Computational Materials Science 155 (2018) 197–208

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

# Initiation of heterogeneous Schrock-type Mo and W oxide metathesis catalysts: A quantum thermochemical study

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## ARTICLE INFO

*Keywords:*
Thermochemistry
Initiation
Mechanism
DFT
Tungsten
Molybdenum
Metathesis
Olefin
Ethylene
Propylene
Activation
Heterogeneous catalyst
Computational chemistry
Silica
Thermodynamics
Carbene
Schrock
Alkylidene
Molecular simulation

## ABSTRACT

Three mechanistic pathways were explored theoretically to study the electronic features and thermodynamics behind the initiation of silica-grafted molybdenum and tungsten oxide metathesis pre-catalysts in light olefins (ethylene and propylene) to form Schrock-type carbene structures. At 298 K and 1 atm, the investigated activation process was found to be exothermic for all but one of the carbene species, where the pathway involving a secondary carbene center and liberating acetone as a byproduct was more favorable (by about 10 kcal/mol) than the process involving a primary carbene center and evolving propionaldehyde. The most exothermic carbene to form (−20.9 kcal/mol) had its both propylidene and propoxy groups bonded through their secondary carbon atoms. A competing pathway suggested for an ethylene feedstock and tungsten-based catalyst, which involved the production of acetaldehyde was also viable. The generation of carbene species from the W-based pre-catalyst was less exothermic than the Mo-based pre-catalyst, however. The computational data with the activation pathways at hand stressed the benefits of initiation at low temperatures, the presence of adjacent trapping heterogeneities for the acetone or propanal by-products, and the beneficial role of the presence of an isopropoxy ligand. The localized-orbital locator maps indicated the polar covalent characteristics of the metal–carbene bonds, which were polarized towards the C atom. The analysis of the density of states indicated the destabilization of the highest occupied molecular orbitals (HOMOs) of the pre-catalysts upon carbene generation, where the alkylidene fragment and transition metal both contributed to the HOMO of the carbene complex.

## 1. Introduction

Ethylene and propylene are the most largely produced (organic) chemicals and main building blocks of the petrochemical industry [1–3]. In industry, they are predominantly produced via thermal cracking or catalytic cracking of hydrocarbons [4–8]. However, the propylene production from the conventional sources and butene products from steam crackers cannot suffice their steadily growing demands in the market [9,10]. This provokes on-purpose technologies, e.g., to generate 30% of global propylene from unconventional sources in 2025 [2].

In spite of the wide applications of heterogeneous catalysts and their promising operational benefits over homogeneous catalysts [11–15], the initiation of heterogeneous catalysts often lacks an essential piece of knowledge, i.e., the identification of the true active species [16,17]. This is particularly relevant to the direct transformation of alkenes to higher olefins over trifunctional single-site catalysts [18].

Single-atomic Mo and W species grafted into the porous silica materials are efficient metathesis catalysts [19–24]. Considerable efforts have been applied to explain the plausible mechanisms of cross-metathesis between olefin molecules [25–29]. The detailed structural description and the relevant mechanism for the generation of active species are still controversial and various, requiring further confirmation as a useful piece of knowledge for any rational catalyst design [29–31]. The quantum chemical studies render as helpful complementary tools in this regard [32]. Many theoretical studies [33–44] have then addressed the identification and initiation of the Mo-based pre-catalysts, such as $MoO_3/\gamma\text{-}Al_2O_3$, $MoO_3/SiO_2$ and $MoO_3$/HZSM-5. Comparably, the W-based counterparts, e.g., in a model W/ZSM-5 catalyst [45], have been investigated much less extensively.

Combined quantum theory and experiment led Guo et al. [46] to assume that $MoO_x$/SBA-15 contained tetrahedrally coordinated dioxo

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https://doi.org/10.1016/j.commatsci.2018.08.031
Received 12 April 2018; Received in revised form 5 August 2018; Accepted 14 August 2018
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$MoO_4$ moieties as the dominant precursors of active site. The authors found that a pentahedrally coordinated monooxo counterpart was only present in diminutive quantities. Meanwhile, they highlighted that the relative composition of these molybdena species differ with different catalyst preparation methods. Raman and infrared (IR) measurements [47] and further computational assessments [48] have also shown the coexistence of tetra- and pentahedrally coordinated molybdena species in the $MoO_x/SiO_2$ catalysts. More strictly, e.g., Lee and coworkers [47] noted that the number of oxo bonds in the surface metal oxide $MO_x/SiO_2$ materials varied with the group number or oxidation state: the dehydrated surfaces of the group 6 metal oxides possessed mainly dioxo structures while minor amounts of monoxo species were also present on these catalysts. As an exception ($WO_x/SiO_2$), comparable quantities of dioxo and monoxo $WO_4$ species were found on the surface, with their ratio depending on the temperature.

Amakawa et al. [30,49–51] presented operando infrared spectroscopic and microcalorimetric data to interpret the olefin reactivities on the $MoO_x$/SBA-15 catalyst. The authors proposed a new mechanism, which was based upon the presence of Schrock-type metal–alkylidene species on the surface. The mechanism starts with the protonation of alkene by the effect of the Brønsted acidity of the supported molybdenol (Mo—OH) groups as the pre-catalyst [30]. The initiation (activation) of the pre-catalyst then flows in a one-pot process, which involves acid--base oxidation–reduction, byproduct capture, and oxidative addition steps (vide infra). Although the new mechanism was presented based on the experimental findings with propylene over $MoO_x$/SBA-15, it is expected to assume that the same steps are involved in the activation of similar W-based catalysts with ethylene or propylene as the feedstock. Indeed, the industrial practice for olefins production via metathesis relies almost entirely upon the W-based catalysts. On the other hand, the metathesis reaction with ethylene as the feedstock is relatively more important in industry than a propylene counterpart. The mechanism on W-based catalysts with both ethylene and propylene feeds would therefore be of particular relevance. As far as we are aware, no theoretical work has appeared on any of these reaction systems.

Having the above-mentioned motivation in mind, we addressed the thermochemical and molecular-level features of the suggested mechanism for the silica-grafted Mo oxide catalyst within the environment of the paramount light olefins (ethylene and propylene). In addition, we carried out simulations of all activation steps for the corresponding silica-supported W oxide catalyst with both ethylene and propylene as the feedstock. The simulation results are explained in terms of several descriptors including the thermochemical and thermodynamic changes, localized-orbital locator (LOL) maps, density of state (DOS) profiles, natural bond orbital (NBO) charges, IR vibrations, and so forth. To the best of our knowledge, this is the first modeling attempt to provide comparative fundamental insights into these critically important reaction systems.

## 2. Computational method

The cluster modeling approach [52–56] was employed for the simulations. The cluster model of silica was taken from the established crystallographic data for beta cristobalite [57], which has been recognized as a reliable representative model [57–62] for nano-structured silica materials as employed in several previous studies [55,63–66]. The simulation of the pre-catalyst was implemented by grafting of the hydroxylated metal species (molybdenum or tungsten) on the surface of the inorganic support, where the support nanocluster was a 1 T ($SiO_4H_3$) group saturated with boundary hydrogen atoms relaxed in the same direction as would be expected in a real crystal for the next removed silicon atom. Complementary calculations proved that the cluster model employed was accurate enough compared to larger clusters of the precatalyst within the energetic alterations at hand. The quantum chemical calculations were implemented by NWChem 6.5 [67] and Multiwfn 3.3.8 [68], and the molecular graphics were provided using Mercury 3.3 [69–72].

All of the computations (optimizations and frequency calculations) were implemented using the hybrid M06 density functional [73] together with the Def2-TZVP basis set [74–76]. The related effective core potential (ECP) was employed to account for the underlying relativistic effects. This computational framework, which incorporates a hybrid functional with a balanced polarized triple-zeta basis set [53–55,77–88] and the adopted cluster modeling approach [53–56,84,89] are known to be sufficiently accurate for the simulation of systems containing both the main group elements and transition metals [77,88,90–93]. The same computational approach was applied to estimate the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) energy levels using the frontier molecular orbital (FMO) theory [94]. The partial charges were obtained at the same level of theory using the natural bond orbital (NBO) population [95] analysis. The electronic features at the bond critical points (BCPs) were analyzed within the framework of the quantum theory of atoms in molecules (QTAIM) [96–100] at the M06/DZP [101–103] level of theory. The electronic chemical potential ($\mu$) within the FMO theory framework is defined as follows [104–109]:

$$\mu = -\chi = -(I + A)/2 = (E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}})/2 \tag{1}$$

where $\chi$ denotes the electronegativity, $I$ represents the ionization potential and $A$ signifies the electron affinity. Furthermore, the chemical hardness ($\eta$) can be calculated as follows [108–110]:

$$\eta = (I - A) = (E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}) \tag{2}$$

Eventually, the global softness can be calculated as [106,107]

$$\sigma = 1/\eta \tag{3}$$

These indices are helpful in commenting on the reactivity of the complexes.

## 3. Results and discussion

The generation of the active carbene species from the pre-catalyst has been identified as a demanding process as the original metal oxide should be converted to an alkylidene through an in situ one-pot reaction pathway [30]. Fig. 1 shows three 7-step reaction pathways on Mo or W pre-catalysts: (1) for ethylene reaction, (2) for propylene reaction at the primary carbon atom, and (3) for propylene reaction at the secondary carbon atom. We labeled the involved species in the first pathway as A1M through H1M in which 1 refers to the pathway number and M is either Mo or W. The backbone of the reaction pathways was presented by Amakawa and coworkers [30] for an Mo-based pre-catalyst and propylene feedstock, assuming a tetrahedral dioxo pre-catalyst. Aside from the computational exploration of their mechanism, we also extended the reaction pathways to alternative systems with ethylene feedstock and those involving the more common W-based catalyst. Other plausible configurations of the carbene species were also taken into account, leading to the consideration of ten alkylidene species (H1Mo–H5Mo and H1W–H5W). The metal atoms (Mo and W) in as-prepared pre-catalysts occur in their highest oxidation state (6+) in form of highly dispersed surface oxide species [30]. This oxidation state remains unchanged in species B, is reduced (to 4+) on C, D, and E, and is re-oxidized to the initial oxidation state on F, G, and H series of structures. The initial protonation of alkene produces ethoxide, propoxide, and isopropoxide species in the pathways 1–3, respectively. Correspondingly, three types of by-products will be desorbed: (1) acetaldehyde, (2) propionaldehyde (propanal), and (3) acetone.

The optimized geometries of the carbene structures are shown in Fig. 2. Other optimized geometries are presented in Fig. S1. As such, total of 42 structures were calculated. After the desorption of the oxygenated by-product, an intermediate with a three-coordinated metal ion is formed. The oxidative addition of the second olefin molecule to this coordinatively unsaturated metal ion (facilitated by the prior formation

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