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## Kinetic modeling of methane dehydroaromatization chemistry on Mo/Zeolite catalysts in packed-bed reactors

Canan Karakaya, Huayang Zhu, Robert J. Kee\*

Mechanical Engineering, Colorado School of Mines, Golden, CO 80401, USA

## HIGHLIGHTS

- Detailed reaction mechanism for methane dehydroaromatization on Mo/H-ZSM5 catalysts.
- 50-step reaction mechanism represents bifunctional catalysis on Mo<sub>2</sub>C and zeolite-acid sites.
- Model is validated using previously published data from packed-bed reactors.

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## ABSTRACT

This paper develops a detailed chemical kinetics reaction mechanism to represent methane dehydroaromatization (MDA) chemistry on bi-functional Mo/zeolite catalysts. The model is validated using a range of previously published results from packed-bed experiments. The reaction mechanism consists of four methane activation reactions on Mo<sub>2</sub>C sites. The resulting gas-phase hydrogen and ethylene continue to react on Brønsted acid sites within the zeolite structure using 46 reaction steps. In addition to the desired benzene formation, the model also predicts the formation of toluene, naphthalene, and other side products. In addition to reaction kinetics on the catalyst surfaces, the packed-bed model incorporates a Dusty-Gas model that accommodates ordinary and Knudsen diffusion as well as pressure-driven advection. Because the model represents essentially all published reports of MDA performance, it is reasonably expected that the model can be applied as a predictive tool to support reactor and process development.

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## 1. Introduction

The object of this paper is to develop and validate a detailed micro-kinetic reaction mechanism that represents the methane dehydroaromatization (MDA) to produce benzene. The specific focus is on the chemistry and performance of bi-functional molybdenum-zeolite catalysts. The approach in this paper is concerned primarily with modeling, but the results are validated using previously published experimental results from packed-bed reactors (Wong et al., 2012; Yao et al., 2008; Korobitsyna et al., 2013; Lu et al., 2010; Cui et al., 2011).

Recent advances in discovery and recovery technologies are contributing to increasing the abundance and lowering the cost of natural gas. In addition to direct use such as in combustion, there is increasing interest in using natural gas for the production of liquid fuels and fine chemicals. Oxidative coupling of methane to produce ethylene is one route to fuels synthesis. Indirect processes, such as

Fischer–Tropsch, are well known and commercially practiced. However, in principle, non-oxidative dehydrogenation processes can be more efficient.

In 1993 Wang et al. discovered that methane can be converted to aromatics using a Mo/H-ZSM5 catalyst in a continuous flow packed-bed reactor (Wang et al., 1993). These results demonstrated the production of H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> under non-oxidative conditions at elevated temperatures and atmospheric pressure. Globally, the process can be represented as



Although MDA is thermodynamically limited (i.e., equilibration of Eq. (1) limits conversion), high C<sub>6</sub>H<sub>6</sub> selectivity can be obtained. Following Wang's initial paper, numerous studies have reported the effects of reaction conditions (Honda et al., 2003; Yao et al., 2008; Zaikovskii et al., 2006; Cui et al., 2011) as well as the catalyst functionality (Borry et al., 1999; Kim et al., 2000; Ding et al., 2001; Liu et al., 2012) to increase selectivity and yield. Recent review papers discuss current MDA technology and future prospects (Ma et al., 2013; Majhi et al., 2013).

\* Corresponding author. Tel.: +1 303 273 3379.

E-mail address: [rjkee@mines.edu](mailto:rjkee@mines.edu) (R.J. Kee).

The MDA process is usually based on bifunctional transition-metal-incorporated zeolite catalysts. Although a variety of transition metals (e.g., Mo, W, Re, V, Ga) have been incorporated into zeolite structures (e.g., H-ZSM5), Mo is found to have the best MDA performance in terms of benzene selectivity. The reaction is typically carried out at temperatures in the range of 700 °C–800 °C, with typical Mo loading in the range of 1%–15% (Aboul-Gheit and Awadallah, 2009; Lu et al., 2010; Cui et al., 2011). Methane conversion is typically in the range of 10%–12%, with the maximum thermodynamically possible conversion being around 14% at 700 °C.

Among the various Mo-doped zeolite structures, such as HSAPO-34, H-ZSM5, HY (Wong et al., 1996), HMCM-36 (Wu et al., 2005), HMCM-22 (Ma et al., 2001; Wong et al., 2012), and HMCM-49 (Wang et al., 2004), H-ZSM5 and HMCM-22 are found to be the most-selective catalysts for benzene formation (benzene selectivity is typically in the range of 50%–80%). The benzene selectivity is generally attributed to zeolite channel dimensions that are close to the atomic diameter of C<sub>6</sub>H<sub>6</sub> (Zhang et al., 1998). Despite high benzene selectivity, the overall reaction yield is low and formation of heavy aromatics and coke precursors is a common problem. Rapid catalyst deactivation can occur within a few hours. Although H-ZSM5 and HMCM-22 deliver similar benzene selectivity, the unique cage structure of HMCM-22 is found to be more tolerant to coke formation and catalyst fouling (Shu and Ichikawa, 2001).

Previous theoretical studies (e.g., density functional theory) concentrate at the atomic level on individual catalytic reactions at the zeolite acid site (Zhou et al., 2007; Nguyen et al., 2011; Zhou et al., 2012). However, there has been relatively little research on the development of comprehensive and detailed kinetics for the MDA process. Wong et al. proposed a multi-step reaction scheme for the formation of aromatics over Mo/HMCM-22 and Mo/H-ZSM5 catalysts (Wong et al., 2012). However, that paper did not report a unique set of rate expressions for the detailed reaction steps. Rather, a regression analysis was used to adjust individual reaction-rate parameters for different reactor operating conditions. The present paper begins with the general reaction pathways proposed by Wong et al. but goes on to develop a more detailed and quantitative reaction mechanism (Wong et al., 2012). Rate expressions for individual reaction steps are determined such that the mechanism represents a wide range of published experimental measurements.

## 2. Practical aspects of MDA processes

Because of unavoidable catalyst deactivation by carbon deposits, practical MDA processes must contend with some inherent transient behaviors. Fig. 1 qualitatively illustrates a typical operating cycle. The catalyst is initially fabricated as a mixture of Mo and zeolite particles, which in this form have very little catalyst activity. During an induction period, methane flowing over the catalyst carburizes the Mo, forming a molybdenum-carbide complex on the

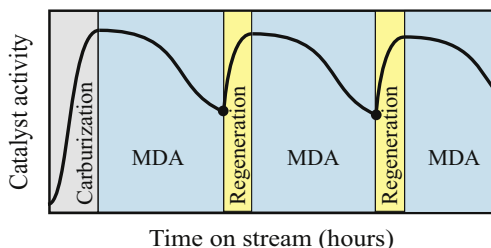


Fig. 1. Qualitative illustration of transient catalyst activity in an overall gas-to-liquid cycle using MDA.

zeolite surface. After the desired catalyst activity is achieved during the carburization induction period, the MDA process begins. However, in addition to producing the desired benzene and hydrogen, carbon deposits act to degrade the catalyst activity. At some point (typical on the order of hours), the catalyst is degraded to the point that it must be regenerated. Regeneration, using, for example H<sub>2</sub>, can remove deposits and restore the activity to nearly the initial activity that was achieved after the initial Mo carburization. Thus, the MDA process can be resumed, but with the accompanying carbon-deposit deactivation behavior. The MDA and regeneration cycles can be repeated numerous times (Ma et al., 2013).

The present paper is specifically focused on the nominally steady performance (few hours) before the catalyst activity is significantly degraded. The paper is not concerned with the kinetics of the Mo-carburization process or the regeneration chemistry. Experimental MDA catalyst performance is typically reported during the quasi-steady period before catalyst deactivation. Such published results are used in the present model development and validation. It must be understood that the “steady” behavior is approximate, but usually persists for a few hours. Although carburization, degradation, and regeneration are clearly important to practical technology and are scientifically interesting, the kinetics for these processes are outside the scope of the present paper.

## 3. Bi-functional Mo/H-ZSM5 catalyst

It is now well established that MDA takes place on bi-functional Mo/zeolite catalysts. Methane is first activated on Mo sites, primarily forming H<sub>2</sub> and small olefins (C<sub>x</sub>H<sub>2x</sub>). The aromatization process continues on zeolite acid sites by hydride transfer, oligomerization, and β-scission reactions to form C<sub>6</sub>H<sub>6</sub>. Additionally, H<sub>2</sub> as well as side products including ethane (C<sub>2</sub>H<sub>6</sub>), toluene (C<sub>7</sub>H<sub>8</sub>), and naphthalene (C<sub>10</sub>H<sub>8</sub>) are formed (Wong et al., 2012).

### 3.1. Mo sites

Although it is generally established that CH<sub>4</sub> is first activated on the Mo sites, the specific Mo configuration, its oxidation state, its interaction with zeolite Brønsted acid site, and the dimerization kinetics are not completely understood. Nevertheless, it is clear that Mo structure and its catalytic activity depend on the synthesis method (Wong et al., 1996; Borry et al., 1999; Lacheen and Iglesia, 2005). The Mo/H-ZSM5 catalyst can be prepared by an impregnation method or by physically mixing MoO<sub>3</sub> with zeolite powders (Borry et al., 1999). Early studies suggested that MoO<sub>3</sub> is the catalytically active center where CH<sub>4</sub> dimerization occurs, forming C<sub>2</sub> olefins or paraffins and H<sub>2</sub> (Xu et al., 1995a, 1995b).

In a series of papers considering Mo/H-ZSM5, Iglesia and coworkers reported that the catalyst preparation method significantly affects the catalyst structure (Borry et al., 1999; Kim et al., 2000; Ding et al., 2001; Lacheen and Iglesia, 2005). For catalysts prepared by impregnation, the MoO<sub>3</sub> structure is formed initially during calcination at temperatures between 241 °C and 343 °C, with MoO<sub>3</sub> migrating into the zeolite channel. In the case of physical mixing, migration of MoO<sub>3</sub> into the zeolite channels takes place at higher temperatures (Borry et al., 1999; Lacheen and Iglesia, 2005). The Mo within the zeolite framework is determined to be in the form of a dimer (Mo<sub>2</sub>O<sub>5</sub>)<sup>2+</sup>, associating with two Brønsted acid sites (Ding et al., 2001). Monomeric bidentate (MoO<sub>2</sub>)<sup>2+</sup> with a single Mo atom is anchored into the cage structure through oxygen bridges (Ma et al., 2005). According to DFT simulations (Zhou et al., 2007; Xing et al., 2010), the particular Mo structure in monomeric or dimer form within zeolite framework is determined by the zeolite Si-to-Al ratios. For high Si-to-Al ratios, the monomeric bidentate (MoO<sub>2</sub>)<sup>2+</sup> is less stable than the dimer (Mo<sub>2</sub>O<sub>5</sub>)<sup>2+</sup>.

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