Article

Probing the Catalytic Active Sites of Mo/HZSM-5 and Their Deactivation during Methane Dehydroaromatization

Molybdenum supported on zeolite HZSM-5 (Mo/HZSM-5) is an effective bi-functional catalyst for methane dehydroaromatization (MDA) that allows direct conversion of methane into aromatics. In this work, Wang et al. determine the forms, locations, and deactivation sequence of the active sites in Mo/HZSM-5 and prepare more stable MDA catalysts accordingly.

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HIGHLIGHTS

The crystal size-dependent catalytic behaviors of Mo/HZSM-5 in MDA are explained

Preferential deactivation of MoC_x sites over acid sites in Mo/HZSM-5 is observed

Encapsulating MoC_x particles in zeolite greatly increases the life of the catalyst

iDPC-STEM provides direct evidence for the migration and evolution of Mo species

Article

Probing the Catalytic Active Sites of Mo/HZSM-5 and Their Deactivation during Methane Dehydroaromatization

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SUMMARY

Molybdenum supported on zeolite HZSM-5 is the most studied catalyst for methane dehydroaromatization. However, the nature of its catalytic sites and their deactivation mechanisms remain unclear and controversial. Here, we report further insights into this system: first, the crystal size of HZSM-5 determines the form and location of the catalytic active MoC_x species, and thus the catalyst performance; second, MoC_x sites are preferentially deactivated over acid sites, when supported on nano-sized HZSM-5; third, MoC_x particles that are traditionally considered detrimental to the reaction can serve as active sites, if they are properly protected from coke deposition. These findings lead us to develop an “encapsulation” strategy, which reconciles the deactivation rates of the MoC_x and acid sites, enabling a full utilization of both sites, and consequently leading to a 10-fold increase in catalyst lifetime. Encapsulation also allows us to design experiments to confirm the catalytic role of the acid sites.

INTRODUCTION

Methane dehydroaromatization (MDA) is a promising method to directly convert methane into aromatics and hydrogen, without the participation of oxygen.^{1–4} However, there are 2 major obstacles that hinder the application of MDA: the thermodynamically limited conversion of methane (~10% at 700°C) and the rapid deactivation of the catalyst.⁵ The thermodynamic limitation can be partially overcome by *in situ* removal of the produced hydrogen, using membranes^{6–8} or metal particles⁹ to drive the reaction toward methane conversion. The rapid deactivation of the catalyst, however, is a more complicated issue to overcome. The most studied catalyst for MDA is molybdenum supported on an acidic zeolite HZSM-5 (Mo/HZSM-5).^{10,11} It is generally believed that Mo/HZSM-5 is bi-functional, catalyzing the dehydrogenation of CH₄ at the Mo sites and the subsequent oligomerization/cyclization of C₂H_x intermediates at the Brønsted acid (BA) sites of HZSM-5, while the 10-member-ring (10-MR) micropores of HZSM-5 provide a shape-selective environment to yield aromatics.^{9,12} Spectroscopic¹³ and electron microscopic characterizations¹⁴ reveal that during the preparation of Mo/HZSM-5, MoO₃ species migrate into the micropores of HZSM-5 in the form of single-Mo oxide cluster (Mo(=O)₂(OH)⁺) bonding to the [AlO₄][–] site in the zeolite framework. According to recent studies,^{15–19} the MDA reaction has an activation/induction period, during which the initially atomically dispersed Mo oxide species react with CH₄ and convert into catalytically active molybdenum carbide (MoC_x) species, and a subsequently formed “hydrocarbon pool” provides organocatalytic centers for the production of aromatics. The quick

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deactivation of Mo/HZSM-5 is generally simply attributed to the easy formation of coke that blocks the channels of HZSM-5.^{16,20}

Despite extensive research that has reached some consensus on this reaction, many questions about the nature of the catalytic active sites^{13,15,18,21–25} and their deactivation mechanism remain.^{16,26,27} First, although MoC_x species are generally considered the active sites, their exact form is unclear and controversial.^{13,18,21,24,25} Are they molecules, clusters, or particles? What are their sizes and locations? If different forms of MoC_x coexist, then what are their respective roles in the reaction? Kosinov et al.²⁵ concluded that MoC_x species inside zeolite channels are the active sites, whereas MoC_x particles on the zeolite outer surface are “spectators” that only produce coke. Is this conclusion valid? The same group later reassigned the active sites from MoC_x to single Mo atoms,¹⁵ which shows the complexity of this question. Second, it is conceivable that for a bi-functional catalyst, using both types of active sites to their full capacity (avoiding prior deactivation of one over the other) is the key to avoiding rapid deactivation. However, there is a lack of studies on the sequence of deactivation of two active sites in Mo/HZSM-5. Are the Mo sites or the BA sites deactivated first? If one site is deactivated more quickly than the other, can we develop a method to reconcile their deactivation rates, to make full use of both sites? Third, the reported MDA performances of various Mo/HZSM-5 catalysts are often inconsistent under similar reaction conditions, likely due to different crystal sizes of zeolites.²⁸ What is the exact impact of the size of the HZSM-5 crystal on the deactivation of the catalyst and why? Fourth, the roles of the BA sites in catalyzing MDA are also under debate. Unlike the generally accepted bi-functional mechanism, the recently proposed “mono-functional” mechanism suggests that the primary function of the BA sites is to drive the dispersion of Mo species into the zeolite micropores, whereas they are not really required for MDA.²⁵ Is it possible to design an appropriate experiment to provide better insights into this controversy?

The purpose of the study reported here is to answer these outstanding questions by carefully characterizing a series of Mo/HZSM-5 catalysts at different stages of the MDA reaction. We investigate the effect of the size of the HZSM-5 crystal on the MDA performance and find that a prior deactivation of the MoC_x sites over the BA sites takes place in small crystals (~60 nm along the *b*-axis) but not in large crystals (>400 nm). This finding leads us to probe the migration and evolution of Mo species, using atomic-resolution transmission electron microscopy. The results show that at the end of the induction period, the produced MoC_x species exist mainly in the form of particles on the outer surface of small HZSM-5 crystals, or mainly in the form of clusters inside the microporous channels of large HZSM-5 crystals, explaining their crystal size-dependent catalytic behavior. On the basis of these observations, we speculate that protecting the MoC_x particles on small HZSM-5 crystals from direct deposition of coke would make both types of active sites resistant to deactivation, thereby extending the lifetime of the catalyst. To verify this hypothesis, we prepare a novel MDA catalyst that contains MoC_x particles encapsulated between the zeolite HZSM-5 and silicalite-1 thin layers and exhibits a significantly improved (~10-fold longer) lifetime, and thus a much higher total yield of aromatics, compared with conventional Mo/HZSM-5. An important conclusion from this experiment is that contrary to the traditional view that only MoC_x clusters inside micropores are active sites, MoC_x particles outside the 10-MR channels can also catalyze the reaction when they are encapsulated within the zeolite crystals. This new insight allows for the design of a control experiment to verify that the BA sites are indispensable for MDA.

Figure 1. MDA Performance of Various Mo/HZSM-5 Catalysts

Shown are (A) Mo/Z5(2), (B) Mo/Z5(60), (C) Mo/Z5(400), and (D) Mo/Z5-C. Top and bottom panels show methane conversions and benzene yields, respectively, as functions of time on stream. On each panel, black squares represent the fresh Mo/HZSM-5 catalyst, and red circles represent the spent Mo/HZSM-5 mixed with fresh Mo/SiO₂. Black-dotted lines are used to guide the eyes to easily identify the differences in methane conversion and benzene yield between the samples.

RESULTS AND DISCUSSION

Crystal Size-Dependent Behaviors of Mo/HZSM-5

This study involves 4 HZSM-5 (Si/Al $\approx$ 40) samples, including 3 with distinct dimensions along the *b*-axis (i.e., the straight channel direction) at $\sim$ 2, $\sim$ 60, and $\sim$ 400 nm that are synthesized using previously reported methods,^{29,30} and a commercial one consisting of micron-sized crystals. The same amount of Mo species was loaded onto the 4 HZSM-5 samples (Mo/Al = 0.5, in molar; $\sim$ 2.0 wt% Mo loading), following a standard procedure using (NH₄)₆Mo₇O₂₄·4H₂O as a precursor, at 700°C (see [Experimental Procedures](#) for details). The prepared Mo-loaded samples are denoted as Mo/Z5(2), Mo/Z5(60), Mo/Z5(400), and Mo/Z5-C, respectively, in which the number in parentheses refers to the thickness of the zeolite crystals along the *b*-axis. Electron microscopy images of the 4 Mo/zeolite samples are presented in [Figure S1](#). Powder X-ray diffraction (PXRD) revealed the absence of the bulk crystalline phase of Mo ([Figure S2](#)), and X-ray photoelectron spectroscopy (XPS) showed the presence of Mo(VI) oxide species in all fresh Mo/HZSM-5 catalysts, regardless of the zeolite crystal size ([Figure S3](#)).

The MDA reaction was performed using a fixed-bed reactor at atmospheric pressure and 700°C under a flow of a CH₄/N₂ mixture (50:50 in volume, 10 mL/min). The reaction always underwent an induction period, as indicated by the high consumption of methane but no aromatics detected in the effluent ([Figure 1](#)). It is known that during the induction period, the initial Mo oxide species are carburized by methane to form MoC_x that is the actual catalytic active sites for the subsequent MDA process.^{11,21,24} At the end of the induction period, when aromatics began to emerge (30 min on-stream), the evaluated catalysts gave similar methane conversions of $\sim$ 10% that were close to the thermodynamic limits ([Figure 1](#)). Although they were deactivated rather quickly as the reactions proceeded, we observed a clear trend in which the deactivation rate increased as the size of the zeolite crystal decreased ([Figure 1](#); [Table 1](#)). This trend was confirmed by analyzing the accumulated products during the reaction, which showed that the total yield of aromatics increased with

Table 1. Deactivation Behaviors of Various Mo/HZSM-5 Catalysts in MDA Reaction

	$t_{0.5}$ (h) ^a	t_{deact} (h) ^b	α (g _{Cat} mol _{CH₄} ⁻¹) ^c	Si/Al ^d	Mo Content (wt%) ^d
Mo/Z5(2)	1.26	2.04	17.78	42.24	1.97
Mo/Z5(60)	1.64	2.88	13.66	41.84	2.09
Mo/Z5(400)	2.53	4.56	8.85	37.10	2.06
Mo/Z5-C	2.85	5.46	7.86	39.78	1.99
MoC _x /HZS(60)	20.52	40.66	1.09	38.43	2.20
MoC _x /HSS(CO)	N/A	N/A	N/A	N/A	1.46
MoC _x /HZS(CO)	18.44	43.33	1.66	53.81	0.98

ICP, inductively coupled plasma spectrometry; MDA, methane dehydroaromatization.

^aTime elapsed for 50% reduction in methane conversion from the end of the induction period.

^bTime elapsed until methane conversion <2% from the end of the induction period.

^cDeactivation coefficient: $\alpha = \tau_0/t_{0.5}$ (contact time: $\tau_0 = 22.4$ g_{Cat} h mol_{CH₄}⁻¹ (30.69 g_{Cat} h mol_{CH₄}⁻¹ for MoC_x/HZS(CO)).

^dDetermined by ICP.

increasing HZSM-5 crystal size, as a consequence of extended catalyst lifetime (Figure 2). It is worth noting that in zeolite-catalyzed reactions, small zeolite crystals usually have longer lifetimes than larger crystals, due to their shorter diffusion lengths that facilitate the mass transfer and larger external surface areas to accommodate more coke before the entrances of micropores are blocked^{31–35}; this was indeed the case when the 4 HZSM-5 samples were used to catalyze the conversion of methanol to olefins (see Figure S4). Therefore, the opposite effect of zeolite crystal size observed for the MDA reaction suggests an unusual catalyst deactivation mechanism.

We mixed the spent, deactivated Mo/HZSM-5 (methane conversion <1%) with SiO₂-supported MoO₃ (Mo/SiO₂) that does not have MDA activity and heated the mixture under a flow of helium at 700°C for 1 h. Interestingly, this process largely restored the MDA activity of the spent Mo/Z5(2) and Mo/Z5(60) (Figures 1A and 1B), but did not restore it for Mo/Z5(400) and Mo/Z5-C (Figures 1C and 1D). Based on these results, we speculate that the deactivation of Mo/HZSM-5 with small zeolite crystals takes place only at the Mo sites, while the BA sites remain “alive”; therefore, supplying fresh MoO₃, which migrates from SiO₂ into the micropores of HZSM-5 upon heating through the specific interaction with BA sites²⁵ can regenerate the bi-functionality and thus the catalytic activity. In contrast, when Mo/HZSM-5 with large zeolite crystals is deactivated, the BA sites are “dead,” making it impossible to restore the activity simply by replenishing Mo species.

Identification of the Deactivation Sites

To understand the observed crystal size-dependent behaviors, we probed the evolution of the Mo sites and the BA sites, using XPS, temperature-programmed desorption of ammonia (NH₃-TPD), proton nuclear magnetic resonance (¹H-NMR), and atomic-resolution electron microscopy. For simplicity, we focus our discussions here on Mo/Z5(60) and Mo/Z5(400), which represent small and large zeolite crystals, respectively. The XPS spectra indicated that as the reaction proceeds, a transition from Mo(VI) oxide to MoC_x occurred in both catalysts, and the transition was nearly complete at 30 min on-stream (see Figure S5). According to NH₃-TPD (see Figure S6) and ¹H-NMR (see Figure S7), the number of BA sites in HZSM-5 was significantly reduced upon loading Mo, due to the proton transfer from the zeolite framework to MoO₃,³⁶ and during the induction period of MDA, the BA sites were restored along with the transition of MoO₃ to MoC_x. Interestingly, we observed a remarkable

Figure 2. Cumulative Methane Conversion and Product Distribution of Various Catalysts

(A) Mo/Z5(2).
(B) Mo/Z5(60).
(C) Mo/Z5(400).
(D) Mo/Z5-C.
(E) MoC_x/HZS(60).
(F) 520°C-regenerated MoC_x/HZS(60).
(G) MoC_x/HZS(CO).

difference between Mo/Z5(60) and Mo/Z5(400) when they were deactivated: the former retained a certain amount of accessible acid sites, but the latter did not (see Figure S6). This result confirms our speculation based on catalytic data.

Two scanning transmission electron microscopy (STEM) techniques, the high-angle annular dark-field STEM (HAADF-STEM) and integrated differential phase contrast STEM (iDPC-STEM) were used to detect the formation of MoC_x particles on zeolite surfaces at low magnification and probe the in-channel Mo species at atomic resolution, respectively. According to HAADF-STEM, there was no bulk phase of MoO₃ in fresh Mo/Z5(60) (Figure 3A), while iDPC-STEM revealed that Mo was atomically dispersed in the micropores (Figure 4A). After 30 min on-stream, small irregular particles (1–5 nm) emerged on Mo/Z5(60) (Figure 3B), and some particles with high crystallinity were determined to be β-Mo₂C from their lattice fringes (see Figure S8).³⁷ Considering the pore sizes of HZSM-5 (<0.6 nm),³⁸ these particles must be located at the external surfaces of zeolite crystals, meaning that Mo has migrated from the micropores to the outer surfaces during the induction period; this was confirmed by iDPC-STEM, which showed the disappearance of Mo from micropores (Figure 4B). A rough calculation based on the sizes, number, and density of observed MoC_x particles (>1 nm) showed that >70% of the total supported Mo species were transformed into particles on the crystal surfaces of Z5(60) at this stage (see Figure S9). With prolonged reaction times, these MoC_x particles steadily agglomerated and grew into larger particles (5–20 nm) (Figure 3C).

In comparison with the case of Mo/Z5(60), many fewer MoC_x particles emerged on Mo/Z5(400) after the induction period (Figures 3D and 3E) and even after deactivation (Figure 3F), despite the longer time on-stream (600 min), suggesting that most Mo species remain in the micropores of HZSM-5 during the reaction. Because the crystals of Mo/Z5(400) were too thick for atomic-resolution imaging, we used the focused ion beam (FIB) technique to cut thin slices out of the bulk crystals (Figures 4C and 4F). The FIB-prepared specimens not only allow atomic-resolution imaging

Figure 3. HAADF-STEM Characterization of Mo/HZSM-5 Catalysts

- (A) Fresh Mo/Z5(60).
(B) Mo/Z5(60) after the induction period (30 min) of the reaction.
(C) Deactivated Mo/Z5(60) after 300 min of reaction.
(D) Fresh Mo/Z5(400).
(E) Mo/Z5(400) after 30 min of the reaction.
(F) Deactivated Mo/Z5(400) after 600 min of reaction.

but also ensure that the observed features are from the “inside” of the crystal, avoiding interference from crystal surface species (note that STEM renders projection images). The HAADF-STEM image of fresh Mo/Z5(400) acquired from the FIB-prepared specimen showed widely distributed diffuse bright contrast, as indicated in [Figure 4D](#), which arose from the atomically dispersed Mo species in the micropores (both straight and sinusoidal 10-MR channels), and the iDPC-STEM image resolved the Mo species residing in the straight 10-MR channels ([Figure 4E](#)). After 30 min on-stream, Mo/Z5(400) showed a similar, diffuse bright contrast throughout the HAADF-STEM image of the FIB-prepared specimen ([Figure 4G](#)), indicating that Mo species remained highly dispersed inside the HZSM-5 crystals at the end of the induction period, and this was confirmed by iDPC-STEM, which showed the persistence of Mo species in the micropores ([Figure 4H](#)).

The XPS data of Mo/Z5(60) indicated a markedly increased Mo/Si ratio after 30 min on-stream (see [Table S1](#)). Because XPS is a surface-sensitive technique, this result provides further evidence that the Mo species migrated from the inside of the zeolite crystals to the external surfaces. For Mo/Z5(400), the XPS-determined Mo:Si ratio did not vary significantly during the reaction, which is also consistent with the STEM observations.

We performed carbon monoxide (CO) chemisorption to measure the number of the accessible MoC_x sites on Mo/Z5(60) at different stages of the MDA reaction, using a previously established procedure.^{39–41} We found that as the reaction proceeded, the number of accessible MoC_x sites and the methane conversion both decreased, with a positive linear correlation ([Figure S10](#)). This result suggests that the decrease in MDA activity of Mo/Z5(60) is related to the reduction in available MoC_x sites, which is the result of the combined effect of the growth of MoC_x into particles and the deposition of coke on these particles.

Figure 4. STEM Images of Mo/HZSM-5 Catalysts

(A and B) iDPC-STEM images of (A) fresh Mo/Z5(60) and (B) Mo/Z5(60) after 30 min of reaction, showing that the initially atomically dispersed Mo species migrate out of the 10-MR channels of HZSM-5 during the induction period.

(C–E) STEM images of Mo/Z5(400).

(C) Low-magnification HAADF-STEM image showing the whole slice extracted from a single catalyst crystal by FIB.

(D) Enlarged image of the area highlighted in (C).

(E) iDPC-STEM image.

(F–H) STEM images of Mo/Z5(400) after 30 min of reaction.

(F) Low-magnification HAADF-STEM image, showing the whole slice extracted from a single catalyst crystal by FIB.

(G) Enlarged image of the area highlighted in (F).

(H) iDPC-STEM image.

The diffuse bright contrast observed in (D) and (G) comes from Mo species atomically dispersed in the zeolite crystal. The red arrows in (A), (E), and (H) indicate in-channel Mo species, which are oxide species in (A) and (E) and carbide species in (H). The yellow arrow in (G) indicates a MoC_x particle formed at the surface of the zeolite crystal.

These characterization results indicate that MoC_x produced during the induction period has 2 different forms: either particles (>0.7 nm) on the surfaces of zeolite crystals or clusters (<0.7 nm) in the micropores. The possible reason for Mo species to be more prone to forming particles on external surfaces, when supported on small-sized HZSM-5, is that smaller zeolite crystals have a larger specific surface area and thus more abundant surface acidic or defective sites that can initially anchor more Mo species on zeolite surfaces (see Table S1), promoting MoC_x particles to nucleate and grow therein. The shorter diffusion lengths of smaller crystals also facilitate the migration of Mo species from the micropores to the outer surfaces. It has been reported that MoC_x particles on the outer surfaces of zeolite crystals can easily induce coke deposits.²⁵ High-resolution TEM showed that in deactivated Mo/Z5(60), MoC_x particles were densely covered by a graphite layer with thicknesses of 3–4 nm (see Figure S11). Therefore, the rapid deactivation of Mo/Z5(60) was actually due to the quick deposition of hard coke on MoC_x particles, despite the BA sites remaining active, whereas the deactivation of Mo/Z5(400) was mainly caused by the gradual formation of soft coke that blocks the pore entrance, making both in-channel MoC_x and BA sites inaccessible. This explains the different catalytic behaviors of Mo/Z5(60) and Mo/Z5(400).

Preparation of a Stable Catalyst by Encapsulating MoC_x Particles in Zeolite Crystals

Previous studies generally assume that only MoC_x clusters inside the micropores are catalytic active sites, whereas MoC_x particles on the zeolite surface are “spectators”

that do not contribute to the MDA but only produce cokes.^{15,25} In our study, although the large majority of the Mo species in Mo/Z5(60) has transformed into MoC_x particles after 30 min on-stream, benzene is continuously yielded for the next hour, which suggests that MoC_x particles are also catalytic active sites, despite their much shorter lifetime, compared to in-channel MoC_x clusters.

According to the experimental results discussed in the earlier sections, smaller HZSM-5 crystals have larger external surfaces and shorter diffusion lengths, which makes their BA sites more tolerant to coke formation, but also leads to the easy formation and deactivation of MoC_x particles on zeolite crystal surfaces, thereby accelerating the loss of overall MDA activity. This understanding inspired us to design and prepare a stable catalyst that combines the advantages of small zeolite crystals with “protected” MoC_x particles. Specifically, we took Mo/Z5(60) crystals out of the reaction bed after the induction period (30 min on-stream) and used them as “seeds” to grow a thin layer of silicalite-1 on their surfaces in a tetrapropylammonium hydroxide (TPAOH) solution under hydrothermal conditions (see [Experimental Procedures](#) for synthetic details). During the seeded growth process, HZSM-5 crystals are partially etched from the center of the crystal, forming a hollow structure. We denote the modified catalyst as MoC_x/HZS(60), in which MoC_x particles are encapsulated within core-shell structured zeolite crystals and sandwiched between the hollow ZSM-5 core and a silicalite-1 shell ([Figures 5B and 5D](#)). We hypothesize that this encapsulation effectively protects the catalytic active MoC_x particles from direct exposure to coke deposition and from further agglomeration, thus extending their lifetime to match that of the BA sites.

HAADF-STEM showed that MoC_x/HZS(60) consisted of hollow zeolite crystals ([Figure 6A](#)) in which the MoC_x particles were encapsulated in the zeolite matrix and well aligned ([Figures 6B and C](#)). These images provide direct evidence that MoC_x particles, originally located on the surfaces of the HZSM-5 crystals, were fully covered by a newly grown layer of silicalite-1, as illustrated in [Figure 5D](#). The electron diffraction performed on an isolated MoC_x/HZS(60) crystal showed a single-crystal diffraction pattern ([Figure 6D](#)), indicating the epitaxial growth of the silicalite-1 shell over the HZSM-5 core. Note that, despite the growth of the silicalite-1 shell, the overall diffusion length along the *b*-axis remains short for MoC_x/HZS(60), due to the hollow structure generated in the HZSM-5 core at the same time, therefore retaining all of the advantages of small zeolite crystals. The HAADF-STEM image taken from the [100] incidence confirmed the short diffusion length along the *b*-axis, in which the encapsulated MoC_x particles were also clearly observed ([Figure 6E](#)). The elemental line-scanning profile by energy-dispersive X-ray spectroscopy (EDS) indicated that the silicalite-1 shell was ~25 nm thick ([Figure 6F](#)). Both the HAADF-STEM ([Figure 6C](#)) and EDS data ([Figure 6F](#)) revealed that MoC_x particles were not located exactly between the hollow ZSM-5 core and a silicalite-1 shell, but ~15 nm inward from their boundary, due to the fact that the dissolved aluminosilicates recrystallized on HZSM-5 surfaces before the formation of the silicalite-1 shell. The XPS did not detect surface Mo species in MoC_x/HZS(60), confirming the successful fabrication of an isolation layer for MoC_x particles (see [Table S1](#)). In addition to protecting the active MoC_x particles from direct exposure to coke deposition, the silicalite-1 shell also acts as a passivation layer to eliminate the acid sites at the catalyst surface, which has proved to be an effective method for reducing coke formation.⁴² MoC_x/HZS(60) contains only MoC_x and no MoO₃ because the residual MoO₃ species are removed by the alkaline solution during the growth of the silicalite-1 shell; meanwhile, the organic structure directing agent (TPAOH) can be removed *in situ* from MoC_x/HZS(60) during the preheating of the MDA reaction (700°C in N₂) (see [Figure S12](#)).

Figure 5. Schematic Illustration of Deactivation Pathways and the “Encapsulation” Strategy

(A–D) The scenario for small zeolite crystals as represented by Mo/Z5(60).

(A) Fresh Mo/Z5(60).

(B) Mo/Z5(60) after the induction period of the MDA reaction.

(C) Deactivated Mo/Z5(60).

(D) MoC_x/HZS(60).

(E–H) The scenario for large zeolite crystals as represented by Mo/Z5(400).

(E) Fresh Mo/Z5(400).

(F) Mo/Z5(400) after the induction period of the MDA reaction.

(G) Deactivated Mo/Z5(400).

(H) MoC_x/HZS(400).

Blue dots represent atomically dispersed Mo oxide species; small red dots represent MoC_x clusters residing in the microporous channels; big red dots represent MoC_x particles located on the surface of zeolite crystals; brown represents the deposition of the coke species; green represents the zeolite ZSM-5; purple represents the zeolite silicalite-1 shell.

MoC_x/HZS(60) exhibited a much more stable MDA activity, in comparison with its parent catalyst Mo/Z5(60), validating the hypothesis that protecting the active MoC_x particles can improve the resistance of the catalyst to deactivation. Specifically, Mo/Z5(60) was deactivated (methane conversion <2%) within 180 min, whereas MoC_x/HZS(60) retained activity (methane conversion >2%) after 2,000 mins on-stream, corresponding to a lifetime ~10-fold longer (Figure 7; Table 1). Compared to Mo/Z5(60), MoC_x/HZS(60) afforded higher selectivity to aromatic products, and produced less coke (Figure 2), by benefiting from surface passivation.⁴³ MoC_x/HZS(60) converted 76.5 mmol/g_{cat} of CH₄ with a cumulative benzene yield of 50.3 mmol/g_{cat}, which was 11 times higher than Mo/Z5(60); this value is ~5 times higher than that of the best-performing conventional catalyst, Mo/Z5-C, which has a cumulative benzene yield of 10.3 mmol/g_{cat} (Figure 2).

Figure 6. Electron Microscopy Analysis of MoC_x/HZS(60)

(A–C) HAADF-STEM images at different magnifications, showing the hollow zeolite structure and well-aligned, encapsulated MoC_x particles. In (B and C), the image was acquired along the [010] zone axis of HZSM-5.

(D) Selected-area electron diffraction pattern of an isolated MoC_x/HZS(60) particle, indicating the single-crystalline nature of the core-shell structured zeolite.

(E) HAADF-STEM image of a MoC_x/HZS(60) particle acquired along the [100] zone axis.

(F) EDS elemental line-scanning profiles along the line marked in (E).

After 2,000 mins of reaction, the encapsulated MoC_x particles in MoC_x/HZS(60) retained the same size (2–5 nm) (see Figure S13) as when the catalyst was first prepared (Figures 6B and 6C). This differs from the case of Mo/Z5(60), in which the MoC_x particles grew on the ZSM-5 crystal surfaces gradually as the reaction proceeded (Figure 3C). This result demonstrates the effectiveness of our “encapsulation” strategy. MoC_x/HZS(60) also differs from Mo/Z5(60) in the deactivation sites. The MDA activity of spent MoC_x/HZS(60) cannot be restored by mixing with fresh Mo/SiO₂ (see Figure S14), indicating that the Mo and BA sites are simultaneously deactivated by “pore blocking.” Thus, our strategy allows the full use of the advantages of small-sized zeolites, which are easily accessible acid sites and have high resistance to coke formation, by avoiding the rapid deactivation of the MoC_x sites. More important, our results demonstrate that MoC_x does not have to reside in the micropores in the form of “clusters” to have MDA activity, while MoC_x “particles” outside the micropores that are usually considered detrimental to the reaction can also act as the active sites, when they are properly encapsulated within the zeolite crystals.

We note that to “protect” the Mo sites, the silicalite-1 shell should be fabricated only after the active MoC_x particles have been formed. In a control experiment, we loaded Mo onto a pre-synthesized core-shell structured HZSM-5@silicalite-1 zeolite. The obtained sample is denoted Mo/HZS(60). Elemental mapping by EDS shows that in Mo/HZS(60), the Mo species are selectively located in the ZSM-5 region (Figure S15), due to their specific interaction with the framework Al. When used for the MDA reaction, Mo/HZS(60) exhibited an only slightly improved lifetime, compared to Mo/Z5(60); large MoC_x particles were observed on the external surfaces of the catalyst after the reaction (Figure S16), indicating

Figure 7. Improved MDA Performance through the Encapsulation Strategy

(A) Methane conversion.

(B) Benzene yields.

(C) Naphthalene yields.

that Mo oxide atomically dispersed in the micropores is highly mobile and cannot be encapsulated. This result reveals that although encapsulating catalytic components in zeolites for improved selectivity and stability is a known strategy,^{44–46} a proper encapsulation procedure is needed to achieve the desired properties in a specific catalytic system.

Figure 8. Characterization and Catalytic Performance of MoC_x/HZS(400)
(A and B) HAADF-STEM images of MoC_x/HZS(400) at different magnifications, showing MoC_x particles in the cavity of the hollow ZSM-5 region that is outlined in (B).
(C and D) MDA performance of MoC_x/HZS(400) and Mo/Z5(400): (C) methane conversion and (D) benzene yield.

The “encapsulation” strategy cannot be applied to increase the lifetimes of Mo/HZSM-5 with large zeolite crystals, due to the different states of MoC_x species. In this study, we also modified Mo/Z5(400), using the same method as was used for converting Mo/Z5(60) to MoC_x/HZS(60). The modified catalyst, MoC_x/HZS(400), has a similar core-shell hollow structure to MoC_x/HZS(60) but with larger crystal sizes (Figure 8A). However, because the MoC_x species in Mo/Z5(400) mainly resided inside the micropores as small clusters (Figure 3E), there were almost no MoC_x particles encapsulated between the hollow HZSM-5 core and the silicalite-1 shell in MoC_x/HZS(400) (Figure 8B). Instead, we found many small MoC_x particles agglomerated in the cavity of hollow HZSM-5 (Figure 8B), likely because during the growth of the silicalite-1 shell, the HZSM-5 crystals were partially etched to form a cavity, leading to the agglomeration of originally isolated MoC_x clusters into particles, as schematically illustrated in Figures 5F and 5H. MoC_x/HZS(400) showed a lower stability in MDA activity than its unmodified counterpart Mo/Z5(400) (Figures 8C and 8D). This is reasonable, considering that MoC_x particles in MoC_x/HZS(400) are not encapsulated, but instead are located at the cavity surface of HZSM-5, where coke deposition can easily take place.

Regeneration of the Catalyst

MoC_x/HZS(60) was deactivated after ~2,500 min on-stream. Calcination in air at an elevated temperature to burn out the coke is a common method to regenerate a

spent zeolite catalyst. However, the regeneration of $\text{MoC}_x/\text{HZS}(60)$ is complicated because the key to its long lifetime is the “protection” of MoC_x particles; these particles can undergo a phase transition during the calcination process and revert back to Mo oxide species dispersed in the micropores. If such a phase transition were to take place, then the regenerated catalyst would behave similar to a conventional Mo/HZSM-5 catalyst, thus losing its structural feature (i.e., encapsulated MoC_x), as well as its longer lifetime, in the next catalytic run.

The thermal analysis performed in air indicates that the coke can be completely burned off at 550°C , whereas the phase transition of MoC_x to MoO_3 takes place starting from 520°C (see Figure S17). Initially, we attempted to regenerate the deactivated $\text{MoC}_x/\text{HZS}(60)$ at 550°C . HAADF-STEM (see Figure S18A) revealed the disappearance of the MoC_x particles along with the regeneration of Mo oxide species; elemental mapping by EDS confirmed that Mo was re-dispersed throughout the zeolite crystal (see Figure S18B). When used in the MDA reaction, the regenerated catalyst showed a similar deactivation behavior to that of unmodified Mo/Z5(60). In the next trial, we reduced the regeneration temperature to 520°C . HAADF-STEM showed that the encapsulated MoC_x particles were well retained at this temperature (see Figure S19A). The 520°C -regenerated catalyst has a slightly lower initial activity, in comparison with other tested catalysts, due to the incomplete removal of coke at this regeneration temperature, whereas it remains much more resistant to deactivation than the unmodified Mo/Z5(60) (see Figures S19B and 19C). This mild regeneration process can be performed repeatedly, without affecting the crystallinity of zeolites or the size and distribution of the encapsulated MoC_x particles (see Figure S20); as a result, the catalyst performs in a stable manner, under multiple regeneration-reuse cycles.

The Catalytic Roles of the BA Sites

It is known that the BA sites of HZSM-5 provide a driving force for the migration of MoO_3 into the micropores during the preparation of the catalyst.^{13,14} However, it remains unclear whether they are catalytically indispensable for MDA. The “hydrocarbon pool” mechanism proposed recently deemphasizes the catalytic role of BA sites, but it does not explain whether the generation of the hydrocarbon pool requires the BA sites.^{15,18}

Under the premise that only the in-channel MoC_x clusters are active sites, the fact that Mo supported on Al-free MFI zeolite (Mo/silicalite-1) is inactive cannot be used as evidence to prove that the BA sites are essential for MDA, because Mo/silicalite-1 does not have in-channel Mo species, due to the lack of BA sites. Now, we have shown that MoC_x particles encapsulated in HZSM-5 crystals are also catalytically active, which makes it possible to rationally design an experiment to investigate the catalytic importance of BA sites.

We loaded MoO_3 onto nano-sized HZSM-5 and silicalite-1 (both ~ 60 nm along the *b*-axis) and then converted MoO_3 to MoC_x using CO at 780°C . Although Mo species were initially located at different sites on HZSM-5 (in the micropores) and silicalite-1 (at the outer surfaces), they formed MoC_x particles at the zeolite outer surfaces in both cases after this conversion (see Figure S21). The use of CO ensures that this conversion is a “clean” process, without generating cokes on MoC_x particles.²⁴ However, we note that using CO to drive this conversion is not very efficient, as the XPS data indicated that the loaded MoO_3 was not fully carbonized under the conditions used (780°C , 6 h) in both samples (Figure S21C). Next, we encapsulated MoC_x particles with a silicalite-1 shell on both samples, using the method described earlier for preparing $\text{MoC}_x/\text{HZS}(60)$, to produce 2 catalysts, $\text{MoC}_x/\text{HZS}(\text{CO})$ and

Figure 9. Comparison between MoC_x/HSS(CO) and MoC_x/HZS(CO)

(A and B) Schematic illustrations of the structures of (A) MoC_x/HSS(CO) and (B) MoC_x/HZS(CO).

(C and D) HAADF-STEM images of (C) MoC_x/HSS(CO) and (D) MoC_x/HZS(CO), showing encapsulated MoC_x particles in both catalysts.

(E and F) MDA performance of the 2 catalysts: (E) methane conversion and (F) benzene yield.

MoC_x/HSS(CO), which constitute a good control experiment because they have the same properties, except that the latter is free of acid sites (Figures 9A and 9B).

HAADF-STEM confirmed that MoC_x particles were successfully encapsulated in core-shell hollow zeolite crystals, for both MoC_x/HZS(CO) and MoC_x/HSS(CO) (Figures 9C and 9D). We notice that the MoC_x particles in MoC_x/HSS(CO) are slightly larger than those in MoC_x/HZS(CO), but we do not think that this causes substantial differences in their catalytic activity. We also notice that the actual Mo content of these 2 catalysts (1.46 wt% for MoC_x/HSS(CO) and 0.98 wt% for MoC_x/HZS(CO); Table 1) is lower than the initial loading of Mo (2 wt%). This result is because the unconverted MoO₃ is removed from zeolite during the growth of the silicalite-1 shell and is consistent with the XPS results (Figure S21C). When used for MDA, MoC_x/HSS(CO) gave low methane conversion and nearly zero aromatics yield; in contrast, MoC_x/HZS(CO) showed high

activity and a long lifetime, and its overall performance was similar to MoC_x/HZS(60) (Figures 2, 9E, and 9F). This result clearly demonstrates that the BA sites are critical for the catalyst to have MDA activity, in which they likely serve as catalytic active sites for (1) the oligomerization/cyclization of C₂H_x intermediates^{9,47} or (2) the formation of “hydrocarbon pool” species,^{15–17} or both (1) and (2). More research is needed to more specifically determine the catalytic role of the BA sites in MDA reactions.

The challenge of understanding the deactivation of a bi-functional catalyst lies in how to identify the respective roles of two types of interacting active sites from the apparent catalytic behavior. In this study, we find that the crystal size of HZSM-5 support has important effects on the catalytic behaviors of Mo/HZSM-5 for the MDA reaction. Nano-sized HZSM-5 crystals have long-lived acid sites, but they tend to generate MoC_x particles on their outer surfaces during reaction. These exposed MoC_x particles are easily deactivated by coke, leading to a rapid loss in the overall MDA activity. Protecting the generated MoC_x particles with a siliceous shell can significantly improve the lifetime and the conversion capacity of the catalyst by almost 10-fold. The as-prepared nano-sized catalyst even far outperforms the conventional Mo/HZSM-5 catalyst that is based on micron-sized zeolite crystals; the MoC_x active sites reside primarily in the micropores and are deactivated together with the acid sites. Our results demonstrate that using both active sites to their full capacity is the key to achieving a long lifetime of the bi-functional catalyst and, more important, that MoC_x particles outside the micropores that are usually considered to be “spectators” to the reaction can act as catalytic active sites as well when encapsulated within zeolite crystals. Control experiments based on two similar catalysts, both having encapsulated MoC_x particles but one with acid sites and one without, demonstrate that in addition to promoting the dispersion of Mo species, the BA sites of the zeolite play an essential catalytic role in producing aromatic hydrocarbons in the MDA reaction.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Professor Yu Han (yu.han@kaust.edu.sa).

Materials Availability

All of the materials generated in this study are available from the Lead Contact without restriction.

Data and Code Availability

This study did not generate or analyze any datasets or code.

Material Preparation

All of the reagents were purchased from Sigma-Aldrich or Alfa Aesar and used without purification. ZSM-5 samples with distinct dimensions along the *b*-axis (~2, ~60, and ~400 nm) were synthesized following the methods reported in the literature.^{29,30} The Si:Al ratios for these samples were maintained at ~40 by the amount of Al precursor used in the syntheses. The as-synthesized ZSM-5 samples were calcined in air at 550°C for 5 h, and then converted to the H-form (HZSM-5).

The Mo/HZSM-5 catalysts—Mo/Z5(2), Mo/Z5(60), and Mo/Z5(400)—were prepared by incipient wetness impregnation, using ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄•4H₂O) as the Mo precursor. Typically, 1 g HZSM-5 was impregnated

in an aqueous solution containing 0.0368 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Mo loading: 2 wt %). The mixture was stirred at room temperature for 8 h and then dried in an oven at 110°C overnight. The obtained powder was further dried at 350°C for 24 h in flowing air and subsequently heated at 10°C/min to 700°C and held at 700°C for 2 h. Mo/silicalite-1 was prepared using the same procedure as described above for Mo/HZSM-5, except that silicalite-1 was used as the support. Mo/SiO₂ was also prepared using the same procedure, except that SiO₂ was used as the support and that the calcination in the last step was performed at 550°C for 5 h.

The preparation of MoC_x/HZS(60) involved 2 steps. In the first step, 0.3 g fresh Mo/Z5(60) (Si/Al = 20) was loaded into a fixed-bed reactor to undergo the MDA reaction for 30 min (see the [Catalytic Reactions](#) section for the reaction conditions). In the second step, the sample was taken out of the reactor and mixed with 3 mL of TPAOH (0.33 M) solution. The mixture was then heated in an autoclave at 170°C under stirring conditions for 10 h. The resulting solid was collected by centrifugation, washed with distilled water, and then added to a prepared TPAOH aqueous solution (0.01 M; 26 mL) containing 1.37 g tetraethyl orthosilicate (TEOS). The mixture was stirred overnight at room temperature, followed by crystallization in an autoclave at 100°C for 24 h. The obtained powder was dried in an oven at 110°C overnight without calcination. MoC_x/HZS(400) was prepared following the same procedure as that described above for MoC_x/HZS(60), except that Mo/Z5(400) (Si/Al = 20) was used as the starting material instead of Mo/Z5(60). Because the growth of a silicalite-1 shell would result in an increase in the Si/Al of zeolite, we used zeolites with a higher Al content (Si/Al = 20) as starting materials, so that the Si/Al ratios in the products were consistent with other catalysts (Si/Al ≈ 40).

To prepare MoC_x/Z5(CO), 0.3 g Mo/Z5(60) (Si/Al = 20) was loaded in a fixed-bed reactor and continuously treated with CO (30 mL/min; 10% CO and 90% He) at 780°C for 6 h. MoC_x/S1(CO) was prepared from Mo/silicalite-1 using the same method.

MoC_x/HZS(CO) and MoC_x/HSS(CO) were prepared following the same procedure used for preparing MoC_x/HZS(60), except that MoC_x/Z5(CO) and MoC_x/S1(CO) were used, respectively, as the “seed” to grow the silicalite-1 shell.

Characterization

(S)TEM imaging and EDS elemental analysis experiments were performed on a Titan Themis Z microscope, operated at 300 kV. HAADF-STEM images were acquired using a HAADF detector with collection angles of 22–135 mrad; iDPC-STEM images were acquired using a 4-quadrant DF4 detector with a high-pass filter applied to reduce the low frequency information and collection angles of 5–21 mrad. FIB was performed using the standard lift-out technique on a dual-beam FIB-SEM (FEI, Helios Nanolab Dualbeam).

PXRD patterns were recorded, using a Bruker D8 Advance instrument with Cu K α radiation (λ = 0.1542 nm) operated at 40 kV and 40 mA with a scanning speed of 0.5°/min. Thermogravimetric analysis was carried out using a TA Q5000 from 30°C–800°C at a heating rate of 10°C/min in air. The composition of the catalysts was obtained using an inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XSP). XPS spectra were collected in a Kratos Supra spectrometer, armed with a monochromatic Al K α X-ray source ($h\nu$ = 1,486.6 eV) in a high vacuum using an aperture slot of 300 × 700 μm .

A NH₃-TPD analysis was conducted in a Quantachrome automated chemisorption analyzer, starting from room temperature up to 800°C, with a ramp of 10°C/min.

A Bruker 600 AVANAC III spectrometer equipped with a 3.2-mm triple resonance CP MAS (magic-angle spinning) Bruker Probe (BrukerBioSpin) was used to record all ^1H NMR spectra. All of the spectra were recorded by collecting 1,024 scans using an adiabatic double-echo refocusing pulse program (zgse.agr) from the Bruker pulse library, with a recycle delay time of 10 s. Bruker Topspin 3.5pl7 software was used for data collection and post-processing.

Catalytic Reactions

The catalytic conversion of methane was performed in a fixed-bed reactor (6 mm inner diameter and 400 mm height) packed with 0.3 g catalyst and quartz wools to support the catalyst. The catalysts were pre-heated to 700°C, at a ramp rate of 10°C/min in a flow of N_2 , followed by the reactions that were performed at atmospheric pressure and 700°C in a 10-mL/min flow of a CH_4/N_2 mixture (50 vol% CH_4 ; N_2 as an internal standard). The transfer lines (stainless steel tubes) were heated and maintained at 200°C to prevent a condensation of the products. The products were analyzed using an online gas chromatograph (Interscience Compact GC) equipped with 2 separate columns and detectors: a thermal conductivity detector on a Molsieve 5-Å column for analyzing light gases (H_2 , N_2 , CH_4 , and CO), and a flame ionization detector on a Plot-Q column for hydrocarbons (aliphatics, benzene, toluene, naphthalene).

Based on the actual content of Mo, 410 mg $\text{MoC}_x/\text{HSS}(\text{CO})$ and 610 mg $\text{MoC}_x/\text{HZS}(\text{CO})$ were used for the reaction to make the total amount of Mo consistent with other catalysts. For the experiments aimed at identifying the deactivation sites, the deactivated catalyst was mixed with the same amount (0.3 g) of fresh catalyst (Mo/SiO_2); the reactions were performed under the same conditions as those described above.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.xcrp.2020.100309>.

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AUTHOR CONTRIBUTIONS

Y.H. conceived and designed the experiments. N.W. prepared, characterized, and evaluated the catalysts and analyzed the data. D.C., X.D., and J.W. participated in the catalyst preparation and catalytic testing. Y.H. contributed to the catalyst characterizations. L.L. performed the iDPC-STEM imaging. A.-H.E. performed the ^1H MAS NMR spectra. J.G. offered valuable suggestions and discussions. Y.H. wrote the manuscript, and all of the authors commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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