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CH_4 dehydroaromatization on Mo/H–ZSM-5: 1. Effects of co-processing H_2 and CH_3COOH

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ABSTRACT

The co-processing of acetic acid with methane ($CH_3COOH/CH_4 = 0.04–0.10$) on Mo/ZSM-5 formulations at 950 K and atmospheric pressure in an effort to couple deoxygenation and dehydrogenation reaction sequences results instead in a stratified reactor bed with upstream CH_4 reforming with acetic acid and downstream CH_4 pyrolysis. X-ray absorption spectroscopy and chemical transient experiments show that molybdenum carbide is formed inside zeolite micropores during CH_4 reactions. The introduction of acetic acid oxidizes a fraction of these carbide moieties upstream while producing H_2 and CO mixtures until completely consumed. Forward rates of CH_4 pyrolysis are unperturbed in the presence of an acetic acid or hydrogen co-feed after rigorously accounting for the reversibility of pyrolysis rates and the fraction of molybdenum carbide oxidized by CH_3COOH implying that all consequences of CH_3COOH and H_2 co-feeds can be interpreted in terms of an approach to equilibrium.

1. Introduction

Natural gas has been purported to be a feedstock for the production of commodity chemicals and fuels currently produced from crude oil [1,2]. Methane, the primary component of natural gas, is chemically inert and its conversion to higher hydrocarbons involves the creation of C–C bonds and H_2 elimination [1,2]. A representative pathway for the non-oxidative conversion of methane is dehydroaromatization (DHA) via high-temperature pyrolysis over catalytic surfaces.

Wang et al. originally reported that H–ZSM-5 modified by aqueous molybdenum oxide leads to near-equilibrium concentrations of aromatics and ethylene during non-oxidative CH_4 reactions at 973 K [3]. Further investigations of CH_4 DHA reactions on Mo encapsulated ZSM-5 catalysts at temperatures ~950 K have reported 8–10% CH_4 conversion with greater than 70% selectivity to benzene and stable catalytic performance at extended reactions times (16 h) [4–13]. Substitution of high-valent metal-oxo species from aqueous solutions into cation exchange sites is limited due to the large size and multiple charge of solvated polyanion clusters, which impair diffusion within zeolite channels at pH levels required for stable aluminosilicate frameworks [14–16]. Borry et al. developed a vapor-phase exchange process that can be used to support Mo oxides (MoO_x) in zeolites to combat this issue [12]. Kim et al. reported a 1:1 Mo/Al stoichiometry corresponding to ion-exchange with Brønsted acid sites using vapor-phase exchange [11]. Hexa-valent Mo forms dimeric $(Mo_2O_5)^+$ species upon vapor-phase ion-exchange with two neighboring Al centers as evidenced by the incomplete exchange of Mo on all Al sites and the presence of residual protons as well as characteristic Raman and X-ray absorptions in these samples [11,12,17]. Upon exposure to CH_4 at 973 K, an induction period is observed in which MoO_x is carburized to form carbidic Mo (MoC_x) with oxygen removed as CO, CO_2, and H_2O as reported by Iglesia et al. and Bao et al. [11,18,19]. Ding et al. reported that $Mo_2O_5^+$ dimers reduce during carburization to form small (0.6–1 nm) MoC_x clusters, similar to the channel diameter within ZSM-5 (0.55 × 0.57 nm), with a fraction of the acidic OH groups, initially exchanged with MoO_x dimers, being regenerated [20]. These small MoC_x clusters contain ~10 Mo atoms and are shown to be stable and to resist sintering or migration to external surfaces during high-temperature (~950 K) CH_4 reactions for several hours [20]. The presence and catalytic involvement in the activation of C–H bonds of these MoC_x clusters has been evidenced by X-ray absorption, X-ray photoelectron, infrared, and NMR spectroscopic investigations [20–23].

Mo–ZSM-5 catalysts have been shown to deactivate during non-oxidative CH_4 DHA reactions due to deposition of

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carbonaceous species [8,24]. Ichikawa et al. reported that a co-feed of CO_2 with CH_4 led to improved stability of the Mo–ZSM-5 catalysts at extended times on stream and postulated that this enhanced stability was due to CO_2 reacting with deactivating carbon species by the reverse Boudouard reaction [25,26]. Liu et al. studied the effects of co-feeding CO_2, CO, and H_2 with CH_4 and reported a drastic cessation of catalytic activity at higher CO_2 pressures ($CO_2/CH_4 > 0.075$) due to oxidation of the active MoC_x species [27]. CO co-feed (CH_4/CO ratio) had no effect on the rate and selectivity of CH_4 DHA reactions. Liu concluded that the presence CO was not responsible for the decrease in reaction rates during CO_2 co-feeding experiments. H_2 co-feed (CH_4/H_2 ratio) led to decreased hydrocarbon formation rates attributed to the reversibility of CH_4 pyrolysis reactions [27].

Methane DHA to benzene at 950 K is equilibrium limited to ~10% conversion with MoC_x clusters activating C–H bonds to remove H-atoms as H_2 and acid sites providing centers for carbon chain growth. Yu et al. postulated that hydrogen removal is the limiting factor in light alkane dehydrogenation reactions on proton- and metal-modified ZSM-5 formulations [28] and that this H-desorption bottleneck results in a very high chemical potential of hydrogen on the surface of the catalyst. Iglesia and co-workers have exploited this phenomenon by using propane as the hydrogen source in hydrodesulfurization reactions over Zn–ZSM-5 catalysts [29–32]. Here, we seek to extend this concept of heteroatom removal reactions by using methane in deoxygenation reactions of low molecular weight oxygenates using MoC_x/ZSM-5 formulations. Co-processing CH_4 with acetic acid using Mo/H–ZSM-5 catalysts results in a staged reactor bed with a fraction of the bed upstream being oxidized by acetic acid to form CO/H_2 mixtures in reforming reactions of CH_4 and the remaining fraction downstream accomplishing CH_4 DHA reactions in presence of the H_2 and CO produced upstream. Forward rates for CH_4 DHA are invariant with respect to catalyst loading and H_2 pressure in presence of hydrogen and acetic acid co-feeds. This research highlights a critical limitation in attempting to couple deoxygenation and dehydrogenation chemistries on Mo/ZSM-5 formulations by co-processing oxygenates and CH_4 – the preferential selectivity to remove oxygen as CO instead of as H_2O.

2. Materials and methods

2.1. Catalyst preparation

A ZSM-5 (Si/Al = 11.7, CBV 2314) zeolite sample was obtained from Zeolyst International in its ammonium form. The silicon-to-aluminum ratio was determined by elemental analysis (Analytical Geochemistry Lab, University of Minnesota). NH_4–ZSM-5 was converted to H–ZSM-5 by treating in dry air (0.67 $cm^3\ s^{-1}$ at NTP conditions, UHP, Minneapolis Oxygen) to thermally decompose NH_4^+ to H^+ and $NH_{3(g)}$ by increasing the temperature from ambient to 773 K at 0.0167 K s^{-1} and holding at 773 K for 10 h. H–ZSM-5 and MoO_3 powders (Sigma–Aldrich, 99.9%) were ground together in an agate mortar and pestle for 0.5 h to form intimate mixtures containing a Mo to Al_f ratio of 0.25. The mixture was heated from ambient to 623 K at 0.0167 K s^{-1} and soaked at this temperature for 16 h in dry air (0.67 $cm^3\ s^{-1}$) to remove water and to disperse MoO_3 on the zeolite's external surface [12,17]. Subsequently, the mixture was heated to 973 K at 0.167 K s^{-1} and soaked at this temperature for 10 h to facilitate molybdenum oxide migration into the zeolite pores [17]. After treatment, the molybdenum-to-aluminum ratio was determined by elemental analysis (Analytical Geochemistry Lab, University of Minnesota). The catalysts were pressed to form pellets which were then crushed and sieved to attain particle sizes between 180 and 425 μm (40–80 mesh) for subsequent use in catalytic reactions.

2.2. Catalytic reactions of CH_4 dehydroaromatization

CH_4 dehydroaromatization reactions were conducted with 0.1–1.0 g of catalyst in a fixed bed, tubular quartz reactor (10 mm inner diameter) at atmospheric pressure and 950 K. The catalyst bed was made stationary by a porous quartz frit. Prior to conducting DHA reactions, catalyst samples were pretreated, to remove water, in Ar (0.21 $cm^3\ s^{-1}$, UHP, Minneapolis Oxygen) by increasing the temperature from ambient to 950 K at 0.167 K s^{-1}. Reactor temperature was set by a split tube furnace (Applied Test System, Series 3210) controlled by an Omega temperature controller (CN7823) with K-type thermocouple feedback (Omega Engineering). A feed gas mixture of CH_4/Ar (90% CH_4 and 10% Ar, 0.21 $cm^3\ s^{-1}$ corresponding to CH_4 space velocity of 684 $cm^3\ g_{cat}^{-1}\ h^{-1}$, UHP, Matheson Tri-Gas) was introduced to the reactor with Ar serving as the internal standard. Liquid acetic acid (AA) (1.52×10^{-7}–4.57×10^{-7} -mol s^{-1}, Fluka, >99.8%) was introduced to flowing gas streams using a liquid infusion pump (Model 100, KD Scientific) and vaporized at 473 K in heated transfer lines. Transfer lines were kept at 473 K to ensure that no condensation of liquid reactants or products occurred. AA or H_2 (5.83×10^{-3}–2.20×10^{-2} $cm^3\ s^{-1}$, UHP, Minneapolis Oxygen) were co-fed with CH_4 once the catalyst was fully carburized and the benzene formation rate reached steady-state, typically after 0.3–3.0 h depending on the catalyst loading. He (1.00×10^{-2}–2.20×10^{-2} $cm^3\ s^{-1}$, UHP, Minneapolis Oxygen) was introduced to the inlet gas feed as an inert for constant CH_4 partial pressure experiments. The reactor effluent was sent via heated transfer lines to a gas chromatograph (GC) (Agilent 7890) equipped with two capillary columns: a bonded polystyrene–divinylbenzene column (HP-PLOT/Q, 30.0 m × 0.32 mm × 0.5 μm, Agilent) connected to a thermal conductivity detector to separate and analyze permanent gases and a (5%-phenyl)-methylpolysiloxane column (HP-5, 30.0 m × 0.32 mm × 0.5 μm, Agilent) connected to a flame ionization detector to separate and analyze hydrocarbons. Ar, serving as the internal standard, was used to calculate CH_4 conversion as well as product formation rates and selectivity. Product selectivity was calculated on a carbon atom basis considering all carbon-containing products with Eq. (1) and *i* as a carbon-containing species, *n* the number of carbon atoms in species *i*, and *F* the molar flow rate. Transient product evolution throughout the course of the reaction was measured with an online mass spectrometer (MS) (MKS Cirrus 200 Quadrupole MS system) connected to the outlet of the GC. The number of removed O atoms during carburization of molybdenum oxide was determined by the cumulative amount of H_2O, CO, and CO_2 as calculated from the transient MS signal. Product formation rates (mol [product] (g-atom Mo s)$^{-1}$) are reported as measured net rates or forward rates, as discussed in Section 3.3.

$$\%S_i = \frac{n_i * F_i}{\sum_i n_i * F_i} \tag{1}$$

2.3. Chemical titration of Brønsted acid sites using dimethyl ether

Chemical titration using dimethyl ether (DME) was performed to determine the number of free Brønsted acid sites on H–ZSM-5 and MoO_x/H–ZSM-5 at various degrees of carburization [33]. The number of accessible acid sites during DHA reactions was investigated by titrating MoC_x/H–ZSM-5 samples at different carburization times (0.1–3.0 h). The samples (0.1 g) were treated in He (0.33 $cm^3\ s^{-1}$, UHP, Minneapolis Oxygen) by increasing the temperature from ambient to 773 K at 0.167 K s^{-1}, soaking for 1 h, and subsequently cooling the sample to 423 K in He flow. A mixture of 50% DME/1% CH_4/49% Ar (UHP, Praxair) was introduced (0.25 cm^3 per pulse) to the catalyst sample by He (0.67 $cm^3\ s^{-1}$)