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Influence of Framework Heteroatoms on Olefin Metathesis Activity using MoO$_3$-MFI Catalysts

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Supporting Information

ABSTRACT: Zeolites with the MFI topology and Si:M (M = Al or 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 metathesis activity against a comparable amorphous silica support. Incorporation of trivalent aluminum or boron heteroatoms into the MFI support had a significant impact on catalytic performance. While strongly acidic sites generated by Al incorporation decreased overall metathesis rates from 1.1x10$^{-7}$ mol/s/gcat to 3.9x10$^{-9}$ mol/s/gcat after 8 h on stream, less polarizable sites generated by B incorporation only decreased the rate to 8.3x10$^{-8}$ mol/s/gcat. 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.

KEY WORDS: 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 8,400 KTA and over 10% of the on-purpose propylene market share. 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 (WO$_3$/SiO$_2$) and the Shell Higher Olefin Process (SHOP) to produce linear alpha alkenes over molybdena on alumina (MoO$_3$/Al$_2$O$_3$). Of the two materials, molybdenum-based catalysts offer great promise for less energy-intensive industrial processes in addition to lowering reaction temperature for fundamental mechanistic and kinetic studies like the current work. Although the mechanism of homogenous reactions catalyzed with organometallic complexes is known to proceed via a carbene catalyst with a metalloccyclobutane intermediate, the nature of heterogeneous oxide precursor sites and how they contribute to metathesis activity continue to be highly debated topics in the open literature. Zeolites present an exciting platform to host oxide centers active for olefin metathesis as both 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 Bronsted acidity, while boron leads to weaker acid sites due to boron’s poor polarizability.

Zeolites have been explored for olefin metathesis in various capacities in the past. Pu Zhao et al. compared tungsten oxide catalysts on different zeolite frameworks, ranging from FFI (ZSM-5) to FAU (USY), concluding that strong acidity assisted metathesis. Xiujie Li et al. admixed zeolite BEA with amorphous alumina in optimal ratios to maximize metathesis activity over molybdenum oxide. Owing to their crystallinity, zeolites have also been popular subjects to study in computational models of metathesis. In a follow up work, Li et al. studied metathesis over Mo/H-BEA system to conclude that reduced molybdenum sites in the presence of aluminum heteroatom pairs were more likely to form active carbines. Handzik 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 into modifying zeolites and zeolite heteroatoms.

In this work, we investigated the impact of heteroatom type and framework substitution extent in Mo-containing MFI zeolites on metathesis activity. The heteroatom content of MFI zeolite supports, defined by the molar Si:M (M = Al...
or B) ratio, 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, associated in the literature with reduced acidity. Catalysts were prepared using incipient wetness impregnation of ammonium heptamolybdate salts, as described by Shu et al. 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% by weight of MoO₃ was used as the active metal across all catalysts, ensuring good dispersion of the metal centers.

Powder X-ray diffraction patterns (Fig. S1) indicated complete dispersion of the molybdenum within the zeolite pores as no MoO₃ crystalline peaks were observed. This was confirmed by Raman spectroscopy measurements (Fig. 1), which only displayed peaks at 968 cm⁻¹ and 976-988 cm⁻¹, corresponding to the O-Mo-O and Mo=O stretches, respectively, of isolated molybdenum species. Complete incorporation of trivalent aluminum heteroatoms into the zeolite framework was verified by 27Al MAS NMR spectroscopy (Fig. S2), so all measured activity can be attributed to molybdenum centers and associated framework aluminum sites.

Catalytic performance was evaluated for a stoichiometric mixture of 2% ethylene and 2% cis- and trans-2-butenes 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-butenes into 1-butenes. Specific reaction rates were calculated in terms of propylene and 1-buten production rates. Steady-state was reached for almost all materials after 4 h on stream (Figure 2), and steady state activity after 8 h is shown in Table 1.

Molybdena species supported on pure silica MFI resulted in propylene production rates nearly three times higher than an equivalent amount of molybdena on amorphous silica. The degree of improvement in activity is consistent with current literature regarding nanostructured silica materials, such as MCM-41 or SBA-15, which showed 4 to 8-fold improvements as supports for 1-octene metathesis over 8% MoO₃/SiO₂. Topka and coworkers attributed the improvements to stabilization of active molybdenum centers due to the added periodic structure of the silica support. These claims are difficult to verify, but Raman spectra of our samples (Figure 1) showed that the wide range of O-Mo-O stretches 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. discovered a highly-strained rhenium site on alumina associated with a

<table>
<thead>
<tr>
<th>Support</th>
<th>Wt% MoO₃</th>
<th>Si:Al Ratio</th>
<th>Propylene Prod. Rate mol/s/gcat</th>
<th>1-Butene Prod. Rate mol/s/gcat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-MFI</td>
<td>1.9%</td>
<td>b</td>
<td>1.1 x 10⁻⁷</td>
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<tr>
<td>B-MFI-67</td>
<td>1.7%</td>
<td>c</td>
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<tr>
<td>SiO₂</td>
<td>2.2%</td>
<td>b</td>
<td>5.2 x 10⁻⁸</td>
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</tr>
<tr>
<td>H-Al-MFI-200</td>
<td>2.1%</td>
<td>212 ± 19</td>
<td>2.6 x 10⁻⁸</td>
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</tr>
<tr>
<td>Na-Al-MFI-20</td>
<td>2.2%</td>
<td>20 ± 2</td>
<td>9.2 x 10⁻⁹</td>
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<tr>
<td>H-Al-MFI-20</td>
<td>2.2%</td>
<td>20 ± 2</td>
<td>3.2 x 10⁻⁹</td>
<td>2.6 x 10⁻⁷</td>
</tr>
<tr>
<td>K-Al-MFI-20</td>
<td>2.0%</td>
<td>22 ± 3</td>
<td>8.0 x 10⁻¹⁰</td>
<td></td>
</tr>
</tbody>
</table>

Figures:

Figure 1: Raman spectra of 2% MoO₃ supported on (a) Si-MFI, (b) B-MFI-67, (c) SiO₂, (d) H-Al-MFI-200, (e) Na-Al-MFI-20, (f) H-Al-MFI-20, (g) K-Al-MFI-20.

Figure 2: Propylene production rate at 100°C at 100mL/min of 2% C₂H₄ and 2% C₃H₈ for 200mg of 2% MoO₃ supported on (a) Si-MFI, (b) B-MFI-67, (c) SiO₂, (d) H-Al-MFI-200, (e) Na-Al-MFI-20, (f) H-Al-MFI-20, (g) K-Al-MFI-20.

Table 1: Compositional analysis and catalytic testing of 2% MoO₃ supported on various supports.

1. By ICP-AES to within 0.2wt% in MoO₃.
2. Al content below detection threshold of 500:1.
4. Measured after 8h on stream.
5. 1-Butene below detectable limits.
larger Raman shift that was also linked to metathesis activity. We therefore posit that the improvement in 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 aluminum-containing samples exhibited a mild decrease of 5 to 20 cm\(^{-1}\) in Raman shift relative to the MoO\(_3\)/Si-MFI spectrum (Figure 1a). It was shown by Hu and Wachs that a downshift by roughly 25 cm\(^{-1}\) in the Raman spectrum for dispersed MoO\(_3\) on titania or zirconia can be attributed to a partial reduction of the molybdenum site\(^{25}\). Therefore, we associate the decrease in Raman shift for MoO\(_3\)/H-Al-MFI-20 with the partial reduction of the molybdenum sites at electron-donating centers, such as Bronsted acids. The incorporation of aluminum sites also increased the rate of 1-butene formation (the isomerization side product), perhaps at the cost of suppressing the olefin metathesis rate, which decreased nearly two orders of magnitude. This result agrees with Spamer et al., who noted that Bronsted acidity plays a detrimental role in olefin metathesis and leads to side reactions\(^{29}\). However, Debecker and coworkers showed that metathesis rate doubles for 6wt% MoO\(_3\) supported on amorphous silica-aluminate prepared by co-precipitating 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, suggested by the difference in the shape of the MoO\(_3\)/H-Al-MFI-20 Raman spectrum (Figure 1f) from both MoO\(_3\)/SiO\(_2\) and MoO\(_3\)/Si-MFI catalysts. It is known in the literature that the difference local alumina topology between Al-MFI and amorphous Al\(_2\)O\(_3\)-SiO\(_2\) can play a significant role in determining reaction selectivity even if both possess strong Bronsted acids. This is why Cu-ZSM-5 is active for NO decomposition whereas Cu-silica-alumina is not\(^{30}\) and also the reason why the two supports differ in octane cracking activity\(^{31}\).

The Al-MFI-200 sample with Si/Al = 200 improved activity by a factor of 10 in comparison to the rate obtained with the Al-MFI-20 sample. In addition, 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 low Si/Al sample 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 activity, though recovery in 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 Bronsted acidity through sodium ion exchange did not fully recover catalyst activity, which was improved over H-Al-MFI-20 only by 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\(_2\)MoO\(_4\) exhibited decreased Mo=O Raman shifts relative to MoO\(_3\), too, did the Mo=O shifts on Na-Al-MFI-20 when compared to their H-Al-MFI-20 counterparts. However, just as in the case of 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 its activity decreased below H-Al-MFI-supported levels.

Replacement of aluminum heteroatoms with boron, previously attributed to have weaker acid sites\(^{29}\), restored activity near that of 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 of 1-butene formation was below detection limits. The Raman spectrum for MoO\(_3\)/B-MFI-67 was also nearly identical to the MoO\(_3\)/Si-MFI sample, albeit at slightly lower Raman shifts due to 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. In addition to enhancing metathesis activity over conventional amorphous supports, zeolite composition can be controlled with great precision to grant mechanistic insight on 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
Experimental details and PXRD patterns are available in the supporting information pdf file.

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REFERENCES


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