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Benchmarked Intrinsic Olefin Metathesis Activity: Mo vs. W

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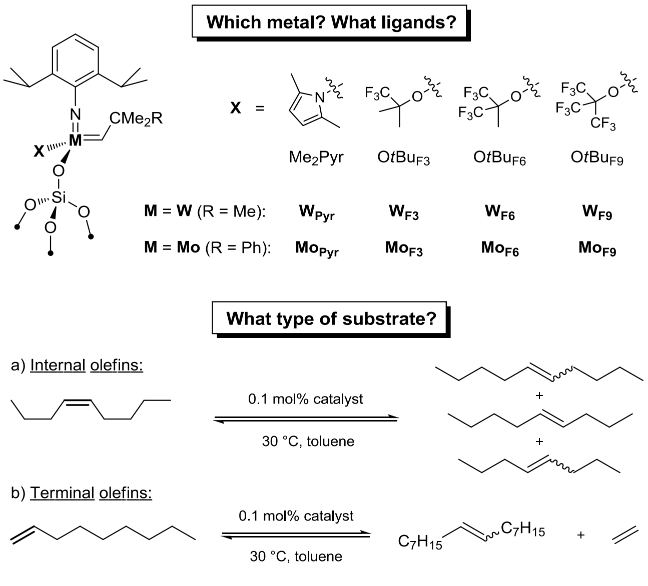
Combining Surface Organometallic Chemistry with rigorous olefin purification protocol allows evaluating and comparing the intrinsic activities of Mo and W olefin metathesis catalysts towards different types of olefin substrates. While well-defined silica-supported Mo and W imido-alkylidenes show very similar activities in metathesis of internal olefins, Mo catalysts systematically outperform their W analogs in metathesis of terminal olefins, consistent with the formation of stable unsubstituted W metallacyclobutanes in the presence of ethylene. However, Mo catalysts are more prone to induce olefin isomerization, in particular when ethylene is present, probably because of their propensity to undergo more easily reduction processes.

Keywords: Olefin Metathesis, Surface Organometallic Chemistry, Benchmark, Activity, Mo vs. W

Introduction

Molybdenum and tungsten are the two key elements for the industrial heterogeneous olefin metathesis catalysts (SHOP, Phillips Triolefin Process, Lummus' OCT, etc.).[1] Both metals also provide the most active homogeneous[2] and well-defined silica-supported[3-5] catalysts based on the Schrock-type alkylidene complexes. However, despite years of research and industrial application, it is still difficult to evaluate the intrinsic activity of Mo vs. W. Indeed, the marked difference in operating conditions for industrial heterogeneous catalysts based on supported MO_3 (100–200 °C for Mo vs. ≥400 °C for W) is likely associated with the initiation steps and the number of active sites,[6] rather than with the intrinsic activity of Mo and W active species. Well-defined silica-supported Mo alkylidenes[7-9] are more active than their W counterparts in propene metathesis,[10-12] however, molecular W alkylidenes are reported to outperform Mo analogs in metathesis of *cis*-2-pentene.[13] The difficulty to compare catalyst activities (rates) is however not surprising considering that these catalysts are both highly active and sensitive to poisons, hence requiring low catalyst loadings and very pure substrates to obtain reliable data (kinetic regime and no deactivation by poisoning). DFT calculations have shown that the main differences between isostructural Mo and W d^0 metathesis catalysts arise from: the difference in the stability of the metallacycles and the difference in energy barriers for the TBP/SP interconversion. In particular, W leads to more stable TBP and SP metallacycles; while the former is on the metathesis pathway, the more stable SP structure is an off-cycle intermediate that contributes to an overall decrease of activity of the catalyst.[14-18]

Recent investigations have shown that well-defined silica-supported alkylidenes, prepared by Surface Organometallic Chemistry (SOMC),[3-5] do not suffer from bimolecular decomposition pathways due to site isolation in contrast to their molecular analogs.[19, 20] In addition, it has been shown in the context of alkyne metathesis that using highly purified substrates is essential for reliable measurement of rates.[21] We thus reasoned that combining SOMC on a series of silica-supported Mo and W imido-alkylidene metathesis catalysts bearing identical ligand sets (*Scheme 1*) with a standardized olefin purification protocol would warranty reproducible metathesis activity measurement, allowing in fine the comparison of the intrinsic activities between Mo and W. This benchmark measurement of activity will be carried out on two prototypical substrates: *cis*-4-nonene and 1-nonene.



Scheme 1. Catalysts and substrates investigated.

Results and Discussion

In order to compare Mo and W catalysts, we have prepared a series of silica-supported Mo imido-alkylidenes ($(\equiv SiO)Mo(=NAr)(=CHCMe_2Ph)(X)$) bearing X ligands with different σ-donating ability ranging from electron-donating Me_2Pyr to highly electron-withdrawing $OtBu_{F9}$ (*Scheme 1*; Ar = 2,6-$iPr_2C_6H_3$; X = Me_2Pyr (**Mo_{Pyr}**), $OtBu_{F3}$ (**Mo_{F3}**), $OtBu_{F6}$ (**Mo_{F6}**), and $OtBu_{F9}$ (**Mo_{F9}**)), as well as the corresponding W analogs reported previously (*Scheme 1*; **W_{Pyr}**, **W_{F3}**, **W_{F6}**, **W_{F9}**; see *ESI* for details).[22, 23] We have then evaluated the performance of these supported complexes in the self-metathesis of *cis*-4-nonene and 1-nonene in batch conditions. The olefins are purified by successive distillation from Na, degassing, and passing through activated neutral alumina prior to a treatment with Selexsorb CD[24] (see *ESI* for details), the latter reagent being key for reaching high and reproducible activity at such low loadings.

Metathesis of *cis*-4-nonene results in the formation of an equilibrium mixture of cis/trans 4-octenes, 4-nonenes, and 5-decenes, corresponding to ca. 50% conversion of nonene (*Scheme 1a*). Since metathesis occurs without initiation, turnover frequency measured at time = 3 min ($TOF_{3\ min}$) is used as a descriptor of the catalyst activity, while time required to reach equilibrium (τ_{equil}) depends on both activity and stability. As shown in *Table 1*, the performance of certain W catalysts (in particular, the least active ones, **W_{Pyr}** and **W_{F3}**) is significantly improved after Selexsorb pretreatment of the olefin as compared to the previously reported data,[22, 23] although the general trend within the series stays unchanged. The results summarized in *Table 1* show that there is hardly any difference in activity between Mo and W catalysts for the same ligand set, the greatest distinction being observed for **Mo_{Pyr}** and **W_{Pyr}**. Interestingly, the activity of Mo catalysts within the series follows the same trend upon changing the σ-donating ability of the X ligand as observed before for supported W[22, 23] and molecular Mo[13] and W[25] catalysts ($Me_2Pyr < OtBu_{F3} < OtBu_{F6} < OtBu_{F9}$).

Table 1. Catalytic activities of silica-supported Mo and W imido-alkylidenes in metathesis of *cis*-4-nonene (*Scheme 1a*).

Cat.	**$TOF_{3\ min}$,^{a,b} min^{-1}**	**τ_{equil},^{a} min**	**Cat.**	**$TOF_{3\ min}$,^{b} min^{-1}**	**τ_{equil}, min**
W_{Pyr}	*23 (9)*	*60 (240)*	**Mo_{Pyr}**	*36*	*60*
W_{F3}	*50 (15)*	*30 (120)*	**Mo_{F3}**	*62*	*30*
W_{F6}	*78 (75)*	*20 (30)*	**Mo_{F6}**	*70*	*20*
W_{F9}	*101 (115)*	*10 (10)*	**Mo_{F9}**	*103*	*10*

[a] *In parentheses: previously reported data (no Selexsorb pretreatment).*[20,21] [b] *$TOF_{3\ min}$ are averages of several catalytic runs and are calculated based on total metal content in the sample considering 100% initiation.*[5]

For 1-nonene, metathesis yields cis/trans 8-hexadecenes and ethylene (*Scheme 1b*). In this case, full conversion can be reached if ethylene is removed from the reaction mixture (see *ESI* for details). The results are summarized in *Table 2* and *Figure 1*. All Mo catalysts demonstrate high activities and perform very similarly with little influence of the pendant X-group. However, in contrast to what is found for *cis*-4-nonene, the initial activity of W catalysts is ca. an order of magnitude lower than that of Mo. The effect of the X ligand on the initial activity is also not strongly pronounced for W. However, it has a significant effect on the overall catalytic performance (number of turnovers) (*Figure 1*), σ-donating X ligands clearly yielding more efficient catalysts. Thus, **W_{Pyr}** catalyst containing electron-donating Me_2Pyr ligand shows remarkably better performance than other W catalysts albeit still worse than its Mo analog **Mo_{Pyr}**. It should be also noted that, while being more active, Mo catalysts display lower selectivity. While selectivity in metathesis product (C_{16}) remains ≥99.5% for all the W catalysts over the course of the reaction, 2–3% of isomeric products (C_{15}, C_{14}…) are formed after 8 h of the reaction for **Mo_{F3}**, **Mo_{F6}** and **Mo_{F9}**, and up to 7% for **Mo_{Pyr}**. In addition, if ethylene is not efficiently released from the reaction mixture (e.g. using a closed vessel), the selectivity can drop even further to reach values as low as 80–85% (**Mo_{Pyr}**), probably indicating that ethylene is responsible (at least in part) for the lower selectivity. The reaction also appears to be slower in this case for both Mo and W.

Table 2. Catalytic activities of silica-supported Mo and W imido-alkylidenes in metathesis of 1-nonene (*Scheme 1b*).

Cat.	$TOF_{3\,min}$,[a] min^{-1} (conv. after 8 h)	Cat.	$TOF_{3\,min}$,[a] min^{-1} (conv. after 8 h)
W_{Pyr}	*2.1 (68%)*	**Mo_{Pyr}**	*14 (96%)*
W_{F3}	*2.0 (24%)*	**Mo_{F3}**	*26 (96%)*
W_{F6}	*1.7 (24%)*	**Mo_{F6}**	*28 (98%)*
W_{F9}	*0.7 (16%)*	**Mo_{F9}**	*20 (98%)*

[a] *$TOF_{3\,min}$ are calculated based on total metal content in the sample considering 100% initiation.*[5]

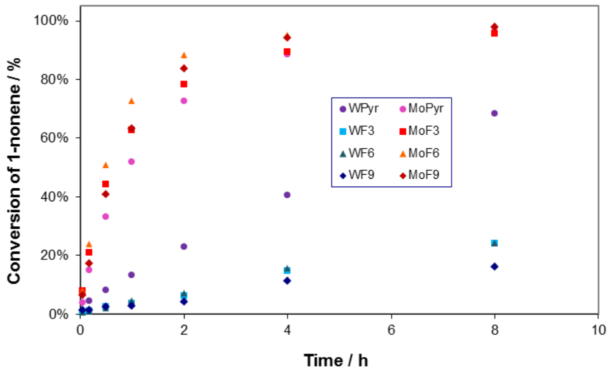


Figure 1. Catalytic performance of silica-supported Mo and W imido-alkylidenes in metathesis of 1-nonene.

The observed difference in activity towards 1-nonene metathesis between Mo and W is in line with the previous findings on catalytic behavior of silica-supported Mo[7-9] and W[10, 11] alkylidenes in the metathesis of propene under flow conditions, where W catalysts are also found to be significantly less efficient than their Mo analogs. We reasoned that the main difference between metathesis of internal (*cis*-4-nonene) and terminal olefins (propene and 1-nonene) arises from the presence of ethylene and the formation of unsubstituted metallacyclobutanes in the latter case. For W, these metallacyclobutanes have been previously shown to be rather stable and reluctant to participate in metathesis, as evidenced by pronounced induction periods.[22] Their stability is also consistent with DFT calculations[17] and with the fact that most isolated and fully characterized metallacyclobutanes are based on W, in both molecular[26] and surface chemistry.[11, 22, 23, 27, 28] In contrast, the stability of Mo metallacyclobutanes is significantly lower,[13, 29, 30] and so far these species have been isolated in only few cases with molecular catalysts[13, 29] and not reported on surfaces. Easier decomposition of Mo metallacycles to form d^0 hydride/alkyl or d^2 species is also likely the reason of lower selectivity observed in this case, as these species can promote double bond migration. Earlier studies have shown that ethylene is particularly prone to induce deactivation of metathesis catalysts.[15, 31] In fact, we have so far failed to observed the formation of metallacyclobutanes in the case of supported Mo catalysts.

Overall, based on the catalytic data discussed above, we conclude that there is no dramatic difference in intrinsic activity between Mo and W alkylidenes towards metathesis of internal olefins and that the lower activity of W catalysts in metathesis of terminal olefins is mainly due to the relatively high stability of unsubstituted metallacyclobutane intermediates that serve as a catalytic off-cycle resting state. Moreover, the better performance of $\mathbf{W_{Pyr}}$ can also be explained using the same rationale, as the presence of σ-donating ligands leads to destabilization of the metallacyclobutane intermediates.[17] This is also in line with the data on the previously reported W catalysts bearing strongly σ-donating ligands, e.g. thiolates[32] and *N*-heterocyclic carbenes,[33] that displayed remarkably high activities in metathesis of terminal olefins.

Conclusions

Using SOMC and careful olefin purification protocol has allowed us to measure the intrinsic activities of Mo and W olefin metathesis catalysts and to compare their relative performance. The set of data reported here can serve as a perfect illustration to the general principles of olefin metathesis catalyzed by group 6–7 d^0 metal alkylidenes found in DFT studies.[14-17, 31, 34] While there is no essential difference in activity between Mo and W in metathesis of internal olefins (given the identical ligand environment and rigorous purification of the substrate), Mo catalysts systematically outperform their W analogs by ca. one order of magnitude in metathesis of terminal olefins, albeit at the expense of selectivity. This differences are rationalized by the formation of stable unsubstituted metallacyclobutanes in the presence of ethylene for W and presumably the easier reduction of Mo. The activity of both Mo and W systems towards internal olefins increases with decreasing the σ-donating ability of the X ligand, which favors TBP over SP. In the case of terminal olefins, destabilization of unsubstituted metallacyclobutane intermediates by introducing σ-donating ligands appears to be a more important factor for W: increasing σ-donating ability of the X ligand leads to the improved overall catalytic performance. The trends identified in this work provide a benchmark in comparing Mo and W and pave the way towards a more rational development of Mo and W-based alkene metathesis catalysts.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

PZ and VM synthesized the catalysts and developed the olefin purification protocol and procedures for testing the catalytic activity. JJS designed and performed the high-throughput experiments with 1-nonene. The manuscript was written by CC, PZ and VM.

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