## Methane Activation by ZSM-5-supported Transition Metal Centers

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Methane Activation by ZSM-5-supported Transition Metal Centers

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Abstract.
This review focuses on recent fundamental insights about methane dehydroaromatization (MDA) to benzene over ZSM-5-supported transition metal oxide-based catalysts (MOₓ/ZSM-5, where M= V, Cr, Mo, W, Re, Fe). Benzene is an important organic intermediate, used for the synthesis of chemicals like ethylbenzene, cumene, cyclohexane, nitrobenzene and alkylbenzene. Current production of benzene is primarily from crude oil processing, but due to the abundant availability of natural gas, there is much recent interest in developing direct processes to convert CH₄ to liquid chemicals. Among the various gas-to-liquid methods, the thermodynamically-limited Methane DehydroAromatization (MDA) to benzene under non-oxidative conditions appears very promising as it circumvents deep oxidation of CH₄ to CO₂ and does not require the use of a co-reactant. The findings from the MDA catalysis literature is critically analyzed with emphasis on in situ and operando spectroscopic characterization to understand the molecular level details regarding the catalytic sites before and during the MDA reaction. Specifically, this review discusses the anchoring sites of the supported MOₓ species on the ZSM-5 support, molecular structures of the initial dispersed surface MOₓ sites, nature of the active sites during MDA, reaction mechanisms, rate-determining step, kinetics and catalyst activity of the MDA reaction. Finally, suggestions are given regarding future experimental investigations to fill the information gaps currently found in the literature.
1. Introduction

The current abundance of natural gas (NG) across the globe, from recent discoveries of large shale gas deposits in North America and methane hydrates beneath permafrost or in shallow sediments along deep-water continental margins, is projected to persist in the coming years due to improvements in both exploration and extraction technologies. Owing to the large surplus, NG is anticipated to serve as the primary energy resource in the transition period, as the global economies transition off oil-based energy generation to renewable energy-based economies of the future. Currently, however, NG is either used as the fuel for power generation and transportation or simply flared to the atmosphere, owing to a deficiency of industrially feasible on-site conversion processes. In the past decades, various attempts have been made to convert methane (CH$_4$), the primary component (~ 70-90%) of NG, to value-added products. A schematic summary of the direct CH$_4$ conversion methods to produce olefins, aromatics and commodity chemicals is presented in Figure 1. Among these processes, literature reports on the following can be found: methane to methanol and formaldehyde via partial oxidation (POM), (ii) methane to ethane and ethylene via oxidative coupling (OCM), (iii) methane to benzene via non-oxidative methane dehydro-aromatization (MDA, also known as DHA), (iv) methane to olefins, aromatics, and hydrogen (MTOAH), and methane to halogenated derivates via methane oxy-halogenation. Note that although there are various indirect processes to valorize CH$_4$ like the industrially employed syngas process, they are simply more capital intensive and exhibit a larger carbon footprint than potential direct conversion processes. Given that a significant portion of the total NG is located in stranded locations, building large scale syngas plants remains unfeasible, leading to hundreds of billions of cubic meters of NG being flared from a lack of direct conversion methods. In the past decade, policymakers have moved to reduce NG flaring practices across the globe by introducing
regulations and initiatives like the popular Zero Routine Flaring by 2030 initiative, further fueling the research on direct catalytic CH₄ valorization processes.

![Figure 1. Direct routes for CH₄ valorization.](image)

Metal oxides supported on ZSM-5 constitute an essential class of versatile catalysts that continues to receive both academic and industrial researchers’ attention owing to the various reactions they catalyze. For example, VOₓ/ZSM-5 catalysts have been studied for selective catalytic reduction (SCR) of NOₓ with NH₃, CrOₓ/ZSM-5 catalysts are effective for oxidative dehydrogenation (ODH) of ethane to ethylene with CO₂, MoOₓ/ZSM-5 have been investigated for non-oxidative methane dehydroaromatization (MDA) and partial oxidation of methane to formaldehyde, WOₓ/ZSM-5 have been examined for methane oxidation and non-oxidative MDA, ReOₓ/ZSM-5 have been studied for the conversion of ethane to benzene and MDA,
ZnOₓ/ZSM-5 catalysts have been found to catalyze the aromatization of alkanes and alcohols\textsuperscript{32}, etc. This review focuses on a subset of the broader zeolite catalysis literature, i.e., ZSM-5-supported transition metal oxides (MOₓ/ZSM-5) where M can be V, Cr, Mo, Re, W or Fe, specifically for MDA to produce benzene. Very recently, ZSM-5 supported group IX (CoOₓ/ZSM-5)\textsuperscript{33} and group X (NiOₓ/ZSM-5)\textsuperscript{34} catalysts have also been found to be active towards MDA reaction. However, they will not be covered in this review since presently little molecular-level information about these catalysts based on \textit{in-situ} and \textit{operando} characterization including Raman spectroscopy, X-ray absorption spectroscopy (XAS), etc is available.

MDA with supported MoOₓ/ZSM-5 catalysts was first reported in 1993.\textsuperscript{8} However, alkanes-to-benzene conversion using zeolite-based catalysts, in general, was actually pioneered in the period of 1974-1989 by a Russian group, which has largely been unrecognized.\textsuperscript{35–37} Compared to other direct, oxidative processes, the non-oxidative environment for benzene production from methane sparked great interest due to its high product selectivity. This pioneering work, since then, has inspired investigations of other similar catalyst systems composed of group V-VII transition metal oxides supported on zeolite.\textsuperscript{7} A few excellent reviews on methane dehydroaromatization (MDA) over zeolite supported transition metal oxide-based catalysts are available in literature\textsuperscript{38–41} and the readers are directed to go over them to gain more insights on the following: (i) development of various conventional (Mo-oxide based catalysts) and novel supported catalysts for MDA, including but not limited to the variation of the zeolite support material (e.g. ZSM-5, MCM-22, MCM-49, NU-87, TNU-9 etc.), (ii) the structure and nature of the active sites; (iii) thermodynamics of MDA reaction with associated MDA reaction mechanism and performance of various catalysts; and (iv) catalyst deactivation, coke formation and regeneration methods.
Despite extensive characterization studies reported on supported MOₓ/ZSM-5 catalysts, many fundamental details such as MOₓ anchoring sites, molecular and electronic structures of MOₓ and their responses to different reactive environments remain moot. The lack of consensus about the fundamental details of supported MOₓ/ZSM-5 catalysts is strongly related to limited in-situ studies since most of the characterization measurements were collected under ambient or ex-situ conditions where the samples are hydrated and not representative of the catalyst structures present under elevated temperatures and reactant gas(es).

The objective of this review is to critically analyze and summarize recent developments in MDA catalysis with emphasis on fundamental in-situ and operando spectroscopy studies in the literature on ZSM-5-supported metal oxide MOₓ (M=V, Cr, Mo, W, Re and Fe) catalysts. Specifically, this review discusses the anchoring sites of MOₓ, molecular and electronic structures of the supported MOₓ sites, the nature of the active catalytic site(s) before and during MDA, reaction kinetics, rate-determining steps, and reaction mechanism of MDA.

2. Anchoring sites of surface MOₓ species on ZSM-5 support.

A plethora of studies has focused on elucidating the location of the dispersed MOₓ sites in the zeolite matrix in ZSM-5-supported catalysts, given the variety of various anchoring sites possible, schematically described in Figure 2. Generally, (Al-OH⁺-Si) sites with IR band between 3608-3610 cm⁻¹ serve as the anchoring sites internally in the 10M pores of ZSM.Outside the pores on the zeolite’s surface, the Si-OH (sometimes denoted as Siex-OH in the literature) indicated by IR band at 3745 cm⁻¹, and Al-OH from extra framework Al (sometimes denoted as Alex in the literature) or Al₂O₃ nanoparticles with IR bands at 3660, 3783 cm⁻¹, respectively, can also serve as the anchoring sites.

It is generally agreed that the metal oxide sites anchor at either the Brønsted acid sites inside the zeolite channels (-Al-OH⁺-Si-) and/or at the external (-Siex-OH), with the
distribution between internal and external anchoring sites dependent on the synthesis method and Si/Al ratio. In past studies, the anchoring sites of supported MOₓ species (such as WOₓ, MoOₓ and ReOₓ) were determined from the titration of residual zeolite protons, where the MOₓ species were assumed to have only one type of site. In contrast, this section on the anchoring sites of supported metal oxides on ZSM-5, emphasized on insights generated via in-situ characterization of the catalysts under dehydrated conditions. Studies undertaken in ambient conditions will not be covered since such hydrated catalysts are not relevant to reaction conditions. A detailed discussion of the literature findings is given below, and a summary of anchoring sites for supported MOₓ/ZSM-5 catalysts is presented in Table 1.

Figure 2. Types of external and internal anchoring sites and their corresponding IR bands, present in H-ZSM-5 zeolite. Hydrogen atoms are not shown here for clarity.
**Supported VOₓ/ZSM-5.** The anchoring sites in VOₓ/ZSM-5 catalysts are affected by the preparation method, as confirmed via *in-situ* (room temperature measurements after high-temperature treatment, without exposing to air) spectroscopic techniques in various reports.⁹,⁴⁶,⁴⁷ Using IR spectroscopy (spectra collected at room temperature, under vacuum, after dehydration at 773 K), it was shown that the samples prepared by impregnation mainly led to the consumption of external silanol groups in the zeolite. In contrast, samples prepared via solid-state reaction of VCl₃ and H-ZSM-5 primarily resulted in the consumption of framework Brønsted acid sites. Moreover, a monotonic decrease in the framework Brønsted acid sites was observed, via *in-situ* IR spectroscopy, with an increase in the V/Al_{framework} ratio, along with complete consumption of external silanol groups during solid ion exchange by sublimation of VOCl₃ onto ZSM-5.⁴⁶ Stoichiometrically, the introduction of each V-atom replaced ~1 proton of the Brønsted acid sites (Al-(OH)^+^-Si) in the zeolite.

**Supported CrOₓ/ZSM-5.** An *in-situ* diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS)⁴⁸ characterization of supported CrOₓ/ZSM-5 (Si/Al=15) catalysts, synthesized by solid-state exchange of various chromium salts (Cr-nitrate, Cr-acetate, Cr-chloride, etc.) and ZSM-5, found that the CrOₓ species are mainly present at the Brønsted acid sites within the zeolitic pores, with a small amount of CrOₓ species present at the external silanol sites of the ZSM-5 support.⁴⁸ In contrast, a recent in-depth study⁴⁹ combining computational, *in-situ*, and *operando* spectroscopic characterization (IR, Raman, Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-vis DRS)) of supported CrOₓ/ZSM-5 catalysts with varying Cr-loading and Si/Al ratios found that CrOₓ species preferentially anchors at Si-OH sites on the external surface of the zeolite at higher Cr- weight loading (above 0.5 weight %) and when the Al-framework site concentration in ZSM-5 was low (Si/Al=140).⁴⁹
**Supported MoO₃/ZSM-5.** It is generally accepted in the literature that both framework Brønsted acid sites (Al-(OH)⁺-Si) and external silanol (Si-OH) groups serve as the anchoring sites for MoOₓ species on ZSM-5.⁵⁰,⁵¹ However, the migration of the MoOₓ between various surface hydroxyl anchoring sites is still unresolved. For example, it was reported from *in-vacuo-in-situ* IR measurements that MoOₓ is equally distributed at both framework Brønsted acid sites and silanol hydroxyls for low loading cases (< 3 wt.%) and preferentially anchored at framework Brønsted acid sites for dehydrated catalysts with 6% MoOₓ/ZSM-5 (Si/Al=25).⁵² In another *in-situ* IR spectroscopy study, on supported 2% MoOₓ/ZSM-5 (Si/Al=25) catalysts synthesized by impregnation, it was found that MoOₓ migrates from external silanols and extra-framework Al-OH hydroxyls to framework Brønsted acid sites Al-OH⁺-Si at elevated calcination temperatures.⁵³ Preparation from a physical mixture of MoO₃ and ZSM-5, however, indicates the presence of residual framework Brønsted acid sites Al-OH⁺-Si even after calcination at elevated temperatures, reflecting a synthesis-dependent anchoring of MoOₓ sites.⁴⁴,⁴⁵ It was also assumed that MoOₓ anchored as surface Mo₂O₅ dimers at two adjacent framework Brønsted acid sites, but no direct supporting spectroscopic information was provided about the structure of the MoOₓ species and the anchoring sites on ZSM-5.⁴⁴,⁴⁵ Moreover, the probability of finding two adjacent Al framework Brønsted acid sites required for anchoring surface dimeric Mo₂O₅ is very low according to Lowenstein’s rule.⁵⁴ Typically, framework Brønsted acid sites in 10M rings are either isolated or separated by at least two Si atoms as in Al-OH⁺-Si-O-Si-OH⁺-Al.⁵⁵ Therefore, enough paired Al-OH⁺-Si-OH⁺-Al sites will not be present for anchoring at high loadings of MoOₓ on ZSM-5 making the anchoring of such dimeric sites very unlikely. More recently, systematic computational and experimental studies on supported MoOₓ/ZSM-5 catalysts have conclusively elucidated the anchoring sites as a function of Mo loading and zeolite Si/Al ratio with *in-situ* IR.⁴²,⁵⁶
spectra demonstrated that the MoO\textsubscript{x} species preferentially anchor at zeolitic Brønsted acid sites for low Mo oxide loading and anchor to external Si-OH sites for higher Mo loadings, indicating external Si-OH sites can also serve as additional anchoring sites. In addition, Mo deposition can also cause some dealumination of the zeolite framework, and a small fraction of MoO\textsubscript{x} can also anchor on the extra-framework Al-OH sites.\textsuperscript{42,56} These findings were also corroborated by a recent \textit{in-situ} IR spectroscopy study.\textsuperscript{57} The MoO\textsubscript{x} sites, generated by physical mixing of MoO\textsubscript{3} and H-ZSM-5 followed by calcination, were found to anchor at Brønsted acid sites of the ZSM-5 support.\textsuperscript{57} Consequently, the surface MoO\textsubscript{x} anchor at multiple surface hydroxyls and not selectively at one kind of surface hydroxyl.

**Supported WO\textsubscript{x}/ZSM-5.** \textit{In-situ} IR study shows that the anchoring sites for WO\textsubscript{x} species on ZSM-5 support depends on the preparation method.\textsuperscript{9} For WO\textsubscript{x}/ZSM-5 catalyst prepared by the solid-state ion exchange method, the Brønsted acid sites Al-OH\textsuperscript{+}-Si were mainly affected, suggesting anchoring of WO\textsubscript{x} species on these sites. The catalysts prepared by the impregnation method, however, were found to be mostly anchored at the external Si-OH surface hydroxyls. In another study\textsuperscript{58}, where the supported WO\textsubscript{x}/ZSM-5 catalyst was prepared by incipient-wetness impregnation of (NH\textsubscript{4})\textsubscript{2}WO\textsubscript{4} (dried at 393 K for 2 h and calcined at 773 K for 5 h), the effect of WO\textsubscript{x} on the Brønsted acidity of ZSM-5 was probed with NH\textsubscript{3}-temperature programmed desorption (TPD). Only a small change in the desorption temperature and peak intensity for NH\textsubscript{3} desorption was noticed, suggesting WO\textsubscript{x} might be anchored to the Bronsted acid sites of the H-ZSM-5 (Si/Al=38) support. This indirect characterization method, however, was unable to distinguish between Brønsted acidity of the ZSM-5 support and new Bronsted acid sites that might have been created by anchoring of the WO\textsubscript{x} species (3 wt.% WO\textsubscript{x}, prepared by incipient-wetness impregnation). A different study proposed that the WO\textsubscript{x} species requires two framework Brønsted
acid sites on ZSM-5.\textsuperscript{31} However, this conclusion was solely based on titration of the residual protons of ZSM-5 support and lacked any direct spectroscopic supporting evidence. In conclusion, identification of anchoring sites in WO\textsubscript{x}/ZSM-5 catalysts is, thus, pending modern \textit{in-situ} characterization measurements.

**Supported ReO\textsubscript{x}/ZSM-5.** The anchoring sites of dispersed ReO\textsubscript{x} for supported ReO\textsubscript{x}/ZSM-5 catalysts have received limited attention. \textit{In-situ} IR studies reported that supported ReO\textsubscript{x} species preferably anchor at the zeolitic Brønsted acid sites, with a small amount of ReO\textsubscript{x} species also anchoring at the external silanols.\textsuperscript{24,59,60} \textit{In-situ} XAS data in the report corroborated the presence of isolated ReO\textsubscript{4} in ReO\textsubscript{x}/ZSM-5\textsuperscript{24}, while no direct evidence regarding the proposed dimeric Re\textsubscript{2}O\textsubscript{y} species\textsuperscript{59} could be found in the literature. Furthermore, it should be noted that dimeric Re\textsubscript{2}O\textsubscript{y} species are volatile\textsuperscript{61,62} and will not remain on the catalyst surface upon formation, especially at elevated temperatures.\textsuperscript{63,64}

**Supported FeO\textsubscript{x}/ZSM-5.** The surface FeO\textsubscript{x} species of the supported FeO\textsubscript{x}/ZSM-5 catalysts were found to be anchored within the zeolitic pores of ZSM-5 and are dependent on the preparation method. Chemical vapor deposition of FeCl\textsubscript{3}, followed by washing and calcination, results in dispersed FeO\textsubscript{x}/ZSM-5 catalysts at high Fe loading.\textsuperscript{65,66} The \textit{in-situ} IR results of these catalysts revealed that the FeO\textsubscript{x} species anchored at the framework Brønsted acid sites. Other studies employing solid-state ion exchange and \textit{in-situ} IR revealed the consumption of framework Brønsted acid sites upon anchoring of FeO\textsubscript{x}.\textsuperscript{9,67} In contrast, \textit{in-situ} IR data of the supported FeO\textsubscript{x}/ZSM-5 catalysts, prepared by the impregnation method, evidenced the preferential anchoring of FeO\textsubscript{x} species at external Si-OH sites.\textsuperscript{9}

**Table 1.** Reported anchoring sites of surface MO\textsubscript{x} species in supported MO\textsubscript{x}/ZSM-5 catalysts based on IR spectroscopy.
### Catalysts, Synthesis Methods, and Reported Anchoring Sites

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<th>Synthesis Method</th>
<th>Reported anchoring sites</th>
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<tr>
<td></td>
<td>Solid-state ion exchange</td>
<td>-Al-OH&lt;sup&gt;+&lt;/sup&gt;-Si-</td>
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<td>CrO&lt;sub&gt;x&lt;/sub&gt;/ZSM-5</td>
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<td>-Al&lt;sub&gt;ex&lt;/sub&gt;-OH&lt;sup&gt;+&lt;/sup&gt;-Si-</td>
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<td>Secondary: -Si&lt;sub&gt;ex&lt;/sub&gt;-OH</td>
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<td>Incipient wetness impregnation of (Cr(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;·9H&lt;sub&gt;2&lt;/sub&gt;O)</td>
<td>-Si&lt;sub&gt;ex&lt;/sub&gt;OH and -Al-OH&lt;sup&gt;+&lt;/sup&gt;-Si-</td>
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<td>MoO&lt;sub&gt;x&lt;/sub&gt;/ZSM-5</td>
<td>Incipient-wetness impregnation of (NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;Mo&lt;sub&gt;7&lt;/sub&gt;O&lt;sub&gt;24&lt;/sub&gt;</td>
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<td>Solid state ion exchange</td>
<td>-Al-OH&lt;sup&gt;+&lt;/sup&gt;-Si-</td>
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<td>Thermal spreading of MoO&lt;sub&gt;3&lt;/sub&gt; onto ZSM-5</td>
<td>-Al-OH&lt;sup&gt;+&lt;/sup&gt;-Si-</td>
<td>57</td>
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<td>Incipient-wetness impregnation of (NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;Mo&lt;sub&gt;7&lt;/sub&gt;O&lt;sub&gt;24&lt;/sub&gt;·4H&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>Incipient-wetness impregnation of (NH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;WO&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>ReO&lt;sub&gt;x&lt;/sub&gt;/ZSM-5</td>
<td>Vapor-phase exchange of Re&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;7&lt;/sub&gt;</td>
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<td>FeO&lt;sub&gt;x&lt;/sub&gt;/ZSM-5</td>
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<td>Solid state ion exchange</td>
<td>-Al-OH&lt;sup&gt;+&lt;/sup&gt;-Si-</td>
<td>9,67</td>
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<td>Incipient wetness impregnation of Fe(NO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;·9H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-Si&lt;sub&gt;ex&lt;/sub&gt;-OH</td>
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### 3. Nature of surface MO<sub>x</sub> sites in supported MO<sub>x</sub>/ZSM-5 catalysts before MDA.

Various literature reports for ZSM-5 supported MO<sub>x</sub> catalysts discuss the nature of metal oxide sites within the zeolitic pores. Typically, *in-situ* and *operando* spectroscopic techniques such as Raman, UV-vis DRS, XAS, etc. have been used to directly probe the structure of the dehydrated and oxidized MO<sub>x</sub> sites before MDA. Earlier non-spectroscopic characterization studies employing the indirect method of titration of surface hydroxyls, however, have also been applied to propose the structure of the MO<sub>x</sub> sites on ZSM-5. A case-by-case discussion of the nature of...
surface MOₙ sites before MDA in group V-VII metal oxides/ZSM-5 catalysts is given in the following subsections. The reader should keep in mind that the nature of sites in supported heterogenous catalysts has historically remained controversial in the broader catalysis field because of different approaches employed in trying to assign supported MOₓ structures. For example, the question of isolated versus dimeric/oligomeric active sites has been heavily debated with regards to CrOₓ/SiO₂-type Phillips catalysts. Simple titration study of Si-OH groups by CrOₓ suggested the co-existence of both isolated CrO₄ and dimeric Cr₂O₇ species on SiO₂. More recent characterization studies employing direct advanced in-situ spectroscopic characterization, however, conclude that only isolated surface CrOₓ sites are present on the SiO₂ support. Likewise, no consensus exists regarding the nuclearity of active Cu sites in zeolite supported CuₙOₙ catalysts used for selective catalytic reduction of NOₓ and methane-to-methanol reactions. In this context, we have critically analyzed the state-of-the art literature reports on ZSM-5 supported MDA catalysts and provided our proposals for the structures of the surface MOₓ sites on ZSM-5 based on the most advanced supporting data available. We, however, tried to analyze key literature from all sides of the debate to provide the reader with a nuanced understanding of the catalytic active sites in these MDA catalysts. The large variety of anchoring sites on the ZSM-5 support suggests that multiple surface MOₓ sites are probably formed for each metal oxide on ZSM-5.

**Supported VOₓ/ZSM-5.** Several molecular structures for dehydrated supported VOₓ species on ZSM-5 have been proposed in the literature. Early electron paramagnetic resonance/electron spin resonance (EPR/ESR) measurements evidenced EPR-active V⁴⁺ oxides present on the zeolite. It was hypothesized that isolated VO²⁺ were present on the cationic sites of zeolites via ESR conducted after various treatments like heat treatment (720 K, 6 h, N₂), adsorption of water, or
adsorption of ammonia.\textsuperscript{74,75} A different study\textsuperscript{47} proposed the presence of VO\textsuperscript{2+} species on both Brønsted acid sites and external silanols. Note, however, that EPR spectroscopy only detects paramagnetic V\textsuperscript{4+} species that may be present in trace quantities and not V\textsuperscript{5+}/V\textsuperscript{3+} species that are EPR silent. Moreover, interpreting EPR signals in supported catalysts to conclude isolated vs. dimeric/oligomeric VO\textsubscript{x} sites is challenging, given that even the EPR of V\textsubscript{2}O\textsubscript{5} single crystals showed significant deviation from expected EPR patterns and exhibited electron sharing between inequivalent V-V neighbors.\textsuperscript{76}

In a relatively-recent in-situ characterization study, the presence of isolated dioxo VO\textsubscript{2+} and dimeric V\textsubscript{2}O\textsubscript{4}\textsuperscript{2+} species located on cationic sites of zeolites for supported VO\textsubscript{x}/ZSM-5 (Si/Al\textasciitilde13.4) were proposed based on in-situ FT-IR, in-situ Raman and EXAFS.\textsuperscript{46} The Raman bands in the 1065-1076 cm\textsuperscript{-1} range were assigned to the terminal V-oxo (V=O) vibration, based on the DFT calculations in the same study.\textsuperscript{46} However, experimental Raman of supported VO\textsubscript{x} catalysts elsewhere in the literature evidences V=O vibrations at lower wavenumbers.\textsuperscript{77} The terminal V=O bond for mono-oxo O=VO\textsubscript{x} sites exhibits only a single Raman band in the 1015-1040 cm\textsuperscript{-1} range, which is much lower than 1065-1076 cm\textsuperscript{-1} scale.\textsuperscript{78,79} The V=O bonds in dioxo O=V-O-V=O are expected to be longer than the V=O bond in mono-oxo O=VO\textsubscript{x} sites and would give rise to V=O vibrations at much lower wavenumbers than 1015-1040 cm\textsuperscript{-1}.\textsuperscript{80} Additionally, the dioxo O=V-O-V=O structure would give rise to both $\nu_s$ and $\nu_{as}$ V=O (a doublet) as well as V-O-V vibrations, which were not observed. The high wavenumber band at 1065-1076 cm\textsuperscript{-1} reported in reference\textsuperscript{46} might either correspond to Si-O-Si vibration or be blue-shifted due to Raman spectrometer not being calibrated. The proposed dimeric surface V\textsubscript{2}O\textsubscript{4}\textsuperscript{2+} species, if present, cannot be present in significant abundance since the in-situ extended X-ray absorption fine structure (EXAFS) spectra\textsuperscript{46} does not exhibit a V-V peak in the second coordination sphere (i.e., V-O-V) at \textasciitilde3 nm.\textsuperscript{81} The X-
ray absorption near-edge structure (XANES) part of the spectrum exhibits a clear pre-edge, which is expected for isolated, non-centrosymmetric sites like the mono-oxo O=VO$_3$ sites. As bridged V-O-V bonds form as in dimeric V$_2$O$_4^{2+}$ sites, the symmetry of the sites should have changed that would lead to a decreased pre-edge intensity. Such a decrease in the pre-edge feature, however, was not observed suggesting that the presence of dimeric surface V$_2$O$_x$ sites in VO$_x$/ZSM-5 catalysts is not supported by the XANES spectra.

The in-situ UV-vis spectra of dehydrated 3% VO$_x$/ZSM-5 (Si/Al=15), prepared by incipient-wetness impregnation, exhibited a strong Ligand-to-Metal Charge Transfer (LMCT) band characteristic of V$^{5+}$ species and a high edge energy value ($E_g \approx 3.5$ eV) in the region of isolated surface V$^{5+}$O$_x$ sites. Oligomeric (VO$_x$)$_n$ sites give rise to $E_g$ values of $\sim 2.8-3.2$ eV and bulk V$_2$O$_5$ exhibits an even lower $E_g \approx 2.3$ eV. The corresponding in-situ Raman spectrum exhibits only a single, sharp Raman band at $\sim 1038$ cm$^{-1}$ that is characteristic of a mono-oxo V=O stretching vibration, which matches the VO$_4$ (O$_3$V=O) coordination of dehydrated surface species on other oxide supports. No supporting evidence was found for isolated, dioxo OV$_5^+(=O)_2$, which would give rise to two bands ($v_s$ and $v_{as}$) at lower wavenumber ($\sim 1000$ cm$^{-1}$), or dimeric V$_2$O$_x$, which would exhibit bridging V-O-V Raman vibrations $\sim 250$ cm$^{-1}$ and V-V features in the second coordination of EXAFS, were found. Therefore, it is expected that surface VO$_x$ sites are present within the zeolitic pores of the ZSM-5-supported catalysts as isolated, mono-oxo (O$_3$V$^{5+}$=O) surface species, as shown in other supported VO$_x$ catalysts. A schematic of the molecular structure of the major dehydrated VO$_x$ site on the ZSM-5 support based on in-situ spectroscopic evidence for supported VO$_x$/ZSM-5 is shown in Figure 3a.
Figure 3. Schematic summary of molecular structures of the major dehydrated MOₓ sites on the ZSM-5 support, based on in-situ spectroscopic (Raman, UV-Vis, x-ray absorption) and DFT. These structures represent surface MOₓ anchored within the zeolitic pores of MOₓ/ZSM-5 catalysts under dehydrated conditions, before MDA reaction, where MOₓ is (a) VOₓ, (b) CrOₓ, (c) MoOₓ, (d) WOₓ, (e) ReOₓ, and (f) FeOₓ. Hydrogen atoms are not shown for clarity. Further details and structures of minor species can be found within respective references of subsections under Section 3.

Supported CrOₓ/ZSM-5. Early characterization studies employing in-situ IR, EPR and Mossbauer spectroscopy under vacuum conditions proposed the presence of both Cr⁺⁵ and Cr⁺⁶ cations for the supported CrOₓ/ZSM-5 catalysts. It is worth noting, however, that Cr⁺⁶ can readily
reduce to Cr$^{+5}$ under vacuum and may give rise to Cr$^{+5}$ signals (e.g., EPR) that are artificially induced by the experimental conditions. Employing *in-situ* XAS (sample sealed in polyethene films under inert atmosphere after treatment with air and taken to the beamline, XAS at 295 K), the supported CrO$_x$/ZSM-5 catalysts prepared via wet-impregnation of Cr-nitrate solution into ZSM-5 were investigated. The presence of Cr-O-Cr coordination indicated the presence of Cr$_2$O$_3$ nanoparticles (NPs) for Si/Al ratios of 29-940. In comparison, only isolated surface CrO$_x$$^{6+}$ sites were evidenced for higher Si/Al ratios (> 940). Based on the intense pre-edge feature in the XANES portion of the XAS spectrum, the possibility of di-grafted, dioxo O$_2$Cr(=O)$_2$ structures present on the ZSM-5 support was proposed for Si/Al ratios of 29-1900. In the same study, complementary EXAFS of the catalysts with Si/Al ~29-1900 corroborated the presence of significant Cr=O bond character in the first coordination shell, but also evidenced weak Cr-O-Cr coordination as in Cr$_2$O$_3$ NPs in the second and third coordination shells. A simplistic schematic, for illustration purpose, of tri-oxo CrO$_x$ structure has also been proposed in the literature, where the bridging Cr-O-support bond shares an electron with one of the three terminal Cr=O bonds. This report warrants some additional discussion since an isolated trioxo Cr(=O)$_3$ structure would be expected to give rise to four Raman vibrations located at ~908 ($v_s$), 933 ($v_{as}$), 947 ($v_{as}$), and 955 ($v_{as}$) cm$^{-1}$ that have been reported for the gas phase tri-oxo CsBrCr(=O)$_3$ reference compound. Without confirmation from *in-situ* Raman spectroscopy, the surface tri-oxo (O=)$_3$CrO structure cannot be validated and seems highly improbable. The number of Cr=O oxo bonds, however, can be confirmed with Raman spectroscopy during isotopic $^{18}$O$_2$-$^{16}$O$_2$ exchange since a trioxo (Cr=O)$_3$ functionality will give rise to band splitting to 4 bands from the isotopic permutations($(=^{16}$O)$_3$, $(=^{16}$O)$_2$(=^{18}$O), $(=^{16}$O)(=^{18}$O)$_2$ and $(=^{18}$O)$_3$). Recently, dehydrated supported CrO$_x$/ZSM-5 catalysts prepared by solid-state reaction (Si/Al=15, Cr/Al=0.5, 1 and 1.5) and were characterized...
with Raman and UV-Vis DR spectroscopy. The Raman band at ~375 cm\(^{-1}\) was assigned to oligomeric CrO\(_x\). However, elsewhere in the literature, a similar band is actually assigned to the ZSM-5 support.\(^{92,93}\)

In a more recent in-depth study, the dehydrated supported CrO\(_x\)/ZSM-5 catalysts were thoroughly characterized via \textit{in-situ} UV-Vis DR, IR and Raman spectroscopy.\(^{49}\) For 1 wt % CrO\(_x\)/ZSM-5 (Si/Al = 15, 25 and 40) catalyst samples, under O\(_2\) flow at 383 K, Raman bands at 964 and 1033 cm\(^{-1}\) were observed, which were assigned to the di-oxo \(\text{O}_2\text{Cr(═O)}_2\) and mono-oxo \(\text{O}_4\text{Cr(═O)}\) structures within the zeolitic pores, anchored on to Brønsted acid sites. For lower concentration of Al (Si/Al = 140), new bands at 984 and 1017 cm\(^{-1}\) were present, which correspond to dioxo \(\text{O}_2\text{Cr(═O)}_2\) and mono-oxo \(\text{O}_4\text{Cr(═O)}\) structures on Si-sites, respectively, on the external surface of ZSM-5. This observation suggests that lower Al concentration force CrO\(_x\) to become anchored on the Si sites of the external surface. Further, it should be noted that these spectra were different from the spectra obtained under the same O\(_2\) flow but at a higher temperature of 773 K. At 773 K, for all Si/Al ratios (25, 40 and 140), the catalysts exhibit Raman vibrations at 984 and 1017 cm\(^{-1}\), indicating that exposure to gas-phase O\(_2\) at elevated temperatures forces the Cr oxide species within the zeolite pores to migrate to the external surface of the zeolite.\(^{49}\) Migration was only observed when Cr loading was higher than 0.5 wt% since no shift in Raman bands was noticed at lower Cr loading.\(^{49}\) A schematic of the molecular structure of the major dehydrated CrO\(_x\) sites based on \textit{in-situ} spectroscopic (Raman, UV-Vis, x-ray absorption) and DFT for supported CrO\(_x\)/ZSM-5 is shown in \textbf{Figure 3b}.

**Supported MoO\(_x\)/ZSM-5** Multiple MoO\(_x\) structures have been proposed for the supported MoO\(_x\)/ZSM-5 catalysts. From \textit{in-situ} XAS characterization,\(^{45}\) catalysts prepared by thermal spreading of MoO\(_3\) onto a ZSM-5 (Si/Al=19) support, bridging Mo-O-Mo bonds in the second
coordination shell (Mo-O-Mo) were not observed. It can be argued that dimeric ($\text{Mo}_2\text{O}_5^{2+}$) sites were present, and that the absence of a detectable Mo-O-Mo feature was related to destructive interference of the EXAFS signals from Mo and Al neighbors. However, Al is a much lighter element than Mo and, thus, the weaker EXAFS scattering from the Al sites cannot destructively interfere with the much stronger EXAFS scattering from the Mo sites. In the same study, the *in-situ* visible Raman spectra exhibited bands at 970 and 1045 cm$^{-1}$, which were tentatively assigned to dimeric and isolated MoO$_x$ sites, respectively. Dimeric Mo$_2$O$_5$ sites were proposed in another study, where *in-situ* Raman bands at 868 and 962 cm$^{-1}$ were assigned to the Mo-O-Mo stretching mode of dimers and the terminal M=O stretch in isolated mono-oxo O$_4$Mo=O sites, respectively.$^{94}$ In contrast, however, the vibration at 868 cm$^{-1}$ is characteristic of bridging Mo-O-Al/Si vibrations and the vibration at 962 cm$^{-1}$ is related to terminal Mo=O bonds (most likely dioxo MoO$_4$ sites).$^{95–97}$ The oxidation state of the surface MoO$_x$ sites, which some authors tried to characterize with EPR, was not resolved because concrete evidence for the proposed oxidation states could not be obtained.$^{50}$ A more recent *in-situ/operando* XAS spectroscopic study found that the dehydrated MoO$_x$/ZSM-5 catalyst exhibits a strong pre-edge feature with a featureless post-edge regime, which is similar to the Na$_2$MoO$_4$ reference compound consisting of isolated MoO$_4$ sites.$^{98}$ Consequently, it was proposed that the dehydrated MoO$_x$/ZSM-5 catalyst predominantly contains monomeric [MoO$_4$]$^{2-}$ species and that a minor amount of dimeric Mo-oxo species may also be present without any supporting evidence. In another *in-situ/operando* XAS study of MoO$_x$/ZSM-5 catalysts, it was reported that at low Mo loading (< 2 wt. % Mo), only the dispersed Mo-complexes are present within the zeolitic pores, whereas at high Mo loading (5 wt. % Mo) large Mo clusters are also present on the external surface of the zeolite support.$^{99}$
Rigorous characterization studies integrating *in-situ* Raman, UV-vis and DFT calculations have provided a more firm picture of the nature of the dehydrated surface MoO$_x$ sites on ZSM-5.$^{42,56}$ The isolated nature of the dehydrated surface MoO$_x$ sites on ZSM-5 was demonstrated with *in-situ* UV-vis studies that exhibit a high $E_g$ value of $\sim$4.9 eV, which is significantly higher than the $E_g$ value expected for dimeric Mo$_2$O$_x$ ($\sim$4.0-4.2 eV) and oligomeric MoO$_x$ ($\sim$3.5 eV) clusters, and reflects the exclusive presence of isolated surface MoO$_x$ sites.$^{42,56}$ The corresponding *in-situ* Raman spectra of the dehydrated supported MoO$_x$/ZSM-5 catalysts revealed that five distinct surface MoO$_x$ species were present on the ZSM-5 support with the relative population of each surface MoO$_x$ structure dependent on both the MoO$_x$ loading and the Si/Al ratio: (i) isolated, di-oxo (OH)$_2$Mo(O=)$_2$ on single Al site inside the 10M ring, (ii) isolated di-oxo O$_2$Mo(O=)$_2$ on two Al sites within the 10M ring (iii) isolated di-oxo O$_2$Mo(O=)$_2$ on external silanols, (iv) isolated, mono-oxo MoO$_5$ species on Al$_2$O$_3$ nanoparticles/clusters on the external surface, (v) isolated, mono-oxo MoO$_5$ at external defect sites (Si$_{ex}$ and Al$_{ex}$). The resulting molecular structures are summarized in Figure 4. The molecular structural assignments were assisted by detailed DFT calculations (see references $^{42,56}$ for the details). Additionally, crystalline MoO$_3$ NPs can form at high Mo loadings when all the anchoring sites on ZSM-5 are completely titrated. These *in-situ* spectroscopic findings clearly demonstrate the co-existence of multiple types of “isolated” surface MoO$_x$ sites on the ZSM-5 support and rule out possibility of dimeric Mo$_2$O$_x$ species. A schematic of the molecular structure of the major dehydrated VO$_x$ site on the ZSM-5 support based on *in-situ* spectroscopic (Raman, UV-Vis, x-ray absorption) and computational insights for supported MoO$_x$/ZSM-5 is shown in Figure 3c.
Figure 4. Unique isolated surface MoO$_x$ sites present in MoO$_x$/ZSM-5 catalysts. The motivation for the schematic has been drawn from the in-situ spectroscopic and DFT studies reported in references 42,56.

**Supported WO$_x$/ZSM-5.** There is a general agreement in the literature regarding the nature of the dispersed WO$_x$ sites present in dehydrated supported WO$_x$/ZSM-5 catalysts.$^{30,31}$ UV-vis DRS analysis has shown that the surface WO$_x$ sites are isolated owing to the very high $E_g$ value $\sim$5.8 eV (LMCT $\sim$210 nm).$^{30,31}$ Tungsten oxide UV-Vis $E_g$ values $> 5.0$ eV correspond to isolated WO$_x$ sites since the $E_g$ value for dimeric W$_2$O$_x$ ($\sim$4.0 eV) and oligomeric WO$_x$ ($\sim$3.5 eV) are significantly lower. This conclusion is further supported by in-situ EXAFS measurements that did not exhibit a second coordination shell comprising W-O-W linkages.$^{82,100}$ The in-situ Raman spectrum of the
dehydrated supported WOₓ/ZSM-5 catalyst exhibited two Raman bands at ~990 and 1020 cm⁻¹ that have been assigned to isolated dioxo O₂W(O=)₂ and mono-oxo O₄W=O species on ZSM-5, respectively, that match WO₄ and WO₅ vibrations of isolated WOₓ species on other oxide supports. A schematic of the molecular structure of the most likely dehydrated WOₓ site on the ZSM-5 support based on in-situ spectroscopic (Raman, UV-Vis, x-ray absorption) for supported WOₓ/ZSM-5 is shown in Figure 3d.

**Supported ReOₓ/ZSM-5.** Based on in-situ Raman and XAS measurements, it was proposed that supported ReOₓ species on ZSM-5 were present as isolated trioxo ORe(=O)₃ species anchored to one site associated with framework alumina (e.g., Si-O*-Al-O*-Si). The absence of bridging Re-O-Re vibrations for dimeric Re₂O₅, which are expected at ~456 (vₛ) and ~185 (δ) cm⁻¹ in the Raman spectra, and the absence of Re-O-Re in the second coordination sphere in the EXAFS spectra demonstrate that the surface ReOₓ sites are indeed isolated on the ZSM-5 support.

More recent in-situ UV-Vis and Raman characterization studies have provided additional insights about the dehydrated surface ReOₓ sites present in the supported 3% ReOₓ/ZSM-5 (Si/Al-15) catalyst. The in-situ UV-vis spectrum exhibit an E₉ value of ~5.0 eV that is significantly higher than the E₉ value of oligomeric (ReOₓ)ₙ structures at 2.8-3.0 eV and confirms the isolated nature of the surface ReOₓ sites on ZSM-5. The corresponding in-situ Raman spectra of the dehydrated ReOₓ/ZSM-5 catalyst possessed two vibrations at 975 and 1010 cm⁻¹ that were assigned to vₐs(Re=O) and vₗ(Re=O) vibrations, respectively, of a structure containing multiple Re=O oxo bonds. Additional studies involving isotopic ¹⁸O-¹⁶O exchange and DFT calculations are needed to determine the number of Re=O oxo bonds for the supported ReOₓ/ZSM-5 catalysts. A schematic of the molecular structure of the most likely dehydrated ReOₓ sites on the ZSM-5...
support based on *in-situ* spectroscopic (Raman, UV-Vis, x-ray absorption) for supported ReO₅/ZSM-5 are depicted in Figure 3e.

**Supported FeOₓ/ZSM-5.** Preliminary studies on catalysts prepared via CVD or solid-state ion exchange, to achieve a high Fe/Al exchange ratio, evidenced various FeOₓ sites (isolated (O-Fe-(OH)ₓ), isolated (O-Fe=O) in distorted tetrahedral coordination, oxygen-bridged dimeric Fe₂O₃(OH)ₓ, oligomeric FeOₓ clusters, and small Fe₂O₃ nanoparticles).⁶⁵,¹⁰⁵ A recent *in-situ* XAS study, where the absorption data were fitted to crystalline reference compounds, that the FeOₓ sites prior to any treatment were present as a mixture of crystalline hematite (Fe³⁺, α-Fe₂O₃) and magnetite (Fe²⁺, Fe³⁺), Fe₃O₄ phases.¹⁰⁶ Upon heating in a He environment to high temperature, the iron oxide structure was reduced to wüstite (Fe²⁺, FeO).¹⁰⁶ This study, however, could not ascertain if dispersed phases of surface FeOₓ sites or clusters were also present in the catalyst since XAS is a bulk characterization technique that averages the signal over all types of FeOₓ in the catalyst. Further structural insights are needed with application of molecular spectroscopy that can distinguish between the different types of FeOₓ that may be present in the ZSM-5 support (e.g., Raman spectroscopy). A schematic of the molecular structures of the most *likely* dehydrated FeOₓ sites on the ZSM-5 support based on *in-situ* spectroscopic (x-ray absorption) for supported FeOₓ/ZSM-5 are shown in Figure 3f.

### 4. Nature of surface MOₓ sites in supported MOₓ/ZSM-5 catalysts during MDA:

Only a few *in-situ/operando* spectroscopic characterization studies have been reported on the state of the surface MOₓ sites in supported MOₓ/ZSM-5 catalysts during MDA. This is a consequence of the few characterization techniques that can operate under the extreme MDA reaction conditions of 973-1073 K. At such high temperatures, only XAS, XRD and Raman spectroscopy can provide
detailed structural information. Other characterization techniques, however, can be applied at much lower temperatures either before or after reaction.

**Supported VOₓ/ZSM-5.** Only a limited number of studies have reported on the nature of the VOₓ site in supported VOₓ/ZSM-5 catalysts during MDA. *In-situ* X-ray photoelectron spectroscopy (XPS) surface analysis of supported VOₓ/ZSM-5, under vacuum conditions before and after reaction with methane at 1023 K for 3-4 hours (without exposing the samples to air after treatment), found the presence of reduced V³⁺ cations on the spent supported VOₓ/ZSM-5 catalysts. The local geometry and coordination number of these cations, however, cannot be provided by XPS electron spectroscopy.

**Supported CrOₓ/ZSM-5.** Little has been reported on the structure of the activated CrOₓ/ZSM-5 catalysts during MDA. An *in-situ* XPS study (samples were treated under the reaction environment, followed by XPS measurements under ultra-high vacuum, without exposing to atmosphere) with a supported 2% CrOₓ/ZSM-5 (Si/Al = 25) catalyst showed that the initial Cr^Ⅵ⁺ oxide sites became partially reduced under reaction with methane and converted to Cr³⁺ oxide sites that remain catalytically active during methane dehydroaromatization at 1023 K.⁷ A recent *operando* Raman spectroscopy study during MDA along with computational insights,⁴⁹ found that the Raman band at 1033 cm⁻¹ from Cr⁺⁶ mono-oxo species (OₓCr⁺⁶=O) anchored at framework [AlO₄] sites disappeared, suggesting reduction, with appearance of a new Raman band at 1062 cm⁻¹ from organic deposits. The exact nature of the surface Cr sites on ZSM-5 under reaction conditions (CrCₓ vs CrOCₓ) has still not been elucidated, but the initial Cr⁺⁶ sites reduce to Cr⁺³.

**Supported MoOₓ/ZSM-5.** Multiple *in-situ* and *operando*⁴²,⁵⁶ spectroscopic studies have focused on determining the nature of the active surface Mo sites during the MDA reaction.⁵⁷,⁹⁸ It is worth noting that since most of the *operando* spectroscopy studies used XAS to characterize the catalyst,
the presence of crystalline MoO$_3$ NPs cannot be ruled out which complicates the XAS analysis. Additionally, MoO$_3$ NPs are too large to fit into the pores of ZSM-5 and can easily be converted to large MoC NPs, blocking the pores.$^{56}$ Unless Raman spectroscopy was employed to characterize the initial state of the MoO$_x$ in ZSM-5, the presence of crystalline MoO$_3$ NPs in the starting material would not be known. Operando XAS studies revealed that during the MDA reaction, the surface MoO$_x$ sites on the ZSM-5 support: (1) partially carburized to intermediate MoO$_x$C$_y$ oxycarbide clusters, (2) subsequently carburized to MoC$_x$ clusters at longer reaction times, and (3) finally detached from the zeolitic pore to aggregate into Mo$_{1.6}$C$_3$ clusters, which was coincident with the maximum benzene production.$^{107}$ The Mo$_{1.6}$C$_3$ clusters, predominantly on the outer zeolite surface, were then observed to grow further, which appears to be the primary cause of catalyst deactivation. Note that catalyst deactivation from hydrocarbon deposition was recently shown to be reaction parameter-dependent, with higher methane pressures stabilizing the supported Mo/ZSM-5 catalyst.$^{107}$ Moreover, MoC$_x$ agglomeration was shown to be reversible via operando Raman spectroscopy, with the initially isolated surface MoO$_x$ sites essentially completely restored by treatment with gas-phase oxygen post MDA reaction that fully restored the catalytic performance of the supported Mo/ZSM-5 catalysts.$^{42,56}$ Both experimental findings and computational calculations confirm the presence of reduced Mo species such as MoO$_x$C$_y$ and MoC$_x$, which serve as the active sites during the MDA reaction.$^{108-112}$ A recent detailed study employing $^{13}$C-NMR with isotopically-labelled $^{13}$CH$_4$ showed that after activation of 2% MoO$_x$/ZSM-5 and subsequent switching to $^{12}$CH$_4$ (with an Ar purge in between) produced a significant amount of $^{13}$C containing benzene molecules. More than 70% of the benzene molecules formed after the first $^{12}$CH$_4$ pulse contained at least one $^{13}$C atom, indicating the dynamic and active roles of MoO$_x$C$_y$, Mo$_x$C$_y$ and confined carbonaceous species during MDA.$^{110}$
Supported \( \text{WO}_x/\text{ZSM-5} \). \textit{In-situ} XAS\textsuperscript{31} and \textit{ex-situ} high resolution transmission electron microscopy (HR-TEM)\textsuperscript{113} studies found poorly-ordered WC\( \gamma \) (~0.6-1 nm) present inside the zeolitic pores for \( \text{WO}_x/\text{ZSM-5} \) catalysts during MDA. An \textit{in-situ} XPS study examined the oxidation state of \( \text{WO}_x \) species on the ZSM-5 support after exposing the catalyst to MDA reaction environment for different amounts of time.\textsuperscript{7} After 2 h of reaction, slight decreases in the binding energy of W 4f\( _{7/2} \) and W 4f\( _{5/2} \) were observed that are consistent with the formation of W\( ^{+5} \) oxides. Further exposure to MDA reaction environment (~13 h) showed an additional shoulder ~33.5 eV, corresponding to W\( ^{+4} \) site. Interestingly, this study did not evidence the formation of WC\( _x \) via \textit{in-situ} XPS investigation. Further information on the nature of active surface \( \text{WO}_x \) sites during MDA is not available, and additional \textit{in-situ} characterization studies using IR, Raman, XAS, and UV-vis DRS are needed as a function of the synthesis method to bridge this information gap.

Supported \( \text{ReO}_x/\text{ZSM-5} \). The active component of supported \( \text{ReO}_x/\text{ZSM-5} \) for MDA has attracted little attention in the literature. An \textit{in-situ} XAS study\textsuperscript{24} observed that surface \( \text{ReO}_x \) species converted to metallic Re clusters ~8.2 Å in size, at the initial stage of benzene formation. Given that ~8.2 Å is comparable to the pore size of the ZSM-5 support, it is not clear from this study if the reported \( \text{Re}^0 \) clusters were observed outside or inside the pores. The facile reduction of \( \text{Re}^{+7}_x \) to \( \text{Re}^0 \) in reducing environments is well known.\textsuperscript{62}

Supported \( \text{FeO}_x/\text{ZSM-5} \). \( \text{FeO}_x/\text{ZSM-5} \) catalysts were also studied via \textit{operando} XAS.\textsuperscript{106} It was found that benzene only formed after a particular XANES feature was observed.\textsuperscript{106} Although the XANES spectrum was similar to that of the reduced form of iron, some unique features, however, did not match any of the measured reference compounds (Fe\(_3\)C, Fe\(_2\)C\(_5\), or Fe foil).\textsuperscript{106} Therefore, the unique XANES feature was tentatively assigned to a reduced/metallic iron phase that can include variable amounts of oxycarbodic carbon (e.g., FeO\(_x\)C\(_y\)) that was also corroborated with the
resemblance of the FT-EXAFS spectrum taken at the end of the MDA reaction with the spectrum of Fe$_2$C$_2$ and Fe$_3$C standards (similar position of the Fe–C and Fe–Fe scattering paths). Facile reduction of iron oxide to metallic Fe$^0$ in reducing environments is well established. In contrast, only a slightly reduced form of iron oxide (Fe$_3$O$_4$) was reported from in-situ XPS and EPR studies (catalyst conditioned under MDA reaction at 973 K, spectra collected at room temperature) and formation of carbidic/oxy-carbidic Fe-clusters were not detected. In the above studies, the presence of Fe$_3$O$_4$ phase in the MDA reaction mixture treated catalyst was confirmed by matching the XPS and EPR spectra of the treated catalysts with the signals of Fe$_3$O$_4$ bulk phase in the literature.

5. Activity and structure-function relationships of MO$_x$/ZSM-5 catalysts towards MDA:

Comparison of MDA performance of MO$_x$/ZSM-5 catalysts. For a detailed comparison of steady-state catalytic MDA performance of various transition metal-oxide-based ZSM-5-supported catalysts, the readers are directed to an existing review paper in the MDA literature. Although, in the mentioned article, the catalysts’ performance have been compared under different reaction environment, one can clearly see that the MDA activity of MoO$_x$/ZSM-5 catalyst towards benzene production is much higher relative to most other MO$_x$/ZSM-5 catalysts. In the current review, we have tried to critically analyze MDA catalysis literature to generate insights based on reports employing similar reaction conditions or reports where all pertinent experimental information is explicitly reported for us to normalize their data. We compared the benzene production rate per metal atom (turnover frequency (TOF), s$^{-1}$) for the supported group V-VIII oxide/ZSM-5 catalysts in Figure 5 (left-a) and benzene selectivity in Figure 5 (left-b). For the TOF calculation, the reported weight loading of the respective metal atoms was utilized from the original reports. Although it is theoretically possible to back-calculate the TOF from literature
reports if reaction conditions, kinetic parameters and metal oxide loadings are known, we caution the reader against it. TOF should only be calculated when only a single type of site is present, corroborated by molecular spectroscopy (Raman). For example, in a catalyst with a known Mo-loading, if a mixture of crystalline and dispersed phase Mo-sites are present, the CH$_4$ conversion or C$_6$H$_6$ production per Mo atom cannot be calculated accurately. Since Mo in crystalline MoO$_3$ is not active for MDA but ZSM-5 confined Mo sites are, using theoretical Mo-loading will yield erroneous TOF values. Please see Table 2 and relevant discussion in the following sub-section.

**Figure 5 (left-a)** suggests that the supported ReO$_x$/ZSM-5 and MoO$_x$/ZSM-5 catalysts exhibit the highest benzene production TOF values amongst group V-VIII catalysts, with the supported ReO$_x$/ZSM-5 catalyst just barely more active than MoO$_x$/ZSM-5. Although the specific activity of the supported ReO$_x$/ZSM-5 catalyst can be slightly higher than that of the supported MoO$_x$/ZSM-5 catalyst for the MDA reaction, the potential volatilization of ReO$_x$ species during calcination, MDA reaction and catalyst regeneration compromises the practical use of supported ReO$_x$-based catalysts. MDA activity, which is indicated by the trend in TOF for benzene production over supported MO$_x$/ZSM-5 catalysts can be summarized as follows: ReO$_x$/ZSM-5 ~ MoO$_x$/ZSM-5 > WO$_x$/ZSM-5 ~ FeO$_x$/ZSM-5 > VO$_x$/ZSM-5 > CrO$_x$/ZSM-5. Next, the selectivity to benzene is compared in **Figure 5 (left-b)** and shows that CrO$_x$/ZSM-5, MoO$_x$/ZSM-5 and FeO$_x$/ZSM-5 exhibit similar selectivity values of ~70-75%, WO$_x$/ZSM-5 and ReO$_x$/ZSM-5 ~ 50-55%, and VO$_x$/ZSM-5 ~ 30%. Note that the reported selectivity in the case of ReO$_x$/ZSM-5 is for C$_6$-C$_{11}$, and not solely for C$_6$H$_6$.

Structure-function (or nature-performance) relationships can be envisioned for the three most active catalysts (ReO$_x$/ZSM-5 ~ MoO$_x$/ZSM-5 > WO$_x$/ZSM-5) by correlating the *operando* Raman spectroscopy data available in the literature, with the trend in TOF values reported in **Figure 5**
For each catalyst, the initial molecular structure of the metal oxide site present within the 10M ZSM ring is shown in Figure 5(center). The operando Raman spectra Figure 5(right) were used to track the diminishing M=O bands as the metal oxide sites carburized with increasing MDA reaction time. $T_{\text{red}}$ corresponds to the temperature that M=O Raman bands completely vanished, while $T_{\text{C6H6}}$ corresponds to the temperature that benzene was first detected in the MS. Operando Raman data suggests that the tri-oxo ReO$_4$/ZSM-5 sites (1013 cm$^{-1}$) reduced at 500 °C, followed by reduction of di-oxo MoO$_4$/ZSM-5 (993 cm$^{-1}$) at ~680-690 °C, and di-oxo WO$_4$/ZSM-5 (1024 cm$^{-1}$) at above 700 °C. Severe fluorescence was observed for the WO$_x$/ZSM-5 above 700 °C, making it hard to ascertain the exact $T_{\text{red}}$. Likewise, $T_{\text{C6H6}}$ was 664, 781, and 814 °C for ReO$_x$/ZSM-5, MoO$_x$/ZSM-5, and WO$_x$/ZSM-5 catalysts, respectively. The trends in reducibility of the initial dispersed phase, isolated metal oxide sites confined within the ZSM-5 pores, and the benzene production temperatures correlate strongly. In fact, for the Mo/ZSM-5 catalyst with well-defined MoO$_x$ sites, experimental and computational study evidenced that differences in geometries and electronic properties of Mo carbide structures formed from distinct MoO$_x$ anchored on Al and Si sites yielded differences in their catalytic properties.$^{42}$ Specifically, the CH$_4$ activation energy over the Mo carbide anchored on the double Al-atom site was calculated to be 112 kJ mol$^{-1}$, while it was ~140 kJ mol$^{-1}$ for the Mo carbide anchored on Si sites.$^{42}$ Therefore, special attention should be paid to synthesis and in-depth characterization of initial oxide forms of the ZSM-5 supported catalysts.
Figure 5. (Left-a) shows benzene production TOF values for group V-VIII supported MOx/ZSM-5 catalysts. Experimental details for Si/Al=25 can be found in reference 9 and Si/Al=13.4-20 in reference 24. For Si/Al=25, the highest reported CH4 consumption TOF was divided by the stoichiometric factor of six to approximate the benzene production TOF. Lastly, for Si/Al=13.4, the CH4 GHSV is not reported, and relevant experimental details are not available to approximate the value. (Left-b) indicates the selectivity towards benzene production, taken from references indicated in Figure 5(Left-a). * indicates that the reported selectivity is for C6-C11, and not solely C6H6 as for the other catalysts. (Center) shows the molecular structures of isolated MOx within the 10M rings of ZSM-5 support prior to MDA reaction. (Right) shows operando Raman spectroscopy, adapted from reference 84 of the three best MDA catalysts Re~Mo~W, correlating the reducibility of the initial isolated metal oxide site with benzene light-off temperature. The Tred values pertain
Factors affecting MDA performance of MoO$_x$/ZSM-5 catalysts. The relative performance comparison of various group V-VIII transition metal catalysts in the previous section shows that Mo-based catalysts exhibit high activity and stability. Hence, we further analyze various factors (material and process) that can affect the MDA performance of MoO$_x$/ZSM-5 catalysts. The literature reports that included pertinent experimental details are summarized in Table 2 along with key parameters. Table 2 highlights significant variability in MDA activity and selectivity of MoO$_x$/ZSM-5 catalysts across the literature. Nevertheless, the following general conclusions can be drawn from the comparison of data (CH$_4$ conversion and C$_6$H$_6$ selectivity) summarized in Table 2.

a) Effect of Mo loading: The loading of Mo in supported MoO$_x$/ZSM-5 catalysts plays a crucial role in determining the catalyst’s performance towards MDA reaction. The CH$_4$ conversion goes through a maximum with increasing Mo weight loading, reaches the maximum conversion at ~3-4 wt.% loading, beyond which conversion drops. This trend in CH$_4$ conversion can be related to the nature of the MoO$_x$ sites in the catalyst. At low loading (From 0 to ~3-4 wt.%), Mo-oxide is largely present as dispersed, isolated MoO$_x$ sites confined within the zeolitic pores, which are known to be selective active sites for C-H activation. After 3-4% weight loading, further increase in the Mo content results in the formation of crystalline MoO$_3$ particles (nano- and micro scale) mostly on the external surface of the zeolite, which corresponds to the decreased CH$_4$ activity. The maximum Mo loading beyond which MoO$_3$ NPs are formed, however, can be above 3-4 wt.% in certain cases depending on the Al sites, which in turn depend on the Si/Al ratio of
the ZSM-5 support. These crystalline MoO$_3$ are known to form coke on the external surface, which blocks the selective active sites within the zeolitic pores. Although carbided Mo sites are present during MDA reaction, the initial dispersion and structure of MoO$_x$ sites are crucial in determining the observed catalytic performance. On the other hand, the C$_6$H$_6$ selectivity exhibits a very low dependency on Mo loading. The selectivity value increases only slightly with Mo loading (up to 3-4 wt.% loading) and remains approximately constant thereafter.

b) Effect of Synthesis technique: Incipient wetness impregnation (IWI) of an aqueous solution of (NH$_4$)$_6$Mo$_7$O$_{24}$ into ZSM-5 support, followed by oxidative calcination is the most used synthesis technique for MoO$_x$/ZSM catalyst preparation. When done carefully, the IWI method can result in uniform dispersion of the MoO$_x$ phase into the ZSM-5 support. The higher dispersion of MoO$_x$ species from IWI synthesis most likely responsible for the higher MDA activity of those catalysts compared to the ones synthesized via solid-state ion exchange of MoCl$_3$ or a mechanical mixing of MoO$_3$ with ZSM-5 support. In the latter synthesis method, residual crystalline MoO$_3$ nanoparticles are always present and adversely affect the MDA performance. Recently, novel synthesis approach of wetness impregnation assisted with additional treatment in rotavapor, microwave and ultrasound resulted in catalysts with appreciably higher MDA activity, tested up to 4 hours of time-on-stream (TOS). Moreover, solvothermal synthesis utilizing 10 v% ethanol/water as solvent has also been reported to yield catalysts that were more active towards MDA compared to the IWI catalyst, tested up to 15 hours of TOS. Catalysts synthesized using solvothermal approach were claimed to have a higher dispersion of the MoO$_x$ sites on ZSM-5 in the freshly prepared catalysts. Having said that, additional catalyst
characterization studies are required under *in-situ* and *operando* conditions to corroborate the exact reason behind superior performance of catalysts prepared via advanced synthesis techniques instead of the traditional IWI. Additionally, one more investigation compared the effect of utilizing hexamolybdate \([\text{(C}_4\text{H}_9\text{N})_2\text{Mo}_6\text{O}_{19}]\) vs. heptamolybdate \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}\) as the Mo-oxide precursor and found that when hexamolybdate is used as precursor, the \(\text{C}_6\text{H}_6\) selectivity is much improved. 43

c) *Effect of Si/Al ratio:* The Si/Al ratio, which controls the acidity of the zeolite support and the dispersion of the supported metal oxide phase is a crucial parameter in MDA performance of MoO\(_x\)/ZSM-5 catalysts: higher acidity ZSM-5 support with low Si/Al ratio generally leads to a greater number of surface MoO\(_x\) sites and higher MDA activity. The literature converges on the understanding that higher the amount of Brønsted acid sites (i.e low Si/Al ratio), higher the dispersion of isolated MoO\(_x\) sites within the zeolitic pores will be, which leads to superior MDA activity from the dispersed Mo sites confined within the ZSM-5 pores.8,121 This trend further highlights the relevance of characterizing and understanding the nature of dispersed phase sites in MDA catalysts.

d) *Effect of reaction pressure:* Only a limited number of studies have undertaken examining the effect of reaction pressure on the MDA performance of MoO\(_x\)/ZSM-5 catalyst. Recently, it was reported that with increasing reaction pressure, both \(\text{CH}_4\) conversion and \(\text{C}_6\text{H}_6\) selectivity values increase.107 The positive effect of higher reaction pressure towards MDA performance was attributed to the decrease in coke formation/catalyst deactivation rate. Higher pressure aiding MDA kinetics was surprising, as higher pressures are expected to shift the reaction towards the reactant’s side, given the stoichiometry of 6 moles of \(\text{CH}_4\) reactant forming 10 moles of product (1 benzene, 9 hydrogen).
Table 2. MDA reaction performance of Mo/ZSM-5 catalysts reported in the literature. Parameters summarized in the table include Mo loading, catalyst synthesis techniques, Si/Al ratio, and total reaction pressure.

<table>
<thead>
<tr>
<th>Synthesis Technique</th>
<th>Si/Al (wt %)</th>
<th>Mo loading (wt %)</th>
<th>Reaction Conditions</th>
<th>CH\textsubscript{4} conversion (%)</th>
<th>C\textsubscript{6}H\textsubscript{6} selectivity (%)</th>
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<td>Incipient-wetness impregnation of aqueous (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}•4H\textsubscript{2}O</td>
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<td>Time (°C)</td>
<td>Residence Time (h)</td>
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<td>Mechanical Mixing of ZSM-5 with Ammonium Molybdate</td>
<td>Impregnation of Ammonium Paramolybdate</td>
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<td>993</td>
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³⁹: Microwave treatment
⁹: Mechanical mixing of ZSM-5 with ammonium molybdate
⁶: Impregnation of ammonium paramolybdate
⁴: Solid state ion exchange of MoCl₃ with ZSM-5
³: Incipient-wetness impregnation of aqueous (NH₄)₆Mo₇O₂₄
⁸: Solvothermal synthesis
⁵: Solvothermal synthesis utilizing 10 v% ethanol/water as solvent
²: Impregnation of (NH₄)₆Mo₇O₂₄•4H₂O
¹: Physical mixing of MoO₃ and ZSM-5
⁴: Incipient-wetness impregnation of (NH₄)₆Mo₇O₂₄•4H₂O
¹²: Incipient-wetness impregnation of aqueous
6. Kinetics and reaction mechanism of MDA over supported $\text{Mo}_x/\text{ZSM-5}$ catalysts:

**Rate-determining-step (RDS).** The energy associated with the breaking of the C-H bond in the methane molecule (~437±2 kJ/mol)\(^3,125,126\) is extremely high. Such a large energetic barrier requires high temperatures to initiate C-H bond activation, especially for the non-oxidative conversion of methane. The C-H bond breaking of CH\(_4\) is, therefore, generally considered the rate-determining-step in methane chemical reactions.\(^56\) Temperature programmed MDA studies with the CH\(_4\) and CD\(_4\) isotopes demonstrated a significant kinetic isotope effect ($T_p=890$ K for CH\(_4\) and $T_p=1042$ K for CD\(_4\)$) establishing that breaking of the C-H bond of methane is indeed the rate-determining-step.\(^56\)
**Most abundant reaction intermediate (MARI).** Given that the RDS is the activation of the C-H bond upon adsorption of CH$_4$, all subsequent reaction steps will be extremely fast. This is confirmed by the immediate production of benzene and hydrogen over an activated catalyst (i.e., when the induction period is over). Consequently, the population of surface reaction intermediates will be negligible under MDA reaction conditions and difficult to detect spectroscopically. Gas-phase methyl radicals are also generated and their contribution to the MDA reaction must be quantified, but no such reports have appeared to date.$^{39}$

Many studies have proposed ethylene and acetylene as the primary reaction intermediates for the MDA reaction.$^{39,127}$ One of the reasons cited for identifying ethylene and acetylene as reaction intermediates is that benzene is formed upon dosing either of these C$_2$ hydrocarbons over supported MO$_x$/ZSM-5 catalysts. The feeding of ethylene generally produces higher selectivity for toluene, whereas acetylene (as a feed) results in similar selectivity towards toluene and benzene, compared to that of methane. Moreover, the more reactive acetylene molecule exhibited higher benzene formation rates than ethylene.$^{99,108,112}$ It was also shown that acetylene was not observed as a side-product of the MDA reaction, possibly due to its high reactivity. Acetylene easily hydrogenates to ethylene in the presence of hydrogen, which may explain why some authors observed ethylene during MDA while a few observed acetylene.$^{128}$ To circumvent the gas-phase reactions of the acetylene intermediate, recently, low residence times in conjunction with microwave heating instead of conventional (resistive) heating, were used to establish a gas-solid temperature gradient provided by the selective heating and the low gas-solid contact time.$^{129}$ This approach apparently quenched gas-phase reactions and enabled detection of the acetylene and carbon monoxide intermediates in appreciable quantities. Over the same catalyst, acetylene was not detected using conventional heating reactor.$^{129}$ On the other hand, a recent report has cast
doubt on ethylene being the primary intermediate.\textsuperscript{127} It was concluded that ethylene was \textit{not} the major reaction intermediate because the hydrocarbon pool formed in the zeolite matrix during MDA is comprised of less dense and more hydrogenated species than the pool formed from ethylene.\textsuperscript{127} Moreover, the carbonaceous deposits formed from methane were also more reactive than the ones formed from ethylene.\textsuperscript{127} As mentioned above, the RDS is the cleavage of the C-H bond of CH\textsubscript{4} and, consequently, it is highly unlikely that reaction intermediates can be detected via conventional approaches because all steps after the RDS are expected to be extremely fast (especially at/above 973 K).

\textbf{MDA reaction mechanism.} The exact MDA mechanism remains under debate. Literature reports corroborating opposing proposals are available: (1) mono-functional mechanism with Mo sites being solely responsible for all catalytic steps,\textsuperscript{99,112} and (2) bi-functional mechanism where Mo sites activate CH\textsubscript{4} and adjacent framework Brønsted acid sites polymerize and aromatize the C\textsubscript{2} intermediates.\textsuperscript{130–132} The majority of MDA studies with supported Mo/ZSM-5, the most investigated MDA catalyst, reported that the Mo-carbide sites within the pores were responsible for the activation of C-H bond in methane and converting the CH\textsubscript{x} intermediates into ethylene/acetylene. Subsequently, the ethylene/acetylene oligomerization and aromatization to benzene and other aromatic products was proposed to occur on the framework Brønsted acid sites in the zeolite micropores.\textsuperscript{130–132} Alternatively, the mono-functional mechanism\textsuperscript{99,107,112} proposes that both the activation of methane and subsequent reaction of the hydrocarbon pool to benzene exclusively occurs at Mo carbide sites.\textsuperscript{127,133,134} It was recently reported that the supported Mo\textsubscript{x}C\textsubscript{y}/silicalite-1 catalyst, which doesn’t contain Brønsted acidity and has the same topology as ZSM-5, was able to convert methane into benzene and aromatic coke at 973 K. It was, therefore, inferred that framework Brønsted acid sites were not \textit{required} for MDA and that the conversion
of methane to benzene followed a mono-functional mechanism on highly dispersed Mo carbide species embedded in the 10MR zeolite micropores.\textsuperscript{112} The lower catalytic performance of Mo\textsubscript{x}C\textsubscript{y}/silicalite-1 catalyst compared to the Mo/ZSM-5 catalyst was attributed to the lack of Brønsted acid sites that aid in stabilizing and dispersing both the initial MoO\textsubscript{x} and Mo\textsubscript{x}C\textsubscript{y} active sites inside the zeolite pores. The presence of the hydrocarbon pool and hydrocarbon pool mechanism was experimentally verified by pulsing isotopically labelled CH\textsubscript{4} (\textsuperscript{13}CH\textsubscript{4}, CD\textsubscript{4}).\textsuperscript{99,111} A recent computational study also determined that, at least over Mo\textsubscript{x}C\textsubscript{y} sites, the radical hydrocarbon-pool pathway was energetically less demanding and, thus, more favorable.\textsuperscript{135} Currently, the exact mechanism of how the radical hydrocarbon-pool forms and cooperates during MDA to form benzene is not understood and requires further probing using operando spectroscopy studies with high spatial and temporal resolution.\textsuperscript{108}

7. MoO\textsubscript{x}/ZSM-5 Catalyst’s Stability and Deactivation under MDA.

It is well known that ZSM-5 supported MDA catalysts experience systematic deactivation with time on stream due to coke formation leading to pore blockage, and due to larger MoO\textsubscript{x} clusters at the external surface sintering at elevated temperature during reaction. Previously, process-intensification strategies have been proposed to circumvent the catalyst deactivation, which include cycling H\textsubscript{2} feed after CH\textsubscript{4} to reactivate the catalyst,\textsuperscript{120} increasing the reaction pressure to 15 bar to speed up hydrogenation of deposited coke,\textsuperscript{107} O\textsubscript{2}-treatment to reverse both the carbide formation and the agglomeration of Mo nanostructures to regenerate the deactivated catalyst\textsuperscript{42}, and using low temperature H\textsubscript{2}-pre-reduction before carburization to form a higher population of dispersed Mo\textsubscript{x}C\textsubscript{y} species.\textsuperscript{136} The state-of-the art understanding regarding coking of Mo/ZSM-5 catalysts during reaction is that graphite-like external coke is more detrimental to the activity of
the catalyst than internal coke.\textsuperscript{135} External coke formation leads to blockage of the pore openings, which in turn decreases the access of CH\textsubscript{4} to the zeolite channels.\textsuperscript{135}

A noteworthy synthesis approach, aimed at improving Mo/ZSM-5 catalyst’s stability, utilizes continuous solvothermal synthesis method under supercritical conditions and reducing atmosphere to synthesize 5\% Mo/ZSM-5.\textsuperscript{120} Although lacking \textit{in-situ} or \textit{operando} characterization of their material, the study boasts an impressive stable performance of the catalyst for \textasciitilde15 hours on stream. The authors attributed enhanced stability of the catalyst prepared via the novel synthesis route to delayed formation of detrimental so-called hard coke species.\textsuperscript{120} Very recently, however, 0.5\%Mo was successfully loaded onto nano ZSM-5 to yield a single site Mo/ZSM-5 catalyst in contrast to a mixture of Mo phases typically present in traditionally prepared Mo/ZSM-5 catalysts.\textsuperscript{137} This novel nano Mo/ZSM-5 material was shown be to orders of magnitude more stable than regular Mo/ZSM-5 catalysts, with the longest time on stream of 36 hours (3 cycles x 12 hours each), without an appreciable decrease in CH\textsubscript{4} conversion.\textsuperscript{137} However, minor dealumination occurred in the material during multiple cycles, as evidenced by a decrease in unit cell volume.\textsuperscript{137} Note that the degree of dealumination observed in this nano Mo/ZSM-5 catalyst was minuscule compared to that observed in traditionally prepared 1\% Mo/ZSM-5 catalyst. It suffices to say that while this ultra-stable nano Mo/ZSM-5 synthesis approach has significantly improved the catalyst stability, various other synthetic approaches to impart greater stability found in zeolite-synthesis literature include encapsulation of metal ions/atoms during zeolite crystallization,\textsuperscript{138} alkali-stabilized metal incorporation into zeolite pores,\textsuperscript{139} stabilization of extra framework sites via substituted framework atoms to exploit strong-metal-support-interaction (SMSI) phenomena,\textsuperscript{140–142} etc. An excellent, state-of-the-art review of the various strategies to improve zeolite-based catalysts’ stability
towards prolonged operation under harsh reaction conditions, similar to those required for MDA, can be found elsewhere in the literature.¹⁴³

8. Summary and Outlook:

There are still disagreements in the literature of MDA catalysis of supported MOₓ/ZSM-5 catalysts primarily because of information gaps, despite a large number of publications on the topic. While the nature of the dispersed MOₓ sites is much better understood for the group VI metal oxides in supported MOₓ/ZSM-5 catalysts (Cr, Mo, W), more research is still needed for the ZSM-5 supported group V (V)-, group VII (Re)- and group VIII (Fe)-containing catalysts. Under MDA reaction conditions, the initially dispersed, fully oxidized MOₓ sites become reduced to oxycarbide and carbide clusters that represent the catalytic active sites. The surface ReOₓ site becomes reduced to metallic Re⁰. The rds is the breaking of the C-H bond during the CH₄ adsorption step, which makes all subsequent steps kinetically insignificant. In terms of catalytic MDA performance, the supported MoOₓ/ZSM-5 catalyst system appears to be the best candidate amongst all of the group V-VIII metal oxides discussed herein. With regards to the reaction mechanism, the literature leans towards the radical hydrocarbon pool mechanism proceeding with activation and aromatization at mono-functional metal carbide cluster sites. Considerable research on supported MOₓ/ZSM-5 catalysts for MDA is expected in the coming years to address both the unresolved fundamental issues (molecular structures of the dehydrated surface MOₓ sites, anchoring sites of the surface MOₓ sites on the ZSM-5 support, and nature of catalytic active sites under MDA reaction conditions) and applied aspects (increasing benzene yield and deactivation from coking).

Further advancement of the fundamental structure-activity relationships of the MDA catalytic reaction using group V-VIII MOₓ-based ZSM-5 catalysts to guide the rational design and optimization of these catalysts for MDA will require the following:
- Isotopic \(^{18}\text{O}_2-{^{16}\text{O}_2}\) exchange \textit{in-situ} Raman studies to determine the number of terminal M=O oxo bonds present for all the dehydrated surface MO\(_x\) sites on the ZSM-5 support.

- \textit{Operando} Raman and XAS spectroscopy studies to completely understand the molecular structures of the catalytic active sites under the MDA reaction conditions.

- Complementary \textit{operando} Near Atmospheric Pressure (NAP)-XPS, UV-vis DRS, and XAS studies to provide information about the oxidation states of the catalytic active sites during MDA.

- Modulation excitation spectroscopy (MES) and isotope-switch experiments to elucidate the nature of the reaction intermediates and reaction network.

- \textit{Operando} photoelectron photoion coincidence spectroscopy (PEPICO)\(^{144}\) and online synchrotron vacuum ultraviolet photoionization mass spectroscopy (SVUV-PIMS)\(^{145}\) to provide information on the involvement of gas-phase radical species in the MDA mechanism.

- \textit{Operando} UV-Vis analysis of carefully synthesized, oriented ZSM-5-based catalysts have recently shown the ability to unravel structure-function relationships by elucidating chemistries occurring within the zeolite pores versus the external surface.\(^{146}\)

9. **Conflicts of Interest:**

There are no conflicts to declare.

10. **Acknowledgements:**

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11. **Author information**
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The literature on methane dehydroaromatization (MDA) to benzene using ZSM-5 supported, group V-VIII transition metal-based catalysts (MOₓ/ZSM-5) is critically reviewed with a focus on *in-situ* and *operando* molecular insights.