

# Investigation of Cross-Metathesis in Fatty Acid Esters using nanosilica supported- and molecular Mo and W halides and oxyhalides precatalysts

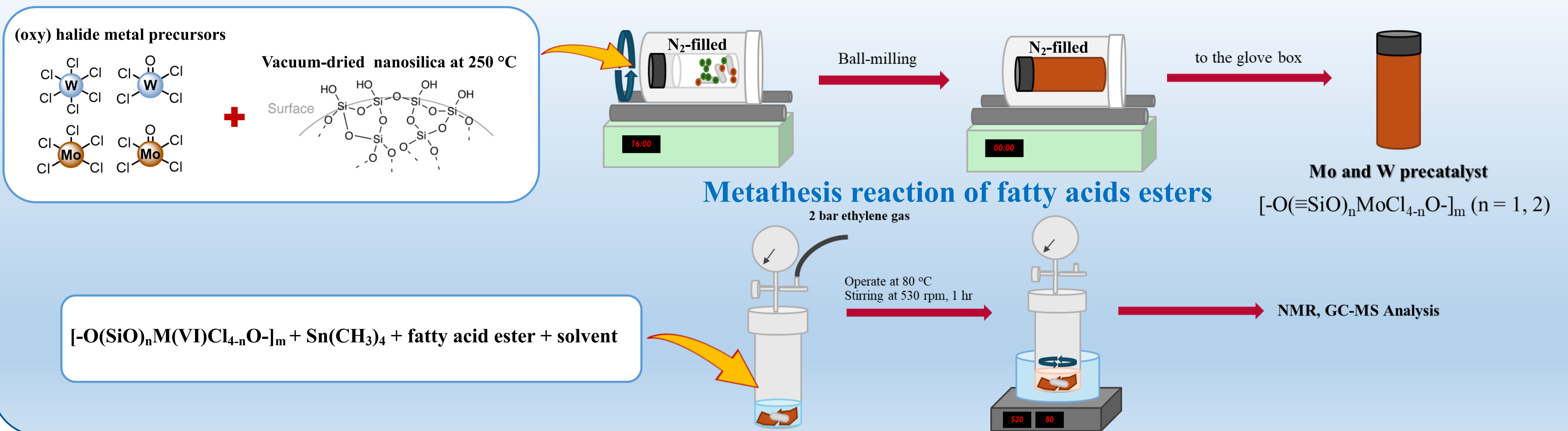
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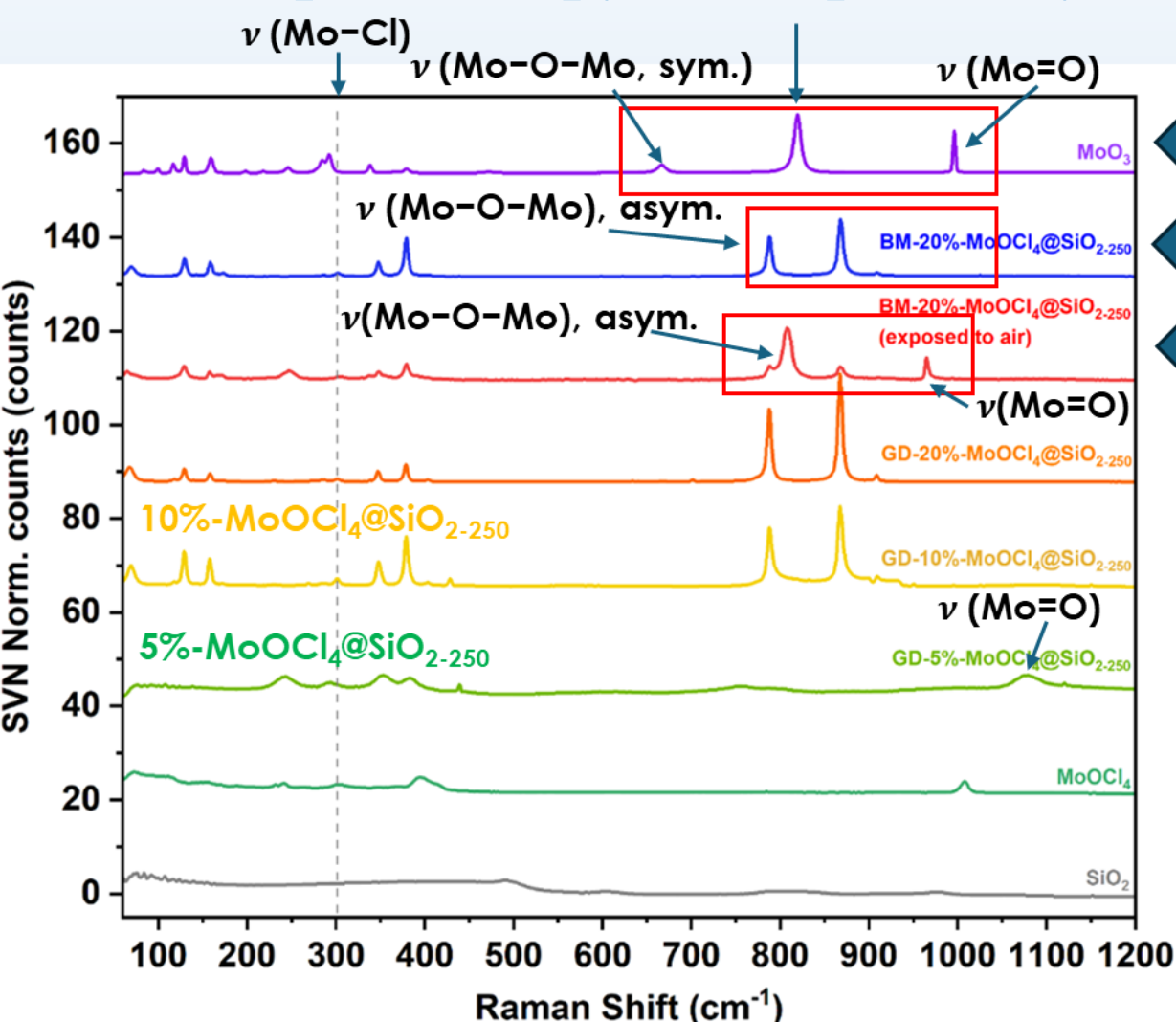
The valorization of biobased feedstocks for the production of high-value chemicals is a rapidly growing field in research chemical chemistry. Unsaturated fatty acid esters (FAEs), derived from the transesterification of fatty acids with alcohols, are abundant, affordable, multifunctional and versatile chemicals. This work explores the cross-metathesis of FAEs such as methyl oleate with ethylene, known as ethenolysis reaction providing C<sub>10</sub> products, 1-decene and 9-decanoate (9-DAME) that have the potential to serve as precursors for lubricants and plasticizers. Although several metathesis catalysts are currently reported for the ethenolysis process, there is still a lack of readily accessible, cost-effective, and efficient catalytic systems. To address this challenge, metal group VI (Mo, W) molybdenum and tungsten (oxy) halides were selected as precursors to generate precatalytic forms. These heterogeneous pre-catalysts are conveniently prepared via a solvent-free mechanochemical approach, which does not require complicated and multi-step synthetic procedures. This study evaluates the efficiency of homogeneous and heterogeneous Mo and W (oxy) catalytic systems activated by tetramethyl tin, an alkylating agent, for the *in situ* generation of metal alkyl species that evolve into catalytically active metal alkylidenes upon heating in ethenolysis reaction. Interestingly, MoOCl<sub>4</sub>, while ineffective as a homogeneous catalyst, displayed remarkable activity and selectivity when supported on nanometric silica. Raman characterization and elemental analysis disclose catalytic structures, which are isolated ( $\equiv$ SiO)Mo(=O)Cl<sub>3</sub> species or polymeric silica supported [-O( $\equiv$ SiO)<sub>n</sub>MoCl<sub>4-n</sub>O-]<sub>m</sub> (n = 1, 2) species, depending on the amount of molybdenum loading on silica. Notably, the analysis also showed that the isolated ( $\equiv$ SiO)Mo(=O)Cl<sub>3</sub> sites exhibit higher catalytic activity compared to the polymeric species. The performance of heterogeneous MoOCl<sub>4</sub> based pre-catalysts was evaluated with various substrates, including polyunsaturated and industrial mixed fatty acid methyl esters derived from palm oil.

## Preparation of Mo and W precatalysts by grafting Mo and W (oxy)chlorides on nanosilica



## Characterization

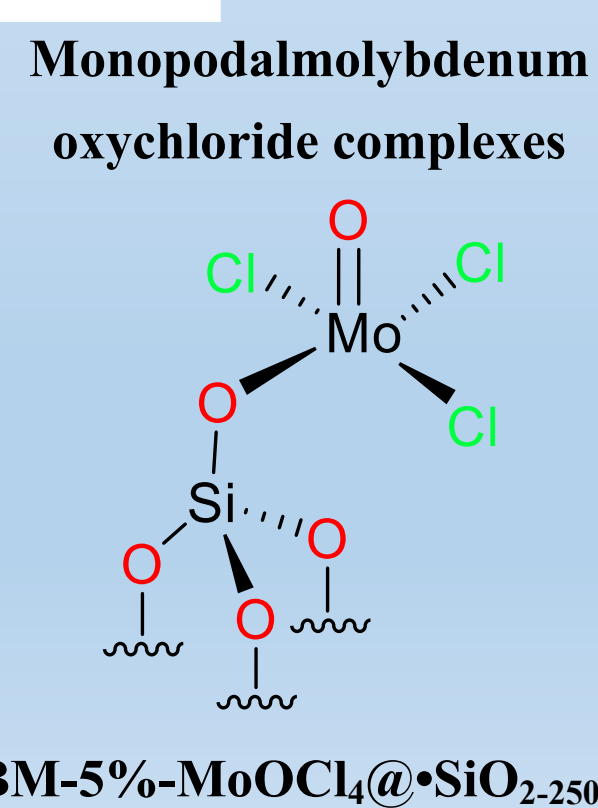
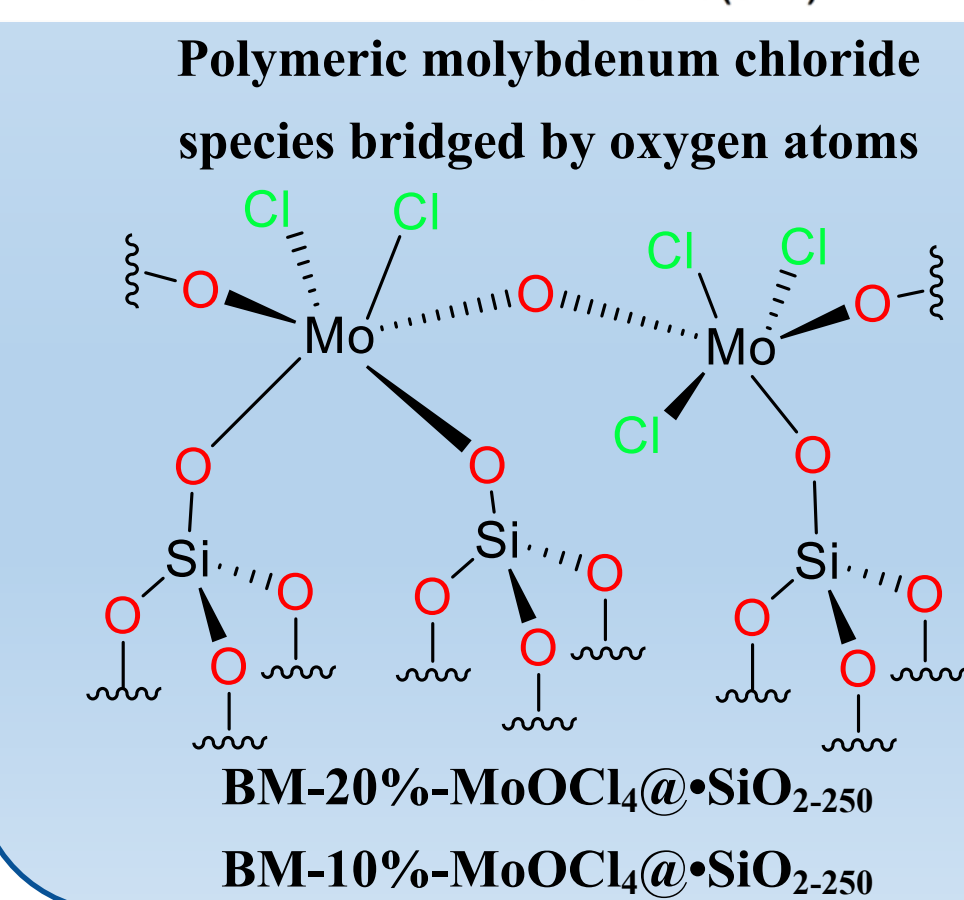
### Raman Spectroscopy of the precatalyst



### Mohr's titration of the precatalyst

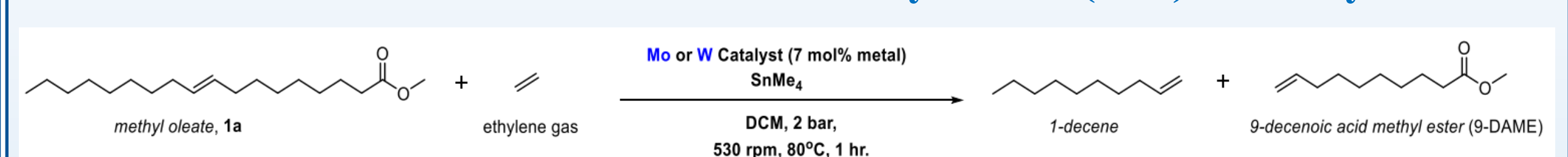
### Mohr's Titration (Chlorine amount determination)

Entry	Catalyst	Cl/Mo molar ratio
1	BM-5%-MoOCl <sub>4</sub> @SiO <sub>2-250</sub>	3.4±0.1
2	BM-10%-MoOCl <sub>4</sub> @SiO <sub>2-250</sub>	3.0±0.1
3	BM-20%-MoOCl <sub>4</sub> @SiO <sub>2-250</sub>	2.5±0.3
4	BM-20%-MoOCl <sub>4</sub> @SiO <sub>2-250</sub> (exposed to air)	1.1±0.1



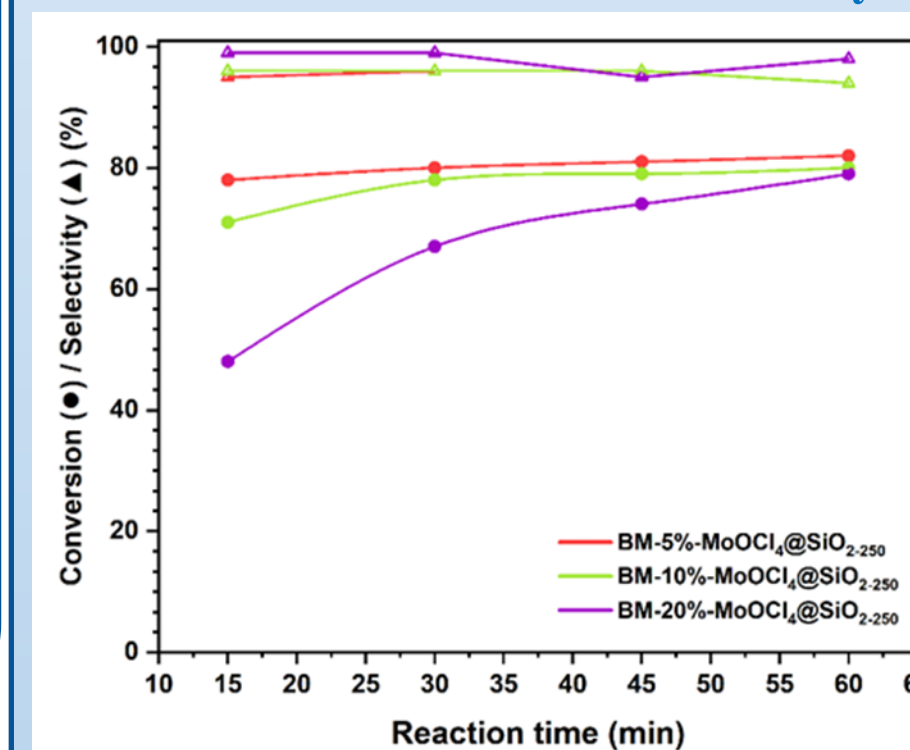
## Results

### Cross metathesis reaction between methyl oleate (MO) and ethylene

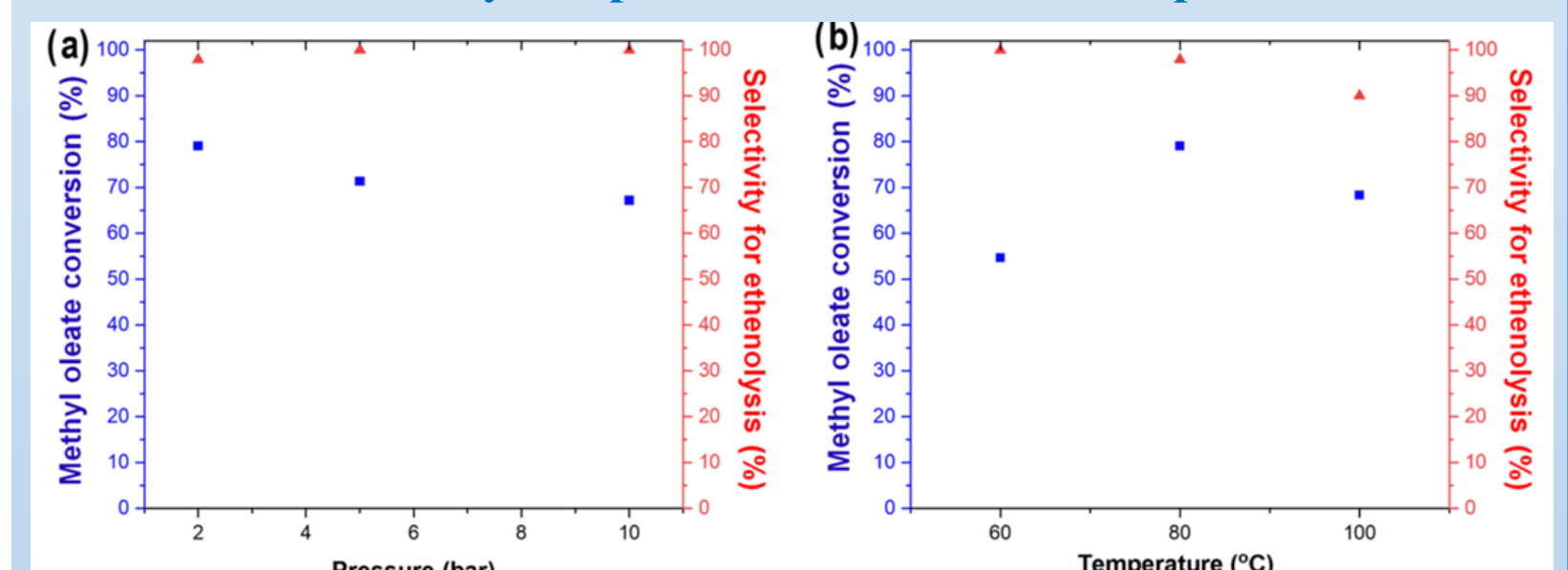


Entry	Catalyst	Conversion (%)	Selectivity in cross-metathesis (%)
1	WCl <sub>6</sub>	13	99
2	WOCl <sub>4</sub>	24	99
3	MoCl <sub>5</sub>	-	-
4	MoOCl <sub>4</sub>	-	-
5	Aerosil silica, SiO <sub>2-250</sub>	-	-
6	BM-20% w/w WCl <sub>6</sub> @SiO <sub>2-250</sub>	46	>99
7	BM-20% w/w WOCl <sub>4</sub> @SiO <sub>2-250</sub>	-	-
8	BM-20% w/w MoCl <sub>5</sub> @SiO <sub>2-250</sub>	62	98
9	BM-20% w/w MoOCl <sub>4</sub> @SiO <sub>2-250</sub>	79	98

### Kinetic profiles of methyl oleate conversion and cross-metathesis selectivity

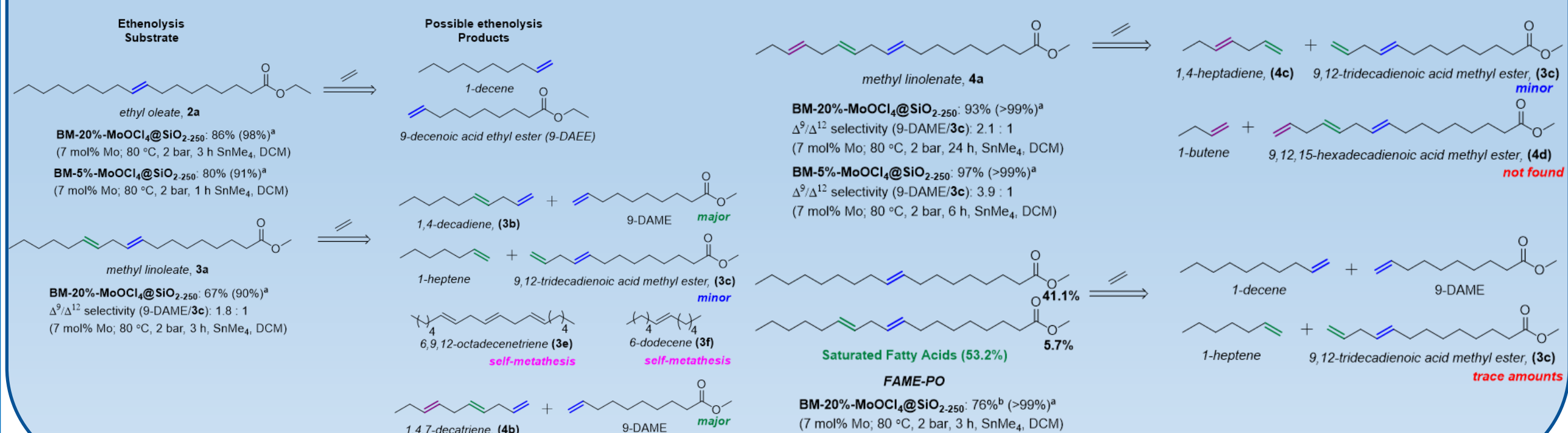


### Effect of ethylene pressure and reaction temperature



Conversion ≈ 80%  
Cross-metathesis Selectivity > 90%

### Application of the catalyst for cross-metathesis of Various Substrates under Optimized Reaction Conditions



## Conclusions

A series of molybdenum (Mo) and tungsten (W) (oxy)halides, both grafted onto nanosilica and in their molecular forms were tested as catalysts for the ethenolysis reaction of unsaturated fatty acid esters. Among all the compounds tested, 20%-MoOCl<sub>4</sub>@SiO<sub>2-250</sub> showed the highest conversion and selectivity. This precatalyst, MoOCl<sub>4</sub>@SiO<sub>2-250</sub>, was prepared through a convenient mechanochemical approach (intimate grinding). Upon *in situ* activation by Sn(CH<sub>3</sub>)<sub>4</sub>, it forms the active catalytic species for the ethenolysis reaction. Raman spectroscopy and Mohr's titration provided insights of the surface structure of the material. By varying the loading of MoOCl<sub>4</sub> on silica produced different surface species, including monopodal molybdenum oxychloride complexes (BM-5%-MoOCl<sub>4</sub>@SiO<sub>2-250</sub>) and polymeric molybdenum chloride species bridged by oxygen atoms (BM-20%-MoOCl<sub>4</sub>@SiO<sub>2-250</sub>). The former exhibited superior catalytic performance achieving equilibrium conversion of methyl oleate within 5-15 minutes. The latter precatalyst, while slightly less efficient, required lower amounts of material, making it more convenient to use. The developed precatalysts were effective for the selective ethenolysis of various (poly)unsaturated fatty acid esters, including industrial FAME mixtures. Preliminary results also indicate that BM-20%-MoOCl<sub>4</sub>@SiO<sub>2-250</sub> is suitable for application in flow reactors. Overall, we believe that systematic exploration and optimization of the structure, loading, and support of readily available heterogeneous ethenolysis precatalysts based on inorganic molybdenum and tungsten compounds are crucial for generating cost-effective and straightforward materials for the valorization of fatty acid esters.

## References

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