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# Formation of Mo-carbene active sites in Mo/Beta zeolite catalysts with different olefins: Theoretical exploration of possible reaction pathways and substituent effects

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## ABSTRACT

Metal-carbenes act as the active sites in varieties of important reactions, and in this work, the possible pathways of Mo-carbene formation in Mo/Beta zeolite were explored by density functional calculations. Four chiral oxametallacyclobutane intermediates of different energies were determined for either propylene or 2-butylene, corresponding to the four independent reaction pathways. The main products were Mo-methylidene for propylene and *syn*-Mo-ethylidene for 2-butylene, respectively. On the basis of energy profiles, the activities of producing the Mo-carbene species were found to decrease in the order of propylene > 2-butylene > ethylene, which were the compromising results of electrophilic and steric effects.

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## 1. Introduction

The Mo-based solid-state materials play vital roles in many important catalytic processes [1–7], including methane aromatization [5] and olefin metathesis [6,7]. Recently, our laboratory performed a series of work and found that the Mo-modified Beta-Al<sub>2</sub>O<sub>3</sub> catalysts exhibited activities in the olefin metathesis reactions [6]. Using multinuclear MAS NMR, XRD and N<sub>2</sub> adsorption, strong interactions between the Mo species and Beta zeolite were observed [7]. It indicates that a large proportion of Mo species will be exchanged into the Brønsted acidic sites, which are probably the catalytic precursors to the olefin metathesis reactions.

As suggested by the Hérisson–Chauvin mechanism [8,9], the initiating and propagating intermediates in olefin metathesis are metal-carbene species. Salameh et al. [10] studied the Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub> olefin metathesis catalysts with various olefins, considering that the generation of metal-carbenes should proceed via the pseudo-Wittig mechanism. Recently, density functional calculations have been performed by the present authors [11] to research into the formation mechanism of metal-methylidene species with ethylene adsorption on Mo/Beta zeolite catalysts. It was found that the Mo-methylidene formation involves two elementary steps with

the second rate-determining and the oxametallacyclobutane structures as the intermediates. However, the actual reaction conditions are much more complex than expected, since three olefins co-exist in the metathesis process of ethylene–2-butylene mixtures to propylene [6]. Which is responsible for the generation of Mo-carbene active sites? Can the product propylene enhance the reaction activity? To the best of our knowledge, these two problems have not been clarified yet, which were attempted to be resolved in this work using density functional methods. The substituent effects of olefins were studied as well, rationalizing the reaction differences of different olefins.

## 2. Computational details

All the computations were performed under Gaussian98 program [12]. The B3LYP density functional level of theory was used [13,14], and the 6-31G(d,p) basis was applied to all the elements except Mo. As the relativistic effects play significant influences in the Mo element, it was treated with LANL2DZ basis, which includes the Hay-Wadt effective core potential (ECP) plus double- $\xi$  basis set [15]. The previous work [16] showed that it is a reasonable combination of basis sets to deal with the late transition-metal systems. Vibrational frequencies at the same theoretical level were calculated to ensure that all the structures are energy minima (no imaginary frequency) or transition states (one characteristic imaginary frequency).

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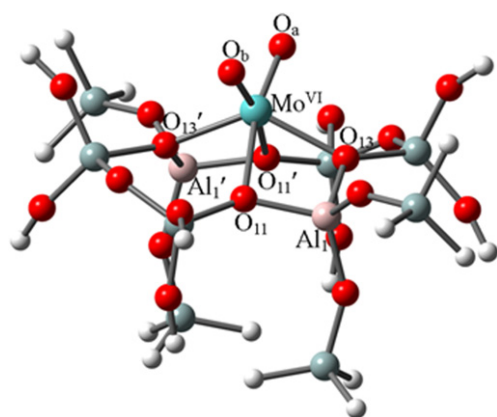


Fig. 1. Structure of the Mo precursor (Mp) embedded in the Beta zeolite cluster.

The Beta zeolite clusters were taken from the framework structure of polymorph A reported by Newsam et al. [17]. As suggested by the  $^{27}\text{Al}$  MQ MAS NMR results [18], the T1 sites rather than the other T sites were preferred to be occupied by the Al atoms and accordingly in the present clusters, two T1 sites were substituted by Al atoms. The proposed  $\text{Mo}^{\text{VI}}\text{O}_2^{2+}$  precursors [11] were exchanged into the Brønsted acidic sites created by framework Al atoms, see Fig. 1. In order to retain the local geometries of Beta zeolite, the boundary OH and  $\text{SiH}_3$  groups were fixed in their crystallographic positions. It should be noted that the present clusters contain 10 T sites and are larger than the 5 T sites of the previous work [19,20].

### 3. Results and discussion

As shown in Scheme 1, the formation of Mo-carbene active sites (Mc) in Mo/Beta zeolite is a two-step process, with the Mo precursors (Mp) and olefins (Ole) as the starting materials. The first step forms the oxametallacyclobutane structures acting as the intermediates (In). The transition states of steps 1 and 2 were designated to be Ts1 and Ts2, respectively.

#### 3.1. Formation of Mo-carbene active sites from propylene

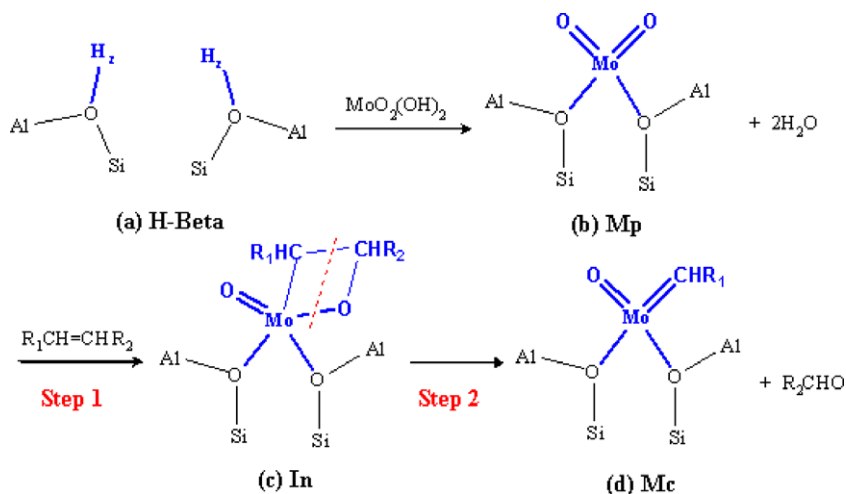
Owing to the different orientations of propylene (Pro) towards the Mo precursors (Mp), four independent reaction pathways exist

with their intermediates shown in Fig. 2. For propylene, its  $\text{CH}_2$  group forms direct bonds with the Mo centers in In(Pro1) and In(Pro2) whereas with the O atoms in In(Pro3) and In(Pro4). In(Pro1) and In(Pro2), In(Pro3) and In(Pro4) differ in the directions of the  $\text{CH}_3$  group and cause chirality in the intermediates [21]. It is different from the situation of ethylene, where the intermediate is non-chiral [11]. Following the reaction pathways of Scheme 1, Pro1 and Pro2 produce the Mo-methylidene species (Fig. 3a), the same as ethylene, while Pro3 and Pro4 produce the Mo-ethylidene species (Fig. 3b and c, respectively). All the structures along the reaction pathways (energy minima and transition states) were given in Figure S1. As to the intermediates, their four-membered oxametallacyclobutane rings were formed by four single bonds; i.e., Mo–O<sub>a</sub>, O<sub>a</sub>–C<sub>1</sub>, C<sub>1</sub>–C<sub>2</sub> and C<sub>2</sub>–Mo with the distances of ca. 1.93, 1.43, 1.52 and 2.26 Å, respectively. The C<sub>2</sub>–Mo distances were shortened to ca. 1.95 Å in the Mo-carbene species, characteristic of double bonds [22–24]. Accordingly, the C<sub>2</sub>–Mo bonds of the Mo-ethylidene species can not rotate freely and thus form the *anti*- and *syn*- conformers (Fig. 3c and b). The *syn*- conformer was more stable than the *anti*- by 6.0 kcal mol<sup>-1</sup> due to the less steric hindrance.

The activation barriers of step 1 were calculated to be 17.1, 16.2, 25.6 and 29.9 kcal mol<sup>-1</sup> in Pro1, Pro2, Pro3 and Pro4, respectively. The larger values in Pro3 and Pro4 were caused by the steric effects of the  $\text{CH}_3$  group, which was adjacent to the Mo = O<sub>a</sub> bond in Pro3 and to the zeolite frameworks in Pro4. The four activation barriers of step 2 were equal to 33.7, 35.2, 28.1 and 22.8 kcal mol<sup>-1</sup> in Pro1, Pro2, Pro3 and Pro4, respectively. The whole reaction heats (from Mp + Pro to Mc + R<sub>2</sub>CHO) were also obtained with the exact values of 15.0, 15.0, 17.6 and 23.6 kcal mol<sup>-1</sup> in Pro1, Pro2, Pro3 and Pro4, respectively. On the basis of the lowest energy barrier in the first step and reaction heats, the second pathway (Pro2) is the most probable to take place and therefore the Mo-methylidene active sites are produced in high proportions by propylene adsorption on the Mo precursors (Mp), the same as ethylene [11]. The two activation barriers of the first pathway (Pro1) are close to those of the second pathway (Pro2) and therefore the first pathway can not be neglected; however, it also produces the Mo-methylidene active sites. The energy profiles of the four reaction pathways from propylene were depicted in Figure S2.

#### 3.2. Formation of Mo-carbene active sites from 2-butylene

As shown in Fig. 2, four different intermediates were formed by the attacks of 2-butylene (But) to the Mo precursors (Mp) in Beta



Scheme 1. The reaction pathway of Mo-carbene formation on the Beta zeolite. (a) H-Beta represents the H-from Beta zeolite; (b) Mp represents the Mo precursor formed by exchanging the  $\text{MoO}_2(\text{OH})_2$  species on the H-Beta zeolite; (c) In represents the oxametallacyclobutane intermediate and (d) Mc represents the product of the Mo-carbene.

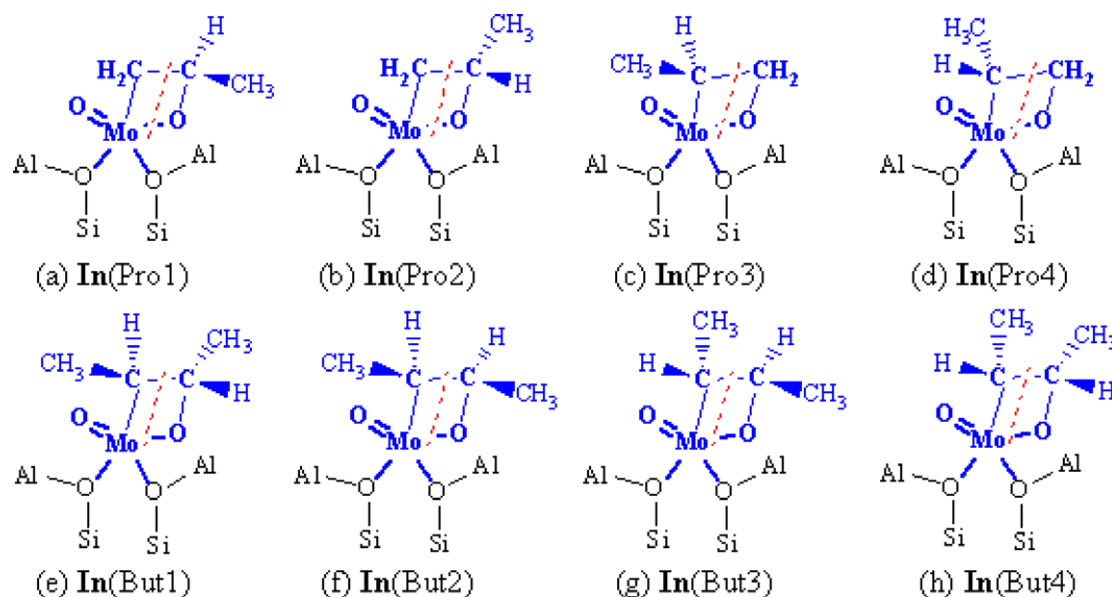


Fig. 2. Schematic presentations of different intermediates arising from the attack of propylene (a–d) and 2-butylene (e–h) to the Mo precursors (Mp).

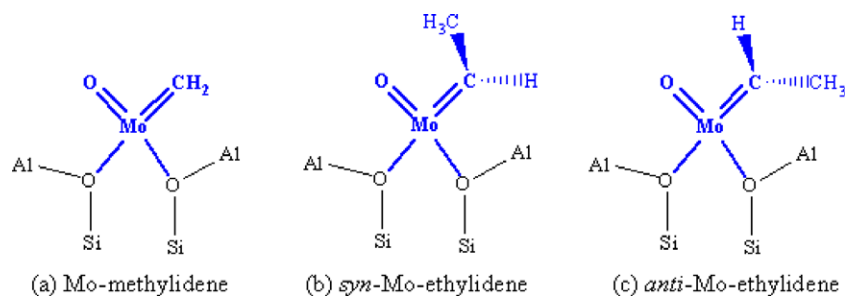
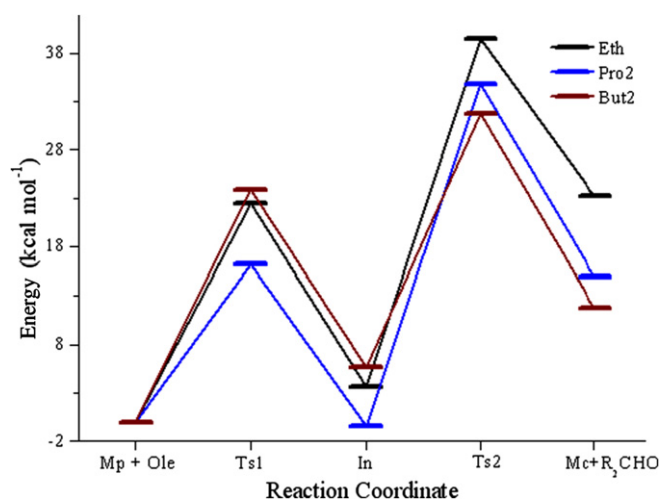


Fig. 3. Several types of Mo-carbene active sites in Mo/Beta zeolites.

zeolite. Two chiral C atoms are present in the intermediates of But1, But2, But3 and But4. Unlike ethylene and propylene, only the Mo-ethylidene species were obtained from 2-butylene. But1 and But2 lead to the *syn*-Mo-ethylidene species (Fig. 3b) whereas But3 and But4 to the *anti*-conformer (Fig. 3c). All the structures along the four reaction pathways (energy minima and transition states) were displayed in Figure S3. The activation barriers of step 1 were calculated to be 24.7, 23.9, 26.7 and 28.5 kcal mol<sup>-1</sup> in But1, But2, But3 and But4, respectively. The CH<sub>3</sub> group at the Mo-C<sub>2</sub> side towards the zeolite frameworks causes the increase of the activation barriers in But3 and But4, especially in But4 where the other CH<sub>3</sub> group is also directed towards the zeolite frameworks. The second reaction pathway (But2) with both CH<sub>3</sub> groups opposite to the zeolite frameworks has the smallest activation barrier. In(But1) and In(But2) were about 8.5 kcal mol<sup>-1</sup> more stable than In(But3) and In(But4). As to step 2, the activation barriers were equal to 26.8, 26.1, 21.8 and 22.9 kcal mol<sup>-1</sup> in But1, But2, But3 and But4, respectively. It was found that the second reaction pathway (But2) has the lowest activation barrier in the first step. Moreover, the second reaction pathway (But2) was the most thermodynamically favored since the reaction heat (from Mp + But2 to Mc + CH<sub>3</sub>CHO) was the lowest among the four reaction pathways. Accordingly, this pathway is the most probable to take place, see the energy profiles in Figure S4.

### 3.3. The reaction activities of different olefins: a comparison

The energy profiles of ethylene (Eth), propylene (Pro2) and 2-butylene (But2) were plotted in Fig. 4. Here the representative Pro2 and But2 were used for propylene and 2-butylene, respectively. Step 1 is an electrophilic [2 + 2] addition reaction [11] and accordingly, Pro2 and But2 should have had smaller energy barriers than Eth due to the presence of the electron-donating CH<sub>3</sub> groups. As aforementioned, large steric hindrances are present in But2, which counteracts the contributions of electrophilicity and even causes slightly larger energy barrier than in Eth. Step 2 is the cycloreversion reaction of the four-membered rings of the intermediates. In Pro2 and But2, the CH<sub>3</sub>CHO fragments are released and therefore cause the severe reduction of steric repulsions, especially in But2. To conclude, the activation barriers of steps 1 and 2 decrease in the orders of But2 > Eth > Pro2 and Eth > Pro2 > But2, respectively. As can be found from Fig. 4, the reaction activities to produce the Mo-carbene active sites decrease in the order of propylene (Pro2) > 2-butylene (But2) > ethylene (Eth), as the compromising results of electrophilic and steric effects. It suggests that the addition of some propylene into the ethylene and 2-butylene mixtures will facilitate the production of Mo-carbene active sites and therefore enhance the metathesis activities of ethylene/2-butylene mixtures to propylene.



**Fig. 4.** Energy profiles for the Mo-carbene formation reactions with different olefins (Ole). In all the cases, the energies of the Mp + Ole complexes were set as the benchmarks.

#### 4. Conclusions

For propylene or 2-butylene adsorption on Mo/Beta zeolite catalysts, the production of the Mo-carbene active sites can proceed via four possible reaction pathways. In each case of propylene or 2-butylene, four intermediates were found which are chiral and of different energies (Fig. 2). Three types of Mo-carbene species (Mo-methylidene, *syn*- and *anti*-Mo-ethylidene) were obtained for propylene, with Mo-methylidene as the main product; Two types of Mo-carbene species (*syn*- and *anti*-Mo-ethylidene) were obtained for 2-butylene with the *syn*-conformer as the main product (Fig. 3). In contrast, there is only one reaction pathway for ethylene leading to one nonchiral intermediate and one product (Mo-methylidene). According to the energy profiles (Fig. 4), the reaction activities of producing the Mo-carbene active sites were found to decrease in the order of propylene > 2-butylene > ethylene. The activity differences among the different olefins (ethylene, propylene and 2-butylene) were caused by the compromising results of electrophilic and steric effects.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.catcom.2008.05.020.

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