In Fig. 11, the time evolution of Mo structures obtained from principal component analyses of near-edge spectra is shown together with the amount of extraframework oxygen as measured by mass spectrometry as the composition of the reactant stream was varied with time. In the left panel, fresh Mo<sub>2</sub>O<sub>5</sub><sup>2+</sup>-ZSM-5 was exposed to a 50% CH<sub>4</sub>/He stream (1 bar, 950 K; 5.8 cm<sup>3</sup> s<sup>−1</sup> g<sup>−1</sup> cat) within the X-ray absorption reactor cell and within a laboratory reactor in separate experiments. The data shown represent the fraction of the Mo atoms present as Mo<sub>2</sub>O<sub>7</sub><sup>2−</sup> and Mo<sub>C</sub><sub>x</sub>, calculated with the use of MgMo<sub>2</sub>O<sub>7</sub> and bulk Mo<sub>2</sub>C near-edge spectra as standards for the near-edge spectral analysis. Changes in the number of O atoms removed coincided with changes in the local coordination and the oxidation state of Mo atoms measured from near-edge spectra.

After catalysts were fully carburized, the reactant stream was changed to a CO<sub>2</sub>/CH<sub>4</sub> mixture with a ratio of 0.025 (shown in the right panel). Here again, changes in the near-edge spectra occurred within the same time scale as the addition of O atoms measured by mass spectrometry (the initial lag in the change in MoO<sub>x</sub> phase measured from X-ray absorption reflects differences in the time required for the new stream to reach the sample). After approximately 2.5 ks, the oxidation of Mo<sub>C</sub><sub>x</sub> clusters stops and CO<sub>2</sub>–CH<sub>4</sub> reforming near the bed inlet and CH<sub>4</sub> pyrolysis near the bed outlet reach steady-state rates. These data do not allow unequivocal structural identification because the predominant Mo phase changes with CO<sub>2</sub> concentration along the reactor. The oxidized Mo phase may form precursor-like MoO<sub>2</sub><sup>2+</sup> species at sufficiently high CO<sub>2</sub> concentrations or MoO<sub>2</sub> clusters, as also occurs during deactivation of bulk Mo<sub>2</sub>C at stoichiometric CO<sub>2</sub>-reforming feeds [28]. The appearance of a pre-edge feature in the near-edge spectra for Mo-ZSM-5 samples exposed to 0.025 CO<sub>2</sub>/CH<sub>4</sub> reactants (Fig. 8) suggests that Mo<sub>2</sub>C oxidizes to volatile MoO<sub>3</sub> within regions of
lower yields as a result of H\textsubscript{2} formed in the CO\textsubscript{2}–CH\textsubscript{4} section of the bed; H\textsubscript{2} decreased equilibrium yields to products and increased hydrogenation rates of surface species, preventing formation of carbonaceous deposits that have been linked to catalyst deactivation.

X-ray absorption and transient addition/removal of O atoms during CO\textsubscript{2} addition/removal to CH\textsubscript{4} streams provided strong evidence that Mo was oxidized to MoO\textsubscript{2}C\textsubscript{y}. Oxidized molybdenum carbide clusters formed remained active for CO\textsubscript{2} reforming below CO\textsubscript{2}/CH\textsubscript{4} molar ratios of 0.1. The structure of the catalyst in CO\textsubscript{2}/CH\textsubscript{4} feeds, determined from multiple scattering simulations of the radial scattering function, resembles that of 0.6 nm MoC\textsubscript{x} clusters with a Mo–O coordinative shell at 0.17 nm. At CO\textsubscript{2} concentrations above 0.1 CO\textsubscript{2}/CH\textsubscript{4}, the catalyst became inactive, oxidative for CO\textsubscript{2} reforming below CO\textsubscript{2}/CH\textsubscript{4} feeds.

Acknowledgments

The authors acknowledge the assistance of Dr. Félix Requejo with the collection and analysis of X-ray absorption data. Portions of this research were carried out at the Stanford Synchrotron Research Laboratory, a national user facility operated by Stanford University on behalf of the US Department of Energy, Office of Basic Energy Sciences. The authors acknowledge partial support by BP as part of the Berkeley-Caltech Methane Conversion Cooperative Program under the stewardship of Dr. Theo Fleisch. Howard Lacheen acknowledges with thanks the financial support of the Ford Corporation through the Ford Catalysis Fellowship administered by the Berkeley Catalysis Center.

References

[30] WinXAS, v. 2.1 licensed by T. Ressler, Fritz Haber Institut der MPG, Dept. of Inorganic Chem., Faradayweg 4-6, D-14195, Berlin, Germany (email: t_ressler@winxas.de).