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Stability, structure, and oxidation state of Mo/H-ZSM-5 catalysts during reactions of CH_4 and CH_4–CO_2 mixtures

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Abstract

$Mo_2O_5{}^{2+}$-ZSM-5 ($Mo/Al_f = 0.4$, $Si/Al_f = 20$) samples prepared by sublimation of MoO_3 were carburized in CH_4 to form MoC_x clusters active in CH_4 pyrolysis and then exposed to different CO_2/CH_4 mixtures. CO_2/CH_4 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 CO_2. Below CO_2/CH_4 ratios of 0.1, the catalyst bed can be described as a CO_2-reforming and pyrolysis reactor in series. In the first segment of the bed, where CO_2 is present, pyrolysis is completely suppressed by reverse Boudouard reactions; pyrolysis reactions begin after CO_2 is completely consumed. CO_2 cannot directly influence rates or deactivation for pyrolysis reactions. Rather, the greater stability observed with CO_2-containing reactants arises solely from the presence of H_2, formed in the CO_2-reforming section, in the pyrolysis regions within the catalyst bed. The evolution of catalyst structure and composition in CO_2/CH_4 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 CO_2/CH_4 ratios greater than 0.1. MoC_x-ZSM-5 samples exposed to CO_2/CH_4 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 MoC_x-ZSM-5 increased from 0.2 to 1.9 eV (relative to Mo^0) after contact with 0.025 CO_2/CH_4 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 MoO_x structures. Radial structure functions resemble those for samples exposed to pure CH_4, which consist of 0.6-nm MoC_x clusters, but show an additional Mo–O coordination shell also detected in bulk β-Mo_2C exposed to ambient air. These data suggest that the inhibition and ultimate suppression of catalytic pyrolysis reactions with CO_2 addition reflect the oxidation of active MoC_x structures, the extent of which increases with increasing CO_2/CH_4 reactant ratios. CO_2/CH_4 reactant ratios above 0.1 lead to conversion of MoC_x to MoO_x structures, which are inactive for both reforming and pyrolysis reactions of CH_4, but which reform active MoC_x after an induction period when exposed to pure CH_4 reactants at reaction conditions.

Keywords: Molybdenum; Carbides; ZSM-5; MFI; CO_2; CH_4; 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 Mo^{6+} salts leads to near-equilibrium yields of ethene, ethane, and benzene during nonoxidative CH_4 reactions with low selectivities for larger unsaturated products, apparently because of steric constraints imposed by MFI channels. MoO_x precursors were shown to form carbide clusters during initial contact with CH_4 at 950 K [16]; these clusters provide the catalytic surfaces required for activation of C–H bonds in CH_4 and for removal of H-atoms as H_2 during both CH_4 conversion to C_2 molecules and sequential conversion of these primary C_2 products to arenes [17]. The exchange of acidic protons with D_2 [18], together with Raman spectroscopy and multiple-scattering simulations of the extended

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fine structure in X-ray absorption spectra [19], provided direct evidence that Mo(VI)-oxo dimers form at exchange sites during sublimation of MoO_3/H-ZSM-5 physical mixtures. These Mo-oxo dimers subsequently convert to active MoC_x structures during CH_4 reactions.

Mo-ZSM-5 catalysts deactivate during nonoxidative CH_4 reactions [20–22] via carbon deposition processes, which become slower as external acid sites on zeolite crystals are selectively titrated by bulky organosilanes [23]. CO_2/CH_4 mixtures lead to slower deactivation than pure CH_4 reactants [24,25], an observation attributed to continuous carbon removal via

$$CO_2 + C^* \rightarrow 2CO + {}^*. \tag{1}$$

A sudden loss of catalytic activity above a threshold CO_2/CH_4 reactant ratio (~ 0.06), reversed upon removal of CO_2 from the CH_4 reactant stream, has also been reported [26]. This sudden but reversible deactivation in CO_2/CH_4 feeds appears to reflect the oxidation of MoC_x instead of carbon deposition processes prevalent with pure CH_4 reactants [27]. At CO_2/CH_4 ratios below these threshold values, CH_4 conversion rates were lower but more stable than those obtained with pure CH_4 reactants. These lower rates reflect, at least in part, kinetic and thermodynamic inhibition by H_2 formed in CH_4–CO_2 reforming reactions; H_2 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 CO_2 as a reactant. Green et al. [28] examined CO_2 reforming on bulk Mo_2C and WC and proposed that CO_2 dissociates at carbon vacancies to form a steady-state concentration of chemisorbed oxygen (O^*) at carbide surfaces. High O^* thermodynamic activities, prevalent at high CO_2/CH_4 ratios, can lead to Mo_2C oxidation to less reactive MoO_x species.

Here we probe CH_4 pyrolysis catalysis and deactivation pathways on carburized $Mo_2O_5{}^{2+}$-ZSM-5 at low CO_2 concentrations by rigorously isolating and examining the kinetic and thermodynamic effects of CO_2 on measured reaction rates. Kinetic factors contributing to decreased hydrocarbon formation rates such as C^* scavenging by CO_2 and H_2 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 CO_2/CH_4 mixtures is due to H_2 alone and not, as previously proposed, CO_2 [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 CH_4 reactants with low CO_2 concentrations and to identify processes leading to the observed effects of CO_2 on the catalytic rates, selectivity, and ultimate reversible deactivation of active Mo-based structures at high CO_2 concentration.

2. Experimental

2.1. Catalyst synthesis

We prepared H-ZSM-5 from Na-ZSM-5 ($Si/Al_f = 20$, Zeochem; Al_f = framework Al) by heating Na-ZSM-5 (2 g) to 823 K at 0.083 $K\,s^{-1}$ in He (2.5 $cm^3\,s^{-1}\,g^{-1}$ Airgas, UHP) and holding at 823 K for 2 h in dry air (2.5 $cm^3\,s^{-1}\,g^{-1}$ 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 NH_4-ZSM-5 by ion exchange with 1 L of $NH_4NO_{3,aq}$ (1 M, Fisher, Cert. ACS) at 353 K for 12 h, followed by washing with 2 L of deionized H_2O. This exchange procedure was carried out three times with fresh solutions; samples were then dried for 12 h at 400 K in ambient air. NH_4-ZSM-5 (5 g) was converted to H-ZSM-5 by heating in 0.5 $cm^3\,s^{-1}\,g^{-1}$ dry air to 773 K at 0.167 $K\,s^{-1}$ and holding for 24 h. H-ZSM-5 and MoO_3 (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_f 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% O_2/He to remove water and to spread MoO_3 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 $Mo_2O_5{}^{2+}$-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 CH_4 and CH_4–CO_2 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% CH_4/Ar (Matheson, UHP, purified with a Matheson MTRP-0019-XX oxygen-moisture trap; 1 bar total pressure, 0.208 $cm^3\,s^{-1}$) mixed with 50% CO_2/He (Matheson, UHP) or H_2 (Airgas, UHP). We held CH_4 partial pressures constant (91 kPa) when using CO_2 or H_2 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. CH_4, Ar, CO, CO_2, and H_2 were separated with a packed column (Agilent Porapak Q, 4.5 m) connected to a thermal conductivity detector. CH_4 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 CH_4 molecules appearing as each product. Unreactive residues or nonvolatile products remaining on catalysts or transfer lines were determined by difference and reported as C_{12+}. CO selectivities are reported as the percentage of the CH_4 converted and appearing as CO (using half the total CO formed, i.e., excluding CO formed in Eq. (1)); in this way,