Reactivity, Selectivity, and Stability of Zeolite-Based Catalysts for Methane Dehydroaromatization

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Non-oxidative dehydroaromatization is arguably the most promising process for the direct upgrading of cheap and abundant methane to liquid hydrocarbons. This reaction has not been commercialized yet because of the suboptimal activity and swift deactivation of benchmark Mo-zeolite catalysts. This progress report represents an elaboration on the recent developments in understanding of zeolite-based catalytic materials for high-temperature non-oxidative dehydroaromatization of methane. It is specifically focused on recent studies, relevant to the materials chemistry and elucidating i) the structure of active species in working catalysts; ii) the complex molecular pathways underlying the mechanism of selective conversion of methane to benzene; iii) structure, evolution and role of coke species; and iv) process intensification strategies to improve the deactivation resistance and overall performance of the catalysts. Finally, unsolved challenges in this field of research are outlined and an outlook is provided on promising directions toward improving the activity, stability, and selectivity of methane dehydroaromatization catalysts.

1. Introduction

Methane is the main component of natural gas (∼95%) and the most abundant source of fossil carbon on Earth.[1] Currently, natural gas is an important source of energy and the primary feedstock for the production of hydrogen and synthesis gas (syngas, CO + H2). Although natural gas is not sustainable in the strict sense,[2] it remains the cleanest among all fossil fuels. In the transition to a renewable chemical industry, natural gas will increasingly become a major source of carbon. Further, in a sustainable fossil-free scenario of low-carbon economy, methane will remain an important and abundant molecule within the chemical industry. Methane is, for example, a major by-product of Fischer–Tropsch synthesis, CO2 hydrogenation, and biomass conversion as well as the main component of biogas.[3–5] The chemical inertness of its strong C–H bonds complicates the selective conversion of methane to higher hydrocarbons and oxygenates. Currently, the main industrial method to use methane as a material feedstock involves the transformation to syngas by steam reforming, followed by processes such as methanol synthesis and Fischer–Tropsch synthesis to obtain liquid fuels and other useful chemicals. A disadvantage of this indirect technology is the high capital cost of reforming plants, making it only economically attractive at a very large scale. An efficient direct process for the conversion of methane to higher hydrocarbons or oxygenates remains one of the “holy grails” of chemistry.[6,7] The approaches to directly convert methane can be categorized into oxidative and non-oxidative methods. Oxidative processes are often met with low product selectivity because of the higher reactivity of targeted products as compared to methane itself, resulting in overoxidation to CO2. Non-oxidative methods are generally more atom-efficient, because, in addition to valuable hydrocarbon products, pure CO2-free hydrogen gas (H2) is obtained, which can be used for instance in fuel cells.[8] Among several alternatives, including non-oxidative coupling of methane to ethylene and deep methane dehydrogenation to solid carbon and hydrogen,[9–12] methane dehydroaromatization (MDA) remains one of the most promising non-oxidative reactions for the direct valorization of natural gas. MDA involves the selective conversion of methane to a mixture of easily transportable aromatics, that is, benzene (predominantly), naphthalene, and toluene. As all other non-oxidative methane conversion reactions, MDA is a highly endothermic process:

$$6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9\text{H}_2 \quad \Delta H^\circ = 532 \text{ kJ mol}^{-1} \quad (1)$$

The strong endothermicity dictates that high temperature is required to obtain a significant benzene yield (Figure 1). For example at a typical reaction temperature of 700 °C, a benzene yield of 11.7% can be achieved. Further, in the whole temperature range of 300–1100 °C graphitic carbon (coke) is the thermodynamically preferred product. These limitations make it necessary to use catalysts for performing the MDA reaction. An efficient MDA catalyst should i) effectively activate stable C–H bonds in CH4 molecules, ii) allow selective production of light aromatics, minimizing the formation of unwanted graphitic carbon (coke), and iii) remain stable at high reaction temperature. Because of these strict catalyst requirements, materials chemistry is at the center of the MDA research.
The first example of suitable catalytic materials was reported in the 1980s. Minachev and co-workers demonstrated that, similar to aromatization of ethylene, ethane, and propane, it is possible to achieve benzene yields as high as 14% from methane at 750 °C in the presence of ZSM-5 zeolites, modified by transition metals (Re, Cr, and Pt among others). In 1993 Wang et al. reported that Mo-modified ZSM-5 is a particularly efficient MDA catalyst. Following these pioneering works, the MDA reaction has been attracting increasing attention from both industry and academia. Besides its obvious commercial potential, MDA represents an intriguing conundrum from the perspectives of catalysis and reactor engineering. Although the reaction mechanism and the nature of the active sites have been actively studied, a complete chemical picture of the reaction is lacking. In recent years, several review papers dedicated to this catalytic system, a complete understanding of the active sites and the roles of the different catalyst components remains lacking. Several important aspects are nevertheless broadly accepted in literature. First, as-prepared Mo/ZSM-5 catalyst regeneration and optimal process parameters are briefly reviewed. Finally, we provide an analysis of possibilities and limitations of zeolite-based catalysts in direct non-oxidative methane conversion and an outlook on the most promising research directions in this field.

2. Structure of the Active Mo-Species

Mo/ZSM-5 is the most studied catalyst for the MDA reaction, which has been at the center of attention for several decades. With Mo/ZSM-5, it is possible to achieve benzene yields close to the thermodynamic limits (5–15% at 600–800 °C) at high benzene selectivity (70–90%) in a broad range of space velocities and methane partial pressures. Despite hundreds of reports dedicated to this catalytic system, a complete understanding of the active sites and the roles of the different catalyst components remains lacking. Several important aspects are nevertheless broadly accepted in literature. First, as-prepared Mo/ZSM-5
catalysts contain highly dispersed Mo(VI)-oxo centers, which are reduced and/or carburized under the reaction conditions giving rise to the active Mo-sites. Second, the Si/Al ratio (and hence Brønsted acidity) of ZSM-5 zeolite plays a critical role in the catalytic activity. Although non-acidic Mo/Silicalite-1 presents low MDA activity, excessive acidity (i.e., low Si/Al ratio) leads to severe coking and catalyst deactivation. Third, zeolite shape selectivity is critical for obtaining high selectivity to light aromatics. While Mo dispersed on non-zeolitic acidic sulfated zirconia displays some MDA activity, such materials are much more selective toward naphthalene and coke than optimal zeolite-based catalysts. Further, only ten-membered-ring (10MR) zeolite topologies such as MFI (ZSM-5), MWW (MCM-22), MEL (ZSM-11), IMF (IM-5), TUN (TNU-9) with pore sizes of about 5.5 Å demonstrate high benzene selectivity. Zeolites with either smaller 8MR pores or larger 12MR pores are not selective and yield coke as the predominant product. Fourth, Mo-based systems are usually significantly more active and selective as compared to other transition metals. Fifth, there are several distinct stages during the MDA reaction over zeolite-based catalysts: induction, quasi-steady-state production of benzene, and deactivation. With this knowledge in mind, we will focus on the structure and evolution of Mo-centers in Mo/ZSM-5 catalyst during its lifetime.

A typical synthesis of Mo/ZSM-5 involves the dispersion of a Mo(VI)-oxo precursor (most often molybdenum trioxide or ammonium heptamolybdate) on the external surface of the zeolite followed by a thermal treatment to enable the diffusion of Mo-species inside the zeolite pores and their interaction with Brønsted acid sites. Dong et al. were the first to demonstrate the migration of MoO3 into the pores of ZSM-5, a process that starts already at 450 °C. The nature of the precursor Mo(VI)-oxo species has been a topic of debate. Figure 2a depicts the proposed structures, a common motive being the exchange of highly dispersed Mo-oxo species with Brønsted acid sites. A recent work by Liu et al., who used integrated differential phase-contrast scanning transmission electron microscopy (iDPC-STEM) to study dispersed Mo-oxo species with Brønsted acid sites, illustrates the isolated nature of Mo-oxo complexes inside the zeolite framework (Figure 2d). Also, zeolites with either smaller 8MR pores or larger 12MR pores are not selective and yield coke as the predominant product. Fourth, Mo-based systems are usually significantly more active and selective as compared to other transition metals. Fifth, there are several distinct stages during the MDA reaction over zeolite-based catalysts: induction, quasi-steady-state production of benzene, and deactivation. With this knowledge in mind, we will focus on the structure and evolution of Mo-centers in Mo/ZSM-5 catalyst during its lifetime.

Operando X-ray absorption spectroscopy has become an essential technique to study nanoscale active sites, including those in Mo/ZSM-5. Using a combination of operando high-energy resolution fluorescence detection X-ray absorption near-edge spectroscopy (HERFD-XANES) and X-ray emission spectroscopy (XES), Lezcano-González et al. followed the evolution of Mo-centers during the lifetime of 4 wt% Mo/ZSM-5 catalyst at 677 °C. The authors concluded that the initially isolated Mo(VI)O2+ species attached to the zeolite framework were converted to metastable Mo(V), Mo(IV), and Mo(III)-oxycarbide species and then detached from the zeolite framework forming Mo(II)C2 clusters. These clusters can diffuse out of the pores and eventually form larger MoC agglomerates on the external surface. By using a pulse reaction technique combined with operando XANES analysis at 700 °C (Figure 2e), we showed that the structure and evolution of the Mo-species strongly depends on the Mo loading. Comparing Mo/ZSM-5 catalysts with Mo loadings of 1 wt% (initially fully dispersed as MoO2+ monomers), 2 wt% (initially...
mainly dispersed as $\text{MoO}_2^{2+}$ monomers with some larger $\text{Mo}_x\text{C}_y$ agglomerates on the external surface) and 5 wt% (similar fractions of dispersed species and surface agglomerates) demonstrated a strong dependence of the performance on the Mo speciation. While the 1 wt% Mo/ZSM-5 sample was only partially reduced at the moment benzene formation was observed, the 5 wt% Mo/ZSM-5 sample started producing benzene after the Mo reduction was complete. Two stages of Mo reduction were identified: an initial fast reduction step followed by a much slower one, which were respectively assigned to removal of oxygen atoms from Mo(VI)-oxo species and detachment of the Mo species from the zeolite framework after complete reduction. Extended X-ray absorption fine structure (EXAFS) and high-angle annular dark-field (HAADF) STEM measurements showed that the Mo phase in 1 wt% Mo/ZSM-5 catalyst did not agglomerate even after 16 h of reaction at 700 °C. Most likely, the Mo-species remain isolated during the whole process of induction, activation, and deactivation. The samples with a higher Mo content showed formation of Mo$_2$C nanoparticles on the external surface.

Agote-Arán et al. combined operando XANES, EXAFS, and powder X-ray diffraction characterization of a 3.8%Mo/ZSM-5 catalyst to demonstrate that as much as 70% of the Mo-species, initially dispersed inside the pores, can be detached from the zeolite framework and agglomerate into larger Mo$_x$C$_y$ species during the reaction. Although these recent operando characterization studies have greatly advanced our understanding of the Mo/ZSM-5 catalysts, the detailed structure of the most active dispersed Mo-species or Mo$_x$C$_y$ clusters responsible for the actual MDA reaction remains to be elucidated.

To summarize, many active site configurations have been proposed to operate in the MDA catalytic cycle. It is likely that
practical catalysts, usually characterized by a relatively high Mo loading, will contain Mo in a diverse range of structures discussed above, each contributing to the catalytic activity.\[65\] Based on the shape-selective nature of benzene formation and microscopic and spectroscopic observations the MDA-active Mo-species are most likely located inside the zeolite pores, while Mo-species on the external surface predominantly form coke.\[30\] Nevertheless, the structure of the most active Mo-species remains one of the main open questions in the MDA field. Fast development of operando spectroscopy characterization makes us confident that this question will be answered sooner than later. It will definitely lead to the development of better catalysts by designing of materials with the maximum number of the most active Mo-sites. Knowing the active site requirements, however, will likely not be enough to design the optimal MDA catalysts. There is a second crucial aspect: the actual reaction mechanism. The complete understanding of the reaction pathway from methane to benzene should allow designing catalysts that, in addition to high activity in methane conversion, would demonstrate low coking selectivity and slow rate of deactivation. Next section is dedicated to discussing and evaluating the existing mechanistic proposals.

3. Reaction Mechanism

Initially in analogy to other zeolite-catalyzed processes carbonium ion and radical mechanisms were proposed.\[18,66\] After three decades of MDA research, there are two main mechanistic proposals remaining: i) a bifunctional mechanism in which C–H bond activation and C–C coupling take place on the Mo active sites, while further aromatization of C\(_2\) intermediate fragments occurs on Brønsted acid sites; and ii) a hydrocarbon pool-like pathway where activation of C–H bonds on Mo sites is followed by the transformation of (hydro)carbon intermediates confined inside the zeolite pores (Figure 3).

The bifunctional mechanism has been widely discussed in the literature and follows conventional high-temperature chemistry of C\(_2\) hydrocarbons, generated by C–C coupling, on Brønsted acid sites. Ethylene is commonly considered as the primary product of C–C coupling and main reaction intermediate, mainly because it is a significant product of the reaction and its selectivity increases during the catalyst deactivation.\[67\] In a recent kinetic study Razdan et al., however, proposed that ethane is the initial product of C–C coupling and acetylene is the key reactive intermediate.\[68\] In addition, Vollmer et al. showed that significantly different reactivities of ethylene and methane over Mo/ZSM-5 at MDA conditions might indicate that ethylene is not the actual intermediate.\[69\] Regardless of the nature of C\(_2\) intermediates, the bifunctional mechanism explains many of the observations, particularly with respect to the superior activity of acidic zeolites toward formation of aromatics.\[70\] There is, however, a significant amount of experimental data contradicting this model. First, several recent studies showed that Mo/Silicalite-1 can also catalyze the MDA reaction.\[16,72\] As Mo-ooxo species bind much stronger to Brønsted acid sites than to silanol groups, another role of zeolite acidity is to improve the dispersion of the Mo sites, which are involved in methane activation. Indeed, upon comparing Mo/ZSM-5 and Mo/Silicalite-1 catalysts Agote-Arán et al. found that the distance between Mo centers and zeolite framework oxygen atoms is significantly longer in Mo/Silicalite-1.\[71\] Thus, the inferior activity of Mo/Silicalite-1 can be explained by the weaker stabilization of highly dispersed Mo and thus the lower activity in methane activation.

Induction period at the early stage of the reaction is likely the key to understanding the MDA mechanism. The induction period has been for a long time exclusively attributed to the reduction and/or carbonization of Mo-oxo precursor phase. A proper kinetic analysis of the MDA reaction is hampered by the absence of a steady-state operating regime, as induction, reaction and deactivation quickly succeed each other.\[72\] Pulsed reaction techniques, which allow titration of surface species are powerful tools for studying such transient processes.\[73\] By limiting the amount of methane supplied to the catalyst, fast transient processes can be resolved, which is often not possible in a continuous flow regime. Jiang et al. applied a pulse reaction technique to show the complex autocatalytic nature of processes taking place during the induction period.\[74\] Partial reduction of Mo\(^{6+}\) and carbon deposition were proposed to take place at the beginning of reaction. A further detailed analysis of several Mo/ZSM-5 catalysts varying in Mo loading by pulsing reaction technique combined with operando and quasi-in-situ spectroscopic characterization led to the identification of three main reaction stages (Figure 4a): i) activation (autocatalytic reduction of Mo(VI) with CO as main carbon-containing product); ii) induction (formation of surface carbon species), and iii) autocatalytic formation of benzene.\[63,75\] We note that rapid carbon deposition at the beginning of the reaction has been observed in continuous flow experiments as well.\[76\] In pulse experiments, the duration of the induction period was nearly independent of the Mo loading. The carbon deposited on the catalyst during the induction period and the resulting zeolite/carbon composites were investigated by a combination of techniques such as Ar adsorption, \(^{13}\)C, and \(^{1}\)H NMR spectroscopy, and EPR spectroscopy. Together these data point to the predominant formation of polyaromatics with a radical character confined in the zeolite micropores (Figure 4b). Isotope experiments with \(^{13}\)CH\(_4\)/\(^{12}\)CH\(_4\) switches demonstrated that the deposited carbon species are involved into the catalytic cycle. As much as 70% of benzene molecules produced directly after an isotope switch contained at least one carbon atom derived from the surface carbon (Figure 4c). Figure 4d shows that this involvement of surface carbon is not related to the reversible nature of the overall reaction.\[63,75\] Although this mechanism shares similarities with the well-established carbocation-based hydrocarbon pool mechanism as commonly assumed for the methanol-to-hydrocarbons reaction,\[77\] the nature of the reactive intermediates and the overall chemical pathway seem different.

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Figure 3. Two proposed reaction mechanisms for the MDA reaction.
Recently, a similar hydrocarbon pool type mechanism was proposed for the conversion of ethane to benzene over Mo/ZSM-5, whereas ethane aromatization over Ga/ZSM-5 proceeded via a different mechanism and metal-free HZSM-5 was not active for the reaction. This finding indicates that even in case of C₂ compounds, being the main initial products of methane activation, the hydrocarbon pool-like mechanism would still be a valid explanation for the reactivity of Mo-zeolite catalysts.

Despite the significant progress, the complete mechanism of the MDA reaction remains unclear. For example, the possibility of both bifunctional and hydrocarbon pool-like mechanisms to co-exist during the MDA reaction cannot yet be ruled out. The structure of the confined (hydro)carbon pool intermediates is not known either and the next section is dedicated to the recent progress in this direction.

4. Structure and Evolution of Deposited Carbon Species

While coke is a widely studied subject in the field of zeolite chemistry, the nature and structure of carbon species formed during MDA has not been resolved yet. Mainly temperature-programmed oxidation (TPO) and thermal gravimetric analysis (TGA) have been used for the characterization of coke deposits formed over Mo/ZSM-5. A common distinction is made between oxidation of Mo-species to MoO₃ (corresponding to a combustion peak at 400–450 °C and weight gain in TGA profiles), “soft coke” (combustion peak at 450–550 °C overlapping with Mo₂C oxidation and corresponding to a weight loss in TGA profiles) and “hard coke” (separate combustion peak at 550–650 °C and weight loss). The two types of coke are usually considered to differ in chemical nature, being formed respectively on Mo and Brønsted acid sites. Such distinction might not be appropriate as, for instance, comparison of DTG profiles and 13C NMR spectra for a series of deactivated Mo/ZSM-5 catalysts showed that all coke species exhibit very similar sp² nature of formed polyaromatic carbon, despite completely different combustion behavior (Figure 5a,b). An explanation for differences in the combustion can be the amount of coke formed in the zeolite micropores. It has been indeed shown that a significant fraction of coke species is formed inside the zeolite micropores. Such distinction might not be appropriate as, for instance, comparison of DTG profiles and ¹³C NMR spectra for a series of deactivated Mo/ZSM-5 catalysts showed that all coke species exhibit very similar sp² nature of formed polyaromatic carbon, despite completely different combustion behavior (Figure 5a,b). An explanation for differences in the combustion can be the amount of coke formed in the zeolite micropores. It has been indeed shown that a significant fraction of coke species is formed inside the zeolite micropores. Furthermore, the combustion behavior of coke strongly depends on the size of zeolite crystals and the nature and location of metal species which catalyze the oxidation of coke. All these findings point at the diffusion-limited nature of coke combustion during TPO and TG characterization, while the chemical specificity of these
methods is questionable. The dissolution of zeolite framework in completely spent Mo/ZSM-5 (Figure 5c) revealed that at late stages of the reaction the carbonaceous deposits form essentially a zeolite-templated carbon material (Figure 5d),[75] that is, particulate microporous carbon framework consisting of curved graphene fragments and featuring short-range order.[86] This result demonstrates that MDA coke is predominantly formed inside the zeolite pores, and that the polyaromatic carbon forms a (semi)connected structure, completely blocking the access to the active sites. The model of zeolite-templated carbon (ZTC) nature of MDA coke species together with the hydrocarbon pool mechanism can explain, for example, the extremely low MDA selectivity of Mo/MOR catalysts (virtually zero benzene yield was observed over Mo/MOR).[30] The structure and connectivity of ZTC materials strongly depends on the topology of the zeolite template,[87] the inability of Mo/MOR to catalyze the MDA reaction might be related to the unsuitable structure of the hydrocarbon pool intermediates formed inside its pores.

At the moment, it is not yet clear how the growth of carbon structures inside the zeolite pores proceeds, how it depends on the zeolite topology, what is the fraction of reactive intermediates in surface carbon during the whole course of the MDA reaction and how to avoid the transformation of the (hydro)carbon intermediates into the extended ZTC-like structures. These aspects are important for designing more deactivation-resistant MDA catalysts and will require further research efforts. The already developed strategies to decrease the deactivation rate of the existing MDA catalysts are discussed in the next section.

Figure 5. a) DTG profiles and b) $^{13}$C MAS NMR spectra of Mo/ZSM-5 catalyst exposed to methane flow at 700 °C for different periods of time. Labeled $^{13}$CH$_4$ methane was used to prepare the samples, except for the samples exposed for 960 min. c) A process of coke liberation from the spent Mo/ZSM-5 catalyst by dissolving the zeolite in HF; d) Scanning electron microscopy (SEM) image of spent Mo/ZSM-5 catalysts with carbon content of 13 wt% and carbon product remained after dissolving the inorganic fraction of spent Mo/ZSM-5 in HF with carbon content of 96 wt%. Ar adsorption isotherm of the obtained carbon material is shown in inset. Adapted with permission.[75] Copyright 2018, American Chemical Society.
5. Process Intensification

The formation of surface carbon, as we outlined above, precedes the formation of light aromatics in the MDA reaction. The further growth of these carbon species into large polyaromatic ZTC-like structures lead to complete catalyst deactivation.

Many approaches to improve the stability of MDA catalysts and overall efficiency of the MDA process have been developed. As shown by Figure 6, all these approaches can be categorized as aiming to mitigate the rate of coke deactivation, to increase the single-pass methane conversion or to achieve both these targets simultaneously. To increase the single-pass methane...
conversion of equilibrium-limited (Figure 1) MDA reaction it is necessary to shift the equilibrium toward the products. Hydrogen-permeable reactors that allow selective removal of hydrogen from the reaction zone have been studied for this purpose. Conventional hydrogen-selective membranes are Pd-based and both pure Pd\(^{[88,89]}\) and Pd–Ag\(^{[90]}\) membranes have shown a significant improvement of methane conversion and the initial aromatic yield. Since the stability of Pd-based membranes under harsh MDA reaction conditions might become an issue, alternative membrane materials such as mixed oxide La\(_3\)W\(_{0.6}\)Mo\(_{0.4}\)O\(_{12.25-\delta}\) have been studied and demonstrated an increased methane conversion as well.\(^{[91]}\) In addition to hydrogen permeable membranes, passive hydrogen-absorbing materials can be used to shift the equilibrium. Kumar et al. found that under MDA conditions Zr reacts with H\(_2\) to yield ZrH\(_{1.75}\) and that the absorbing function of Zr pellets can be efficiently regenerated by treatment in He flow at 700 °C. It was not possible, however, to regenerate the catalytic Mo/zeolite catalyst under these conditions.\(^{[92]}\) A common disadvantage of passive hydrogen removal from the reaction zone is the increased rate of coke formation. The reactions leading to the formation of hydrogen-poor coke species, in accordance with the Le Chatelier’s principle, are more sensitive to the hydrogen concentration than the aromatization itself.\(^{[93]}\)

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\text{6CH}_4 \leftrightarrow \text{1C}_\text{6H}_6 + 9\text{H}_2 \quad \text{Aromatization (2)}
\]

\[
\text{6CH}_4 \leftrightarrow \text{CH}_\text{x(solid)} + 12\text{H}_2 \quad \text{Coke formation (3)}
\]

As a result, in majority of studies dedicated to passive hydrogen removal, an increased selectivity to coke and naphthalene and faster catalyst deactivation were observed. Alternative approaches of active hydrogen removal can be used to overcome this problem. Simple continuous co-feeding of oxidants (O\(_2\), CO\(_2\), CO\(_2 + \text{O}_2\), H\(_2\)O) have been shown to have a promotional effect on the deactivation stability of Mo/zeolite catalysts but in a narrow range of oxidant concentration.\(^{[94]}\) There exist a fine balance between the amount of surface carbon that can be removed and the re-oxidation of the active Mo-phase to the inactive Mo(VI)-species. Another concern, related to the continuous co-feeding of oxidants in fixed-bed reactors, is inhomogeneous distribution of the oxidant along the bed. As experimentally demonstrated by Bhan and co-workers, at 700 °C the reactivity of even mild oxidants such as CO\(_2\) is so high that majority of oxidant molecules are converted with methane in the top zone of the reactor, resulting in the formation of syngas. In the bottom zone of the reactor a conventional MDA reaction in presence of CO and extra H\(_2\) takes place.\(^{[95,96]}\) In view of this effect, non-continuous strategies of oxidant supply have been developed and showed a significant potential. We developed a pulsing protocol for the selective combustion of coke species, where instead of continuous co-feeding of small concentration of O\(_2\) together with methane, short and concentrated pulses of O\(_2\) were periodically fed to the reactor. This strategy allowed overcoming the problem of inhomogeneous distribution of oxygen through the catalyst bed and resulted in a significant improvement of cumulative aromatic yields.\(^{[97]}\) Zhang et al. showed that mechanical mixing of Mo/zeolite 5 with a reducible oxide (Ce\(_{0.9}\)Gd\(_{0.1}\)O\(_3\)) for the chemical combustion of the formed hydrogen is a promising strategy to shift the MDA equilibrium toward aromatic products without excessive formation of carbonaceous deposits.\(^{[98]}\) In this process, the steam formed from hydrogen can oxidize coke precursors and reduce the deactivation rate. The oxide nature of Ce\(_{0.9}\)Gd\(_{0.1}\)O\(_3\) component also makes the combustion regeneration of the hybrid catalysts feasible. Cao et al. demonstrated that using an oxygen-selective membrane, based on Ba\(_0.5\)Sr\(_0.5\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_3\)-δ perovskite, it is possible to uniformly distribute oxygen within the catalyst bed and significantly improve the MDA performance of Mo/MCM-22 catalyst.\(^{[99]}\) Application of catalytic membrane reactors, capable of simultaneously extract hydrogen and distribute oxide ions within the catalyst bed is particularly promising. Morejudo et al. demonstrated that electrochemical co-ionic BaZrO\(_3\)-based membrane reactors (Figure 6a) are effective for this purpose. Comparison of BaZrO\(_3\) membrane reactor with a conventional fixed bed reactor (Figure 6b–d) showed a significantly slower deactivation rate and an increased maximum aromatic productivity at the same time.\(^{[100]}\)

The second group of MDA process intensification strategies is based on shifting the equilibrium toward the reactants to minimize the coke formation rate. As discussed above the reactions of coke formation are more sensitive to approaching the equilibrium and therefore it is possible to selectively mitigate the growth of coke by shifting the equilibrium toward the reactants. Increasing the reaction pressure, first described by Ichikawa and co-workers,\(^{[100,101]}\) is a simple and effective method to retard the deposition of coke and enhance the cumulative yield of hydrocarbon products at the expense of maximum methane conversion. We recently observed an order of magnitude higher benzene productivity of 2%Mo/ZSM-5 catalyst after increasing the pressure of methane from 1 to 15 bar (Figure 6e). Interestingly the improvement of catalyst stability is also accompanied by a higher selectivity toward valuable alkylated aromatics: toluene and xylene (Figure 6f). Elevated pressure operation was found efficient for catalysts with different Mo loading and in a broad range of temperatures and space velocities.\(^{[102]}\) Using isotope labeling, TG-MS and \(^{13}\)C NMR we found that the formation of coke in MDA reaction is a highly reversible process. In fact, as much as 40% of \(^{13}\)C coke species formed after first 20 min of MDA reaction in \(^{13}\)CH\(_4\) flow can be exchanged following 100 min of reaction in \(^{13}\)CH\(_4\) at 5 bar. At elevated pressure, a larger fraction of surface carbon participates in the MDA reaction and it results in a much higher degree of pore utilization and aromatic productivity.\(^{[103]}\)

Other related process intensification strategies include CH\(_2\)-H\(_2\) switch operation and continuous co-feeding of H\(_2\) and CO. Continuous co-feeding of H\(_2\)\(^{[104]}\) can improve the aromatic productivity in the same way as the elevated pressure operation, although the thermodynamic penalty on methane conversion is much higher in case of added H\(_2\). Co-feeding of CO is another efficient method to improve the catalyst stability in a non-oxidative manner and without decreasing the methane conversion.\(^{[105,106]}\) It is not yet completely clear why adding CO leads to a significantly slower coking deactivation of Mo/ZSM-5 catalysts, but a viable hypothesis involves dissociation of CO on Mo-sites and removal of a certain amount of coke precursors as CO\(_2\), while the “extra” carbon atoms participate in the formation of aromatics.\(^{[107]}\) Finally, periodic CH\(_4\)-H\(_2\) switch is one of

\[
\text{6C} + \text{H}_2 \leftrightarrow \text{4H} + \text{C}_\text{6H}_6
\]
the most efficient methods to stabilize the performance of Mo/ZSM-5 catalysts.\footnote{108} In this mode, it is possible to minimize the formation of coke by its intermediate hydrogenation without suppressing the methane conversion level and overoxidation of the active Mo-phase. Using CH$_4$ (15 min)–H$_2$ (45 min) periodic switch operation Sun et al. achieved a stable MDA performance of 5.5%Mo/ZSM-5 catalysts for over 1000 h.\footnote{109} Disadvantages of CH$_4$–H$_2$ switch strategy include the use of excess of hydrogen gas and suboptimal catalyst productivity related to the long regeneration time.

6. Conclusions and Outlook

As demonstrated in this progress report, MDA field has experienced a significant development in the last years. The level of mechanistic and structural understanding has significantly increased; synthetic advances enabled fabrication of more efficient catalytic materials, while novel process intensification techniques allowed improved catalysts stability and aromatic yields. Further developments are nevertheless necessary to bring the MDA process to the level of commercialization. Figure 7 presents our view on the main development directions within the MDA field.

6.1. Catalyst Engineering

The main directions of further MDA development are related to the materials chemistry. As discussed in this progress report the active site requirements for designing active, selective, and stable MDA catalysts are generally known and future advances in high-temperature operando characterization of catalysts will definitely complete the picture. The actual synthetic approaches to meet these requirements, however, have not been developed yet. First of all it is still impossible to achieve a high concentration of dispersed Mo-sites (>0.2 mmol g$^{-1}$) while minimizing the concentration of Brønsted acid sites in order to obtain active, aromatic-selective, and coking-resistant catalytic materials. Several promising synthesis strategies to achieve this target can be identified. First of all, it is now established that Mo(VI)-oxo precursors preferentially interact with two acid sites to form either MoO$_4^{2-}$ monomers or Mo$_2$O$_5^{2-}$ dimers. Also, engineering of siting and distribution of Al atoms within the ZSM-5 framework in such a way that preferably Al pairs are formed is a known technique.\footnote{110} Using ZSM-5 materials with Al centers distributed in pairs followed by a well-defined deposition of Mo-oxo precursors (using for instance CVD approaches\footnote{111}) on the paired Brønsted acid sites to exchange them completely might lead to a high loading of the active Mo-species and minimum residual Brønsted acidity. Second, the exchange of the residual Brønsted acid sites with catalytically inert cations (Ga$^{3+}$, Na$^+$) can be an effective method to minimize the rate of coke formation.\footnote{112} Finally, Mintova and co-workers have recently demonstrated that it is possible to isomorphously substitute framework Si atoms with Mo and W atoms in Silicalite-1 zeolite.\footnote{113,114} Such materials are potentially promising MDA catalysts because of the ultimate dispersion of the active transition metal species and complete absence of Brønsted acidity.

Furthermore, other transition metals such as Co,\footnote{115} Fe,\footnote{116} Mn,\footnote{117} Ni,\footnote{118} Re,\footnote{119} and W\footnote{120} are known to exhibit a substantial MDA activity. These metals are present as reduced metallic, carbide, or cationic centers in working catalysts, but the structure of the active species have not been resolved in the same detail as for Mo. It has also been established that dispersion of these metals in zeolite pores is required for obtaining aromatics, similar with the Mo/zeolite case. Nevertheless, all these metals are significantly less active than Mo and it would be important to establish the reason why Mo is a much better MDA catalyst. This phenomenon can relate to intrinsic activity differences among the transition metals but may also depend on the structure of active sites and their location, leaving room for improvements. Therefore, answering the question about the superior activity of Mo-zeolite catalysts will not only shed light on the chemistry of non-oxidative methane activation but also allow designing better and potentially cheaper catalytic materials. In our opinion, synthesis of different well-defined transition metal sites, confined in zeolite pores, detailed operando characterization, and accurate comparison of their intrinsic C–H activation and C–C coupling activity (as well as hydrocarbon selectivity) combined with DFT modeling of the catalytic pathways is a research direction well worth exploring.\footnote{121–123}

Promotion of Mo/ZSM-5 with a second catalytic metal function is another viable option for designing better MDA catalysts. The majority of transition metals have been evaluated as dopants to Mo/ZSM-5.\footnote{124–126} Significant improvements in stability, activity, and selectivity of Mo/ZSM-5 catalysts were observed with Fe, Co, and Ni.\footnote{127–129} As these metals demonstrate high methane conversion activity (for instance for the decomposition of methane to carbon materials and
hydrogen gas), it is likely that their promotional role is related to increasing the rate of C–H bond activation. Another explanation for the observed improved performance can be the exchange of remaining Brønsted acid sites with metal (oxo) cations, effectively decreasing coking propensity. The influence of a second metal on the performance of Mo/ZSM-5 catalysts is only understood at the phenomenological level and therefore deserves more attention.

Shape selectivity is a critical descriptor of activity and especially selectivity of zeolite-based catalysts. So far, exclusively 10MR zeolite topologies have shown reasonable aromatic selectivity in MDA reaction. One may even draw a parallel with methanol-to-hydrocarbons reaction in which the 10MR zeolites are known to produce a significant amount of BTX aromatics as well.[130] Another explanation for such a significant topology effect should be considered here: different stabilization of Mo-oxo species in different coordination environments. Unlike for many other transition metal–zeolite composites, for instance, Cu/zeolite systems,[131] this aspect has not been studied in Mo/zeolite materials. The zeolite topology can likely have an effect on at least the reducibility of Mo-species, stabilized inside the zeolite pores. Detailed analysis of the effect of zeolite topology on the structure and chemical properties of dispersed Mo-species remains a promising direction in the field of MDA as well.

The textural, morphological and surface structuring of the zeolite component is a promising (and generally underexplored in the context of MDA) strategy to improve the performance of Mo/ZSM-5 catalysts. First of all, external Brønsted acidity strongly affects the performance of zeolite catalysts and leads to the enhancement of unselective reaction pathways, increased coke selectivity, and faster catalyst deactivation.[132] In MDA reaction, the issue of coke formation on the external surface is amplified by the high reaction temperature and accordingly swift graphitization of hydrocarbon fragments in a not shape-selective environment. The inertization of the external surface via i) silylation of the external active sites[133]; ii) removal of acid sites by NH4F treatment[134]; and iii) core–shell structuring with a layer of Al-free Silicalite-1 on top of the ZSM-5[135] have been reported to significantly improve the hydrocarbon selectivity of MDA catalysts.

As with any other reaction of zeolite-catalyzed hydrocarbon conversion, the MDA activity suffers from the slow diffusion of molecules inside the micropores and suboptimal utilization of the zeolite crystal.[136,137] Conventional methods of decreasing the catalyst particle size and hierarchical pore structuring influence the performance of MDA catalysts in a non-linear manner. While shortening the effective diffusion pathway inside the micropores is beneficial for the MDA performance, the excessive external surface area leads to the enhanced rate of coke deposition. This effect results in the existence of optimal zeolite particle size (~2 µm) with larger particles being too diffusion-limited and smaller particles too coke-selective.[138] In case of hierarchical pore structuring, a similar phenomenon results in the presence of optimal proportion between micro- and mesoporosity. To prepare active and hydrocarbon selective catalysts it is necessary to achieve the balance between the effective length of diffusion pathways in micropores and the non-shape-selective conversion of methane on the external surface.[139,140] In addition to conventional hierarchically porous zeolites, in recent years, several novel hollow zeolite structures have been synthesized, used as MDA catalysts and displayed significant deactivation stability and high extent of crystal utilization.[141–143] The promising performance of hollow zeolite catalysts is likely related to a combination of shortened diffusion pathway within the micropores and limited external surface area. Further systematic studies are necessary to determine the optimal (hierarchical and/or hollow) porous structure and identification of textural descriptors similar to the hierarchy factor[144] will likely be useful in this regard.

6.2. Structure and Role of Surface Carbon

The surface carbon plays a key role in both the activity and deactivation of Mo/ZSM-5 catalysts. Provided that the hydrocarbon pool mechanism offers a more suitable model for explaining the reactivity of MDA catalysts, understanding the structure of the surface intermediates is of significant importance. Once the structure of the intermediates is known a rational design of the optimal transition metal–zeolite topology pairs will become much more feasible. Stabilization of organic intermediates in confined space of zeolite micropores is sensitive to the reaction conditions. It means that operando or quasi-in situ spectroscopy efforts will be required to solve the structure of the hydrocarbon pool components.[145] Isotope labeling techniques will be required to distinguish the reactive intermediates from the spectator coke-like species. Finally, impressive recent developments in NMR[146–148] and STEM[149–151] characterization of organic molecules, confined inside the zeolite pores, will definitely be useful for unraveling the fine structural details of MDA intermediates.

6.3. Process Intensification and Regeneration Stability

After three decades of MDA research, it has become clear that industrial application of this reaction would take a certain degree of chemical engineering creativity. Low single-pass methane conversion and quick and inevitable accumulation of heavy carbonaceous deposits require significant process intensification efforts to turn the MDA reaction commercially attractive. Several particularly efficient approaches, including CH4–H2 switch strategy, elevated pressure operation, and use of electrochemical co-ionic membrane reactors have been developed and optimized at the lab-scale. Further progress in this direction, especially related to the long-term stability and up-scaling, is necessary. Although the number of long-term reaction-regeneration studies in MDA field is limited, it is known that oxidative regeneration (combustion of coke in air) is much more harmful toward Mo/zeolite catalysts than reductive regeneration (methanation of coke in hydrogen):

\[ \text{CH}_x + \text{O}_2 \rightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O} \quad \text{Combustion} \quad \text{(4)} \]

\[ \text{CH}_x + \text{H}_2 \rightarrow \text{CH}_4 \quad \text{Methanation} \quad \text{(5)} \]

Nevertheless, air combustion of coke is a much more effective and economically viable strategy[152] and it is the most likely...
future commercial choice. The stability of Mo-zeolite composites upon oxidative regeneration is, therefore, one of the key development directions in the field of MDA. There are several factors, determining the instability of Mo/ZSM-5 during oxidative regeneration: exothermic nature of coke combustion results in a significant overheating during regeneration; evolving water leads to the hydrothermal degradation; and finally the reduced Mo-centers are oxidized to MoO$_3$ during the air regeneration. The strong negative effect of excessive loading of MoO$_3$ on the surface. As a result, the zeolite materials treated with NH$_4$F disfavor oxidative regeneration: exothermic nature of coke combustion results in a significant overheating during regeneration; evolving water leads to the hydrothermal degradation; and finally the reduced Mo-centers are oxidized to MoO$_3$ during the air regeneration.

stability of aluminosilicate zeolite materials is well-documented.$^{[153]}$ Too high concentration of MoO$_3$ results in a chemical reaction with framework aluminum atoms, formation of Al$_2$(MoO$_4$)$_3$ phase, dealumination and eventually collapse of the crystalline zeolite structure. Decreasing the Mo loading to avoid the formation of the Al$_2$(MoO$_4$)$_3$ is an effective strategy to improve the stability of Mo/ZSM-5 composites during high-temperature reaction– oxidative regeneration cycling.$^{[154]}$ In the future, exploring other active transition metals, not aggressive or even capable of stabilizing the zeolite framework,$^{[155]}$ might also be a promising approach for enhancing the regeneration stability of MDA catalysts. Further, improving the thermal and hydrothermal stability of the zeolite matrix itself is another important development line. Indeed, the ideal MDA catalyst should work for thousands of high-temperature reaction and regeneration cycles while retaining the initial structure. Typical degradation mechanisms of zeolitic materials under such conditions are related to the cleavage of Si–O–Si bonds, this process being accelerated by the presence of Al atoms and framework defects.$^{[156,157]}$ Recent synthetic investigations in this direction are therefore focused on decreasing the Si/Al ratio and lowering the number of silanol defects. Several reports have shown that controlled hydrothermal treatment in ammonium fluoride solution is a versatile strategy to lower both the surface Si/Al ratio and number of framework defects.$^{[158,159]}$ The NH$_4$F treatment is particularly efficient for removing Al from the external surface. As a result, the zeolite materials treated with NH$_4$F display a significant improvement of the framework stability.$^{[160]}$

To summarize, methane dehydroaromatization to a mixture of benzene, naphthalene, and toluene is one of the most promising direct gas-to-liquid technologies. Swift coking deactivation and low single-pass methane conversion present a significant hurdle for the commercialization of this process. Further developments in synthesis and operando characterization of MDA catalysts will definitely bring this process closer to the industrial application. For this purpose a number of challenges still need to be solved, including improvement of the long-term reaction-regeneration stability of MDA catalysts, decrease of naphthalene and coke selectivity, increase of single-pass methane conversion, development of effective separation technologies to recover H$_2$ from methane-rich stream prior to its recycling, etc. Apart from the future commercial value, MDA reaction is a fundamentally important chemical problem. The very process of understanding the structure and catalytic action of Mo-sites and complex molecular pathways, underlying the direct conversion of methane to benzene in zeolite pores, will teach us important lessons about the reactions of C–H bond activation and C–C coupling, catalysis in confined spaces, and design of advanced microporous materials.
