Influence of Framework Heteroatoms on Olefin Metathesis Activity Using MoO₃-MFI Catalysts

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S *Supporting Information*

ABSTRACT: Zeolites with the MFI topology and Si:M (M = Al, B) ranging from pure silica to 20:1 were employed as supports for molybdenum oxide centers to catalyze the olefin metathesis reaction of ethylene and 2-butene to form propylene. Pure-silica MFI doubled the metathesis activity against a comparable amorphous silica support. Incorporation of trivalent aluminum or boron heteroatoms into the MFI support had a significant impact on the catalytic performance. While strongly acidic sites generated by Al incorporation decreased the overall metathesis rate from 1.1×10^{-7} mol s^{-1} g$_{cat}$$^{-1}$ to 3.9×10^{-9} mol s^{-1} g$_{cat}$$^{-1}$ after 8 h on stream, less polarizable sites generated by B incorporation decreased the rate only to 8.3×10^{-8} mol s^{-1} g$_{cat}$$^{-1}$. Na$^+$ and K$^+$ ion exchange of the Al-containing MFI partially mitigated the deleterious effect of the strong Al heteroatoms at the cost of altering the molybdenum configuration away from active states, as observed by Raman spectroscopy. This work demonstrates that structured silica supports with weakly acidic heteroatoms are optimal for metathesis activity.

KEYWORDS: *metathesis, zeolite, heteroatom, boron*

Olefin cross-metathesis between ethylene and 2-butene is an important industrial reaction for the production of propylene with an estimated market volume of 8400 KTA and over 10% of the on-purpose propylene market share.[1] Various metal oxide catalysts have been researched for olefin metathesis, including the current Lummus Olefin Conversion Technology for the commercial production of propylene over tungsta on silica (WO₃/SiO₂) and the Shell Higher Olefin Process (SHOP) to produce linear α-alkenes over molybdena on alumina (MoO₃/Al₂O₃).[2] Of the two materials, molybdenum-based catalysts offer great promise for less energy-intensive industrial processes[3] in addition to lowering the reaction temperature for fundamental mechanistic and kinetic studies like the current work. Although the mechanism of homogeneous reactions catalyzed with organometallic complexes is known to proceed via a carbene catalyst with a metallocyclobutane intermediate,[4] the nature of the heterogeneous oxide precursor sites and how they contribute to metathesis activity continue to be highly debated topics in the open literature.[5−9] There is a critical need to understand the underpinnings of heterogeneous metathesis catalysts in order to achieve significant improvements in the process.

The metathesis activity can be controlled by tuning the molybdenum oxide site in a variety of ways, including pretreatments[10−12] and support modification.[13,14] For example, support modification has been demonstrated to influence the metathesis activity by altering the composition in silica–alumina supports,[15] by tuning the support acidity via calcination procedures[16] or dehydration treatments,[17] and by changing the surface of the support through novel synthesis techniques[18] or with mesoporous materials.[19] These studies have all concluded that both the support acidity and metal site structure govern the metathesis activity.

Zeolites present an exciting platform to host oxide centers that are active for olefin metathesis, as both the acidity and structure can be modified with precision. Varying degrees of acidity can be introduced in zeolites through heteroatom substitutions in the silica tetrahedral framework. For example, trivalent aluminum leads to strong Brønsted acidity, while boron leads to weaker acid sites because of boron's poor polarizability.[20]

Zeolites have been explored for olefin metathesis in various capacities in the past. Zhao et al.[21] compared tungsten oxide catalysts on different zeolite frameworks ranging from MFI (ZSM-5) to FAU (USY) and concluded that strong acidity assisted metathesis. Li et al.[22] admixed zeolite BEA with amorphous alumina in optimal ratios to maximize the metathesis activity over molybdenum oxide. Because of their crystallinity, zeolites have also been popular subjects to study in computational models of metathesis. In a follow-up work, Li et al.[23] studied metathesis over the Mo/H-BEA system and concluded that reduced molybdenum sites in the presence of aluminum heteroatom pairs were more likely to form active carbenes. Handzlik[24] investigated computational models of ZSM-5 and concluded that cooperative pairs of aluminum heteroatoms led to improvements in activity. While these idealized model systems may be difficult to achieve experimentally, they nonetheless encourage investigation of modifying zeolites and zeolite heteroatoms.

In this work, we investigated the impact of the heteroatom type and framework substitution extent in Mo-containing MFI zeolites on the metathesis activity. The heteroatom content of MFI zeolite supports, defined by the Si:M molar ratio (M = Al,

B), was varied from pure silica to 20:1. In addition, Al-MFI materials were further modulated by using sodium or potassium as charge-balancing cations, potentially eliminating Brønsted acid sites. Finally, boron was tested as an alternative heteroatom that in the literature is associated with reduced acidity.[20] Catalysts were prepared using incipient-wetness impregnation of ammonium heptamolybdate salts, as described by Shu et al.[25] as an effective way to disperse molybdenum oxides inside MFI for use in the methane dehydroaromatization with up to 6% Mo loading. For this work, 2 wt % MoO_3 was used as the active metal across all of the catalysts, ensuring good dispersion of the metal centers.

Powder X-ray diffraction patterns (Figure S1) indicated complete dispersion of the molybdenum within the zeolite pores, as no MoO_3 crystallite peaks were observed. This was confirmed by Raman spectroscopy measurements (Figure 1),
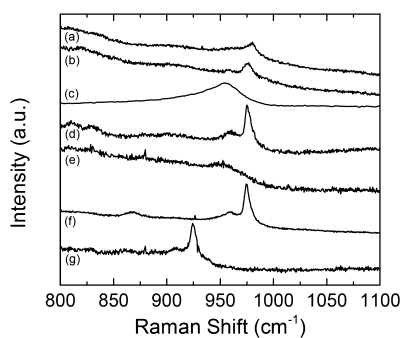

Figure 1. Raman spectra of 2% MoO_3 supported on (a) Si-MFI, (b) B-MFI-67, (c) SiO_2, (d) H-Al-MFI-200, (e) Na-Al-MFI-20, (f) H-Al-MFI-20, and (g) K-Al-MFI-20.

which displayed peaks only at 968 and 976−988 cm^{-1}, corresponding to the O−Mo−O and Mo=O stretches, respectively, of isolated molybdenum species.[26] Complete incorporation of trivalent aluminum heteroatoms into the zeolite framework was verified by ^{27}Al magic-angle spinning (MAS) NMR spectroscopy (Figure S2), so all of the measured activity can be attributed to molybdenum centers and associated framework aluminum sites.

The catalytic performance was evaluated for a stoichiometric mixture of 2% ethylene and 2% cis- and trans-2-butene diluted in helium at 100 °C under differential conditions free of mass transfer limitations. The carbon balance of the reaction was >99%, and no significant side products were observed other than isomerization of 2-butene to 1-butene. Specific reaction rates were calculated in terms of the propylene and 1-butene production rates. A steady state was reached for almost all of the materials after 4 h on stream (Figure 2), and the steady-state activities after 8 h are shown in Table 1.

Molybdena species supported on pure silica MFI resulted in propylene production rates nearly 3 times higher than those with an equivalent amount of molybdena on amorphous silica. The degree of improvement in the activity is consistent with current literature regarding nanostructured silica materials such as MCM-41 and SBA-15, which showed 4−8-fold improvements as supports for 1-octene metathesis over 8% MoO_3/ SiO_2.[19] Topka and co-workers attributed the improvement in activity to stabilization of active molybdenum centers due to the added periodic structure of the silica support.[19] These claims are difficult to verify, but Raman spectra of our samples (Figure 1) showed that the wide range of O−Mo−O stretches
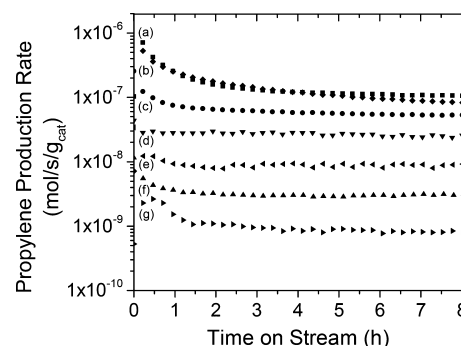

Figure 2. Propylene production rates at 100 °C for a 100 mL/min flow of 2% C_2H_4 and 2% C_4H_8 on 200 mg of 2% MoO_3 supported on (a) Si-MFI, (b) B-MFI-67, (c) SiO_2, (d) H-Al-MFI-200, (e) Na-Al-MFI-20, (f) H-Al-MFI-20, and (g) K-Al-MFI-20.

Table 1. Compositional Analysis and Catalytic Testing of 2% MoO_3 Supported on Various Supports

support	wt % MoO_3[a]	Si:Al ratio	production rate $(mol\ s^{-1}\ g_{cat}^{-1})$[d]	
			propylene	1-butene
Si-MFI	1.9	[b]	1.1×10^{-7}	[e]
B-MFI-67	1.7	[c]	8.3×10^{-8}	[e]
SiO_2	2.2	[b]	5.2×10^{-8}	[e]
H-Al-MFI-200	2.1	212 ± 19	2.6×10^{-8}	[e]
Na-Al-MFI-20	2.2	20 ± 2	9.2×10^{-9}	[e]
H-Al-MFI-20	2.2	20 ± 2	3.2×10^{-9}	2.6×10^{-7}
K-Al-MFI-20	2.0	22 ± 3	8.0×10^{-10}	[e]

[a]As determined by ICP-AES to within 0.2 wt % in MoO_3. [b]The Al content was below the detection threshold of 500:1. [c]B-MFI-67 has a Si:B ratio of 67 ± 1. [d]Measured after 8 h on stream. [e]The amount of 1-butene was below the detection limit.

observed for amorphous silica collapsed into a band at a higher Raman shift for MFI, suggesting stabilization of a more strained molybdenum configuration. In similar findings, Lwin et al.[27] discovered a highly strained rhenium site on alumina associated with a larger Raman shift that was also linked to metathesis activity. We therefore posit that the improvement in the metathesis activity over the Si-MFI support can be linked to a change in the configuration of the molybdenum centers within the zeolite pores.

The addition of aluminum to the MFI framework led to a change in the molybdenum site configuration, as evidenced in the Raman spectra (Figure 1f), where all of the aluminum-containing samples exhibited a mild decrease of 5−20 cm^{-1} in the Raman shift relative to the MoO_3/Si-MFI spectrum (Figure 1a). It was shown by Hu and Wachs[28] that a downshift by roughly 25 cm^{-1} in the Raman spectrum for dispersed MoO_3 on titania or zirconia can be attributed to partial reduction of the molybdenum sites. Therefore, we associate the decrease in Raman shift for MoO_3/H-Al-MFI-20 with partial reduction of the molybdenum sites at electron-donating centers, such as Brønsted acids. The incorporation of aluminum sites also increased the rate of formation of 1-butene (the isomerization side product), perhaps at the cost of suppressing the olefin metathesis rate, which decreased nearly 2 orders of magnitude. This agrees with results reported by Spamer et al.,[29] who noted that Brønsted acidity plays a detrimental role in olefin metathesis and leads to side

reactions. However, Debecker and co-workers showed that the metathesis rate doubles for 6 wt % MoO_3 supported on amorphous silicoaluminate prepared by coprecipitating 5% alumina with silica (corresponding to a Si:Al ratio of 16).[15] This difference in behavior may be due to a change in site topology, as suggested by the difference in the shape of the Raman spectrum for MoO_3/H-Al-MFI-20 (Figure 1f) compared with the MoO_3/SiO_2 and MoO_3/Si-MFI catalysts. It is known in the literature that the difference in local alumina topology between Al-MFI and amorphous Al_2O_3–SiO_2 can play a significant role in determining the reaction selectivity even if both possess strong Brønsted acids. This is why Cu-ZSM-5 is active for NO decomposition whereas Cu-silica-alumina is not[30] and also why the two supports differ in octane cracking activity.[31]

The Al-MFI-200 sample with Si:Al = 200 exhibited improved activity by a factor of 10 in comparison with the rate obtained with the Al-MFI-20 sample. In addition, the 1-butene side product formation decreased below detectable levels, whereas 1-butene formation previously accounted for nearly 8% of 2-butene conversion over MoO_3/Al-MFI-20. However, the sample with a low Si:Al ratio still was 5 times less active than the pure Si-MFI-supported material. Unlike the MoO_3/Al-MFI-20 sample, the number of molybdenum sites on Al-MFI-200 exceeds the number of aluminum heteroatoms (compositional analysis from Table 1 gives a molar ratio of 1.9 Mo per Al). In light of this observation, we propose that not all of the molybdenum sites were negatively affected by the presence of acid sites, leading to some improvement in the activity, though recovery of the activity was still incomplete. This hypothesis can be partially justified by the Raman spectrum (Figure 1d), which exhibited a mild broadening of the peaks found in the Al-MFI-20-supported sample as additional Mo stretches were added away from the aluminum sites.

Eliminating Brønsted acidity through sodium ion exchange did not fully recover the catalyst activity, which was improved over that of H-Al-MFI-20 by only a factor of 3. Akin to the H-Al-MFI materials, this poor metathesis activity relative to aluminum-free catalysts can be partially explained by the change in the molybdenum configuration, as observed in the Raman spectrum. Just as Na_2MoO_4 exhibited decreased Mo= O Raman shifts relative to MoO_3,[32] so too did the Mo=O shifts on Na-Al-MFI-20 compared with their H-Al-MFI-20 counterparts. However, just as in the case of the amorphous-silica-supported catalyst versus MoO_3/Si-MFI, this downward shift in molybdenum Raman stretches may be associated with a decrease in metathesis activity, causing MoO_3/Na-Al-MFI-20 to underperform relative to MoO_3/Si-MFI even as the sodium ion exchange eliminated harmful side reactions. This effect was further amplified for the larger potassium ion. Specifically, MoO_3/K-Al-MFI-20 exhibited further-reduced Raman shifts, and its activity decreased below H-Al-MFI-supported levels.

Replacement of aluminum heteroatoms with boron, previously attributed to have weaker acid sites,[20] restored the activity nearly to that of the pure Si-MFI-supported catalyst even though B-MFI-67 contained more heteroatom substitution than the less-active H-Al-MFI-200. In addition, the acid-catalyzed side reaction to form 1-butene was below the detection limit. The Raman spectrum of MoO_3/B-MFI-67 was also nearly identical to that of the MoO_3/Si-MFI sample, albeit at slightly lower Raman shifts because of mild electron donation from the boron heteroatoms, suggesting that MoO_3/

B-MFI-67 supported a more similar molybdenum site and was therefore similarly active.

In summary, zeolites offer a versatile gateway for tunable olefin metathesis supports. Zeolites exhibit enhanced metathesis activity compared with conventional amorphous supports, and in addition, their composition can be controlled with great precision to grant mechanistic insight into the role of support acidity for olefin metathesis in addition to the importance of creating highly strained molybdenum sites by way of defect engineering. Future work can expand on the catalyst archetypes and trends discussed here to create even more active supports for the next generation of metathesis catalysts.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

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Experimental details and PXRD patterns (PDF)

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Notes
The authors declare no competing financial interest.

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