

# H<sub>2</sub> effect in Cr/PNP-catalyzed ethylene tetramerization: a DFT study

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## Abstract

It is well noticed that hydrogen promotes catalyst activity in Cr/PNP-catalyzed ethylene tetramerization, but the mechanism of this boost is unclear. A density functional theory (DFT) study devoted to exploring this effect was conducted, and conformation changes were carefully taken into consideration to build a clear reaction pathway. Three components in the catalytic cycle was examined in detail: the production of 1-hexene from the metallacycloheptane, the production of 1-octene from metallacyclononane, and the formation of active center on the catalyst. The result indicates that the formation of active center on the catalyst becomes more favorable upon imposition of hydrogen, where hydrogen function as a second ligand. This easing effect could be the key factor leading to the outperformed catalyst activity.

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**Keywords:** ethylene oligomerization \* Cr-PNP catalyst \* DFT calculation \* Hydrogen promoting effect \* active center

## Introduction

Driven by the emerging polyethylene, particularly the linear low-density polyethylene (LLDPE) market, the demand for  $\alpha$ -olefin proliferate rapidly, especially the low carbon number components such as 1-butene, 1-hexene, and 1-octene<sup>[1]</sup>. Compared to the fast development of selective ethylene trimerization<sup>[2]</sup>, which first commercialized as early as 2003 by Chevron Phillips Chemical Company LP<sup>[3]</sup>, the selective ethylene tetramerization catalyst still suffer from relatively low activity and selectivity<sup>[4]</sup>. The first selective ethylene tetramerization catalyst that has the potential to be commercialized was reported by Sasol at 2004<sup>[5]</sup>, using methylaluminoxane(MAO)-activated Cr/PNP catalyst system to give a 1-octene selectivity up to 70%, which

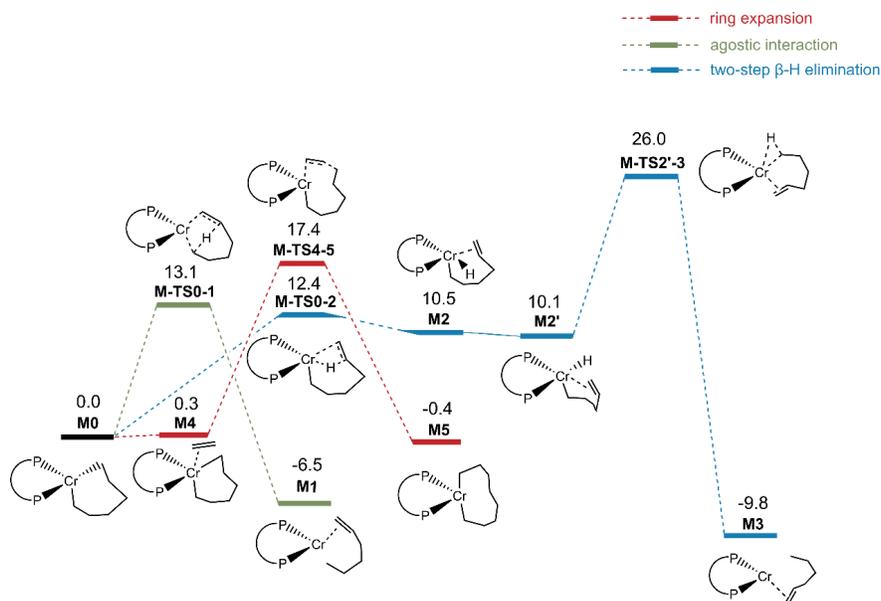
is also the most studied catalyst system up till today. It was noticed then that addition of 2.5 bar of hydrogen to the system alleviated the polyethylene formation without much compromise on selectivity and productivity, but the mechanism is unclear. Further investigation regarding this hydrogen promoting effect remained scarce until 2016 when Jiang *et al.* [6] confirmed that there is a significant improvement of PNP/Cr(III)/MAO catalyst activity on ethylene tetramerization under hydrogen pressure ranging from 0.03 to 0.50 Mpa. A DFT study of hydrogen effect on the Chevron-Phillips trimerization system was conducted by Bahri-Laleh *et al.* at 2017[7], in which hydrogen is believed to participate into the reaction and leads to the formation of alkanes. However, ethylene tetramerization experiments conducted by Jiang *et al.* showed little alkane product in the presence of hydrogen, indicating further investigation is required. Liu *et al.* [8] investigated the effects of hydrogen in PNP/Cr catalytic system using DFT analysis at 2018, in which he proposed that the increase of catalyst activity under hydrogen addition is due to the lowered energy barrier to form metallacyclopentane. However, the energy required for the oxidative addition from quartet bis(ethylene)Cr complex to quartet heterocyclic Cr complex actually increases from 6.6 kcal/mol to 7.0 kcal/mol upon addition of hydrogen, seemingly insufficient to account for the significant increase of catalyst activity. Hydrogen effect on the following reactions leading to the product was also investigated where hydrogen function solely as a second ligand. Based on these previous studies, here we compare competitive reactions from metallacycloalkanes where hydrogen either participate into the reaction to produce alkene, or function as a second coordinated ligand, with conformation changes taken into consideration, to further explore how hydrogen might have affect the ethylene oligomerization process using DFT calculation. We also explore possible hydrogen effect outside the catalytic cycle, namely the formation of catalyst active center to gain the whole picture.

## Results and Discussion

The ethylene oligomerization process adopted into the calculation here is based on a well-accepted metallacyclic mechanism, which was first proposed by Manyik<sup>[9]</sup> at Union Carbide at 1977. The cycle starts with the oxidative coupling of two coordinated ethylene to form a metallacyclopentane intermediate, followed by a  $\beta$ -H transfer to a third coordinated ethylene, from which 1-hexene was released. This mechanism was soon modified by Briggs<sup>[10]</sup> at 1989, proposing that a third coordinated ethylene was inserted into the metallacyclopentane to give a metallacycloheptane, from which  $\beta$ -H eliminate or  $\beta$ -agostic 3,7-H shift take place to yield 1-hexene. This metallacyclic mechanism was experimentally verified using deuterium labeling by Agapie and coworkers<sup>[11]</sup>, and applied to ethylene tetramerization as well, which was also tested with isotopomers by Sasol<sup>[12]</sup>. The probing into the active center of the catalysts, however, remained complicated because of the paramagnetic nature of the various oxidation states of chromium formed during the catalytic cycle<sup>[13]</sup>, but there are more evidences supporting Cr(I)/Cr(III) redox in the tetramerization catalytic cycle<sup>[11a, 14]</sup> using electron paramagnetic resonance and X-ray absorption spectroscopy<sup>[15]</sup>, or self-activating catalysts crystallization<sup>[16]</sup>, so Cr(I)/Cr(III) redox cycle was applied in this study.

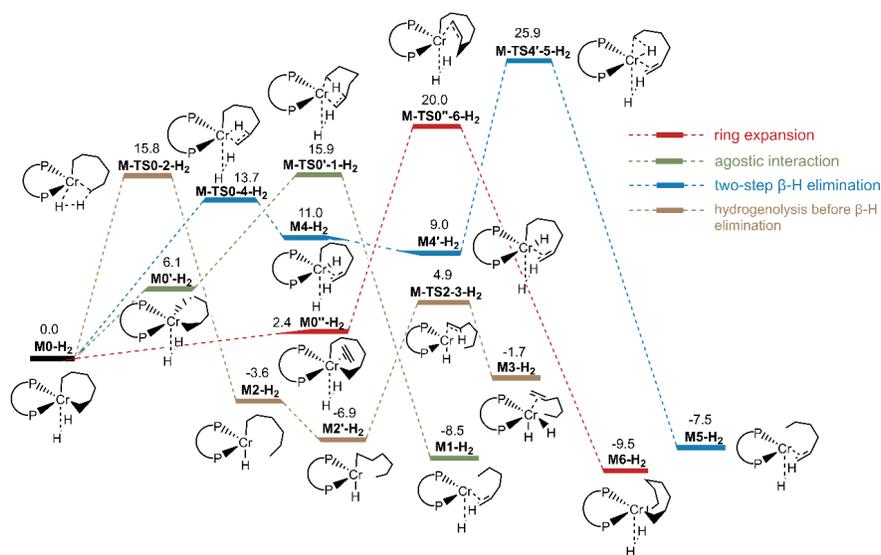
Based on the mechanism given before, the production of  $\alpha$ -olefin may occur via  $\beta$ -H eliminate or  $\beta$ -agostic 3,7-H shift from the corresponding metallacycloalkane, through which hydrogen might modify the energy barriers of the reactions only by coordination and not necessarily involve into the reaction, as Liu stated in the previous studies<sup>[8]</sup>. However, we do believe it is possible to include hydrogen into the reaction process that leads to the production of alkene, in which hydrogen is inserted into the Cr-C bond, offering an hydrogenolysis reaction to give an alkane chain, before  $\alpha\beta$ -H transfer to liberate  $\alpha$ -olefin. The selectivity of the catalyst depends on the relative equilibrium between decomposition and ring expansion of the metallacycloalkane, so the energy required for ring expansion is also calculated. Here we present the energy profiles of these reactions on metallacycloheptane and metallacyclononane with or without hydrogen, attempting to illustrate how hydrogen might affect the reactions. All Gibbs free energies are relative to the starting material plus the corresponding number of free ethylene molecules.

**Ηψδρογεν εφφρεστ ον  $\alpha$ -ολεφιν προδυστιον φρομ μεταλλαςψςλοαλκανες**



**Figure 1.** Relative Gibbs free energy profiles (kcal/mol) to produce 1-hexene from metallacycloheptane without hydrogen

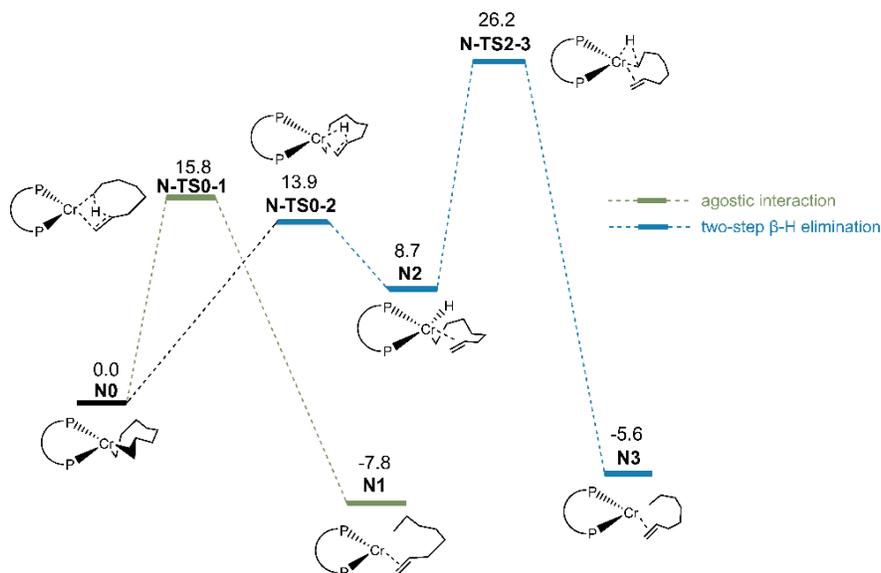
Starting from the metallacycloheptane (M0), there are three possible developments presented in Figure 1, from which two leads to the formation of 1-hexene. 1-hexene could be produced via a one-step  $\beta$ -agostic interaction (M-TS0-1) due to ring flexibility with an energy barrier of 13.1 kcal/mol, or via a two-step  $\beta$ -H transfer incorporated with a conformation change, overcoming energy barriers of 12.4 kcal/mol (M-TS0-2) and 15.9 kcal/mol (M-TS2'-3) for each step. The ring-expansion involves ethylene coordination from M0 to M4, followed by insertion of ethylene to the M-C bond via M-TS4-5 with an energy barrier of 17.1 kcal/mol. Note that both ethylene coordination and ring expansion are endergonic, hence the overall energy barrier for ring expansion without hydrogen should be the sum of the two, namely 17.4 kcal/mol.



**Figure 2.** Relative Gibbs free energy profiles (kcal/mol) to produce 1-hexene from metallacycloheptane

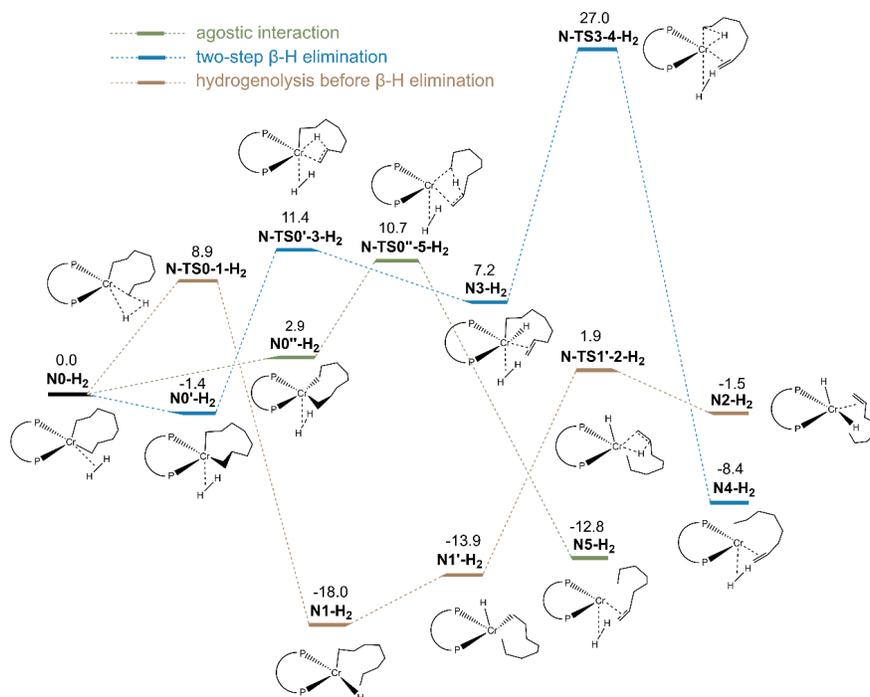
with hydrogen.

When hydrogen is introduced into the system, an additional pathway is included into the calculation, and all energies are referred to  $M0-H_2$ , the Gibbs free energy of which is set to 0 for analysis convenience. The one-step  $\beta$ -agostic interaction via  $M-TS0'-1-H_2$  to liberate 1-hexene has an energy barrier of 9.8 kcal/mol, but an endergonic conformation change of 6.1 kcal/mol from  $M0-H_2$  to  $M0'-H_2$  is necessary to enable the reaction, thus the overall energy barrier rise to 15.9 kcal/mol, which is actually higher than that without hydrogen (13.1 kcal/mol). The two-step  $\beta$ -H transfer occur via two transition states  $M-TS0-4-H_2$  and  $M-TS4'-5-H_2$ , overcoming energy barriers of 13.7 kcal/mol and 16.9 kcal/mol respectively. The hydrogenolysis occur via  $M-TS0-2-H_2$  to give an alkane chain, overcoming an energy barrier of 15.8 kcal/mol. An exergonic conformation change from  $M2-H_2$  to  $M2'-H_2$  occurred to enable further  $\beta$ -H transfer to liberate 1-hexene via  $M-TS2'-3-H_2$ , with an energy barrier of 11.8 kcal/mol. The ring expansion occur through first an endergonic ethylene coordination of 2.4 kcal/mol, followed by an ethylene insertion of 17.6 kcal/mol, both figures higher than those without hydrogen, indicating a higher overall energy barrier.



**Figure 3.** Relative Gibbs free energy profiles (kcal/mol) to produce 1-octene from metallacyclononane without hydrogen.

Similar analysis was conducted on metallacyclononane and presented in Figure 3 and Figure 4. The production of 1-octene through one-step agostic interaction via N-TS0-1 requires an energy barrier of 15.8 kcal/mol. The two-step  $\beta$ -H transfer occur via N-TS0-2 and N-TS-2-3, with energy barriers of 13.9 kcal/mol and 17.5 kcal/mol respectively. Further ring expansion leads to the formation of byproducts and is neglected in this calculation,



**Figure 4.** Relative Gibbs free energy profiles (kcal/mol) to produce 1-octene from metallacyclononane with hydrogen

Upon addition of hydrogen, one-step agostic interaction via N-TS0''-5-H<sub>2</sub> requires an energy barrier of 7.8 kcal/mol. The overall energy barrier required for this agostic interaction includes the necessary conformation change from N0-H<sub>2</sub> to N0''-H<sub>2</sub>, and thus rise to 10.7 kcal/mol, which is still significantly lower than that without hydrogen (15.8 kcal/mol). The two-step  $\beta$ -H transfer starts with an exergonic conformation change from N0-H<sub>2</sub> to N0'-H<sub>2</sub>, enabling the transfer via transition state N-TS0'-3-H<sub>2</sub> and N-TS3-4-H<sub>2</sub> with energy barriers of 12.8 kcal/mol and 19.8 kcal/mol respectively. It is difficult to compare how hydrogen affects this two-step reaction, as one step becomes more favorable yet the other more unfavorable, but since the agostic interaction is generally easier to occur, the reaction might well proceed via the one-step agostic route. The pathway of  $\beta$ -H transfer after hydrogenolysis is also calculated on metallacyclononane. The hydrogen insertion from N0-H<sub>2</sub> to N1-H<sub>2</sub> via N-TS0-1-H<sub>2</sub> requires 8.9 kcal/mol, and the following  $\beta$ -H transfer via N-TS1'-2-H<sub>2</sub> after an endergonic conformation change of 4.1 kcal/mol has an energy barrier of 15.8 kcal/mol.

The energy required for conformation change and coordination is necessary to take into consideration, especially when the transformation is endergonic, as the reaction needs the overcoming of these barriers to occur. Here we present the relevant energy barrier figures with or without hydrogen in Table 1, in which endergonic conformation change are labeled in brackets.

**Table 1.**  $\Delta G$  of the reactions calculated regarding metallacycloheptane and metallacyclononane with and without hydrogen, figures in brackets indicate energy required for necessary conformation change or ethylene coordination

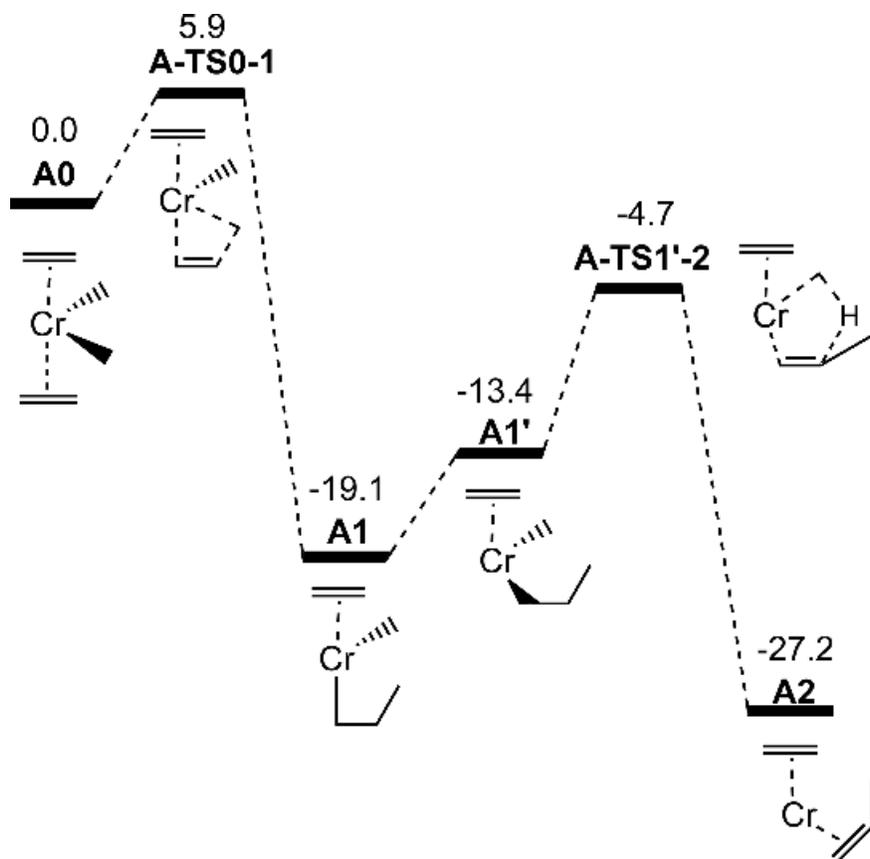
	metallacycloheptane	metallacycloheptane	metallacyclononane	metallacyclononane
	Without hydrogen	With hydrogen	Without hydrogen	With hydrogen
$\beta$ -agostic interaction	13.1	(6.1) 9.8	15.8	(2.9) 7.8
Two-step $\beta$ -H elimination	12.4, 15.9	13.7, 16.9	13.9, 17.5	12.8, 19.8
Hydrogenolysis and $\beta$ -H elimination	-	15.8, 11.8	-	8.9, (4.1) 15.8

	metallacycloheptane	metallacycloheptane	metallacyclononane	metallacyclonona
Ring expansion	(0.3) 17.1	(2.4) 17.6	-	-

The introduction of hydrogen modifies the energy barriers of these reactions, albeit in different directions. For metallacycloheptane, the energies required for possible reactions are generally raised upon addition of hydrogen. The energy required for the agostic 3,7-H shift seems to be reduced from 13.1 kcal/mol to 9.8 kcal/mol, but a conformation change of 6.1 kcal/mol is required, making the overall energy barrier higher than that without hydrogen. It is difficult to determine exactly which pathway is applied to produce 1-hexene without hydrogen, as the energy requirements of the two pathways are similar, but it is clear that  $\beta$ -agostic 3,7-H shift becomes more favorable among the three possible reaction pathways in the presence of hydrogen. For metallacyclononane, the formation of 1-octene via  $\beta$ -agostic hydrogen shift becomes much more favorable as the energy barrier is greatly reduced from 15.8 kcal/mol to 10.7 kcal/mol with the introduction of hydrogen, but the formation of metallacyclononane itself becomes more difficult as the energy required for the ring expansion of metallacycloheptane rises from 17.4 kcal/mol to 20.0 kcal/mol, making hydrogen's full significance to the reaction hard to ascertain. Thus, we turned to explore how hydrogen might affect the formation of the active center on the catalyst in hopes of finding a more conclusive influence.

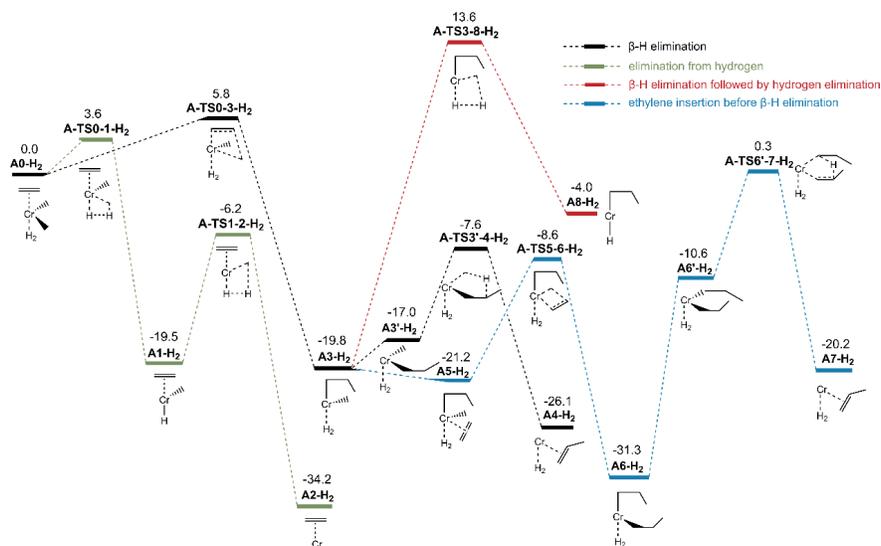
### Hydrogen effect in the formation of active center on the catalyst

Upon addition of MAO, the chromium pre-catalyst is believed to undergo methylation and reduction to form an active center capable to coordinate at least two ethylene in order to form the key intermediate metallacyclopentane<sup>[17]</sup>. A proposed mechanism is used based on previous works by Sasol<sup>[18]</sup>, in which two ethylene molecules both coordinate onto the metal center axially to achieve minimal steric around the active center. Figure 5 shows the Gibbs free energy profiles for the activation process, all figures relative to the starting molecule A0 where two ethylene molecules are just coordinated onto the metal center.



**Figure 5.** Relative Gibbs free energy profiles (kcal/mol) for the formation of active center on Cr/PNP catalyst, where ethylene coordinated both axially.

The process starts with the insertion of one ethylene into the M-C bond via A-TS0-1, overcoming an energy barrier of 5.9 kcal/mol, followed by a conformation change (A1 to A1') of 5.7 kcal/mol and reduction elimination of 8.7 kcal/mol via A-TS1'-2 to give an active species A2. Note that this conformation change is necessary to bring  $\beta$ -H from propyl group close to methyl group to enable further reaction, and both the conformation change from A1 to A1' and the reaction over A-TS1'-2 are endergonic, hence the overall energy required for the formation of active center without hydrogen could be regarded as the sum of the two, namely 14.4 kcal/mol.



**Figure 6.** Relative Gibbs free energy profiles (kcal/mol) for the formation of active center on Cr/PNP catalyst with hydrogen, with hydrogen coordinated onto the metal center opposite the ethylene molecule

When hydrogen is introduced into the system, the reduction elimination could originate from the  $\beta$ -H on the alkyl group, or from the hydrogen molecule, thus enable other possible scenarios to occur. Figure 6 presents the Gibbs free energy profiles with hydrogen adsorbed axially onto the metal center. In this case direct reduction from hydrogen adsorbed onto the metal center to liberate methane off could occur via A-TS0-1-H<sub>2</sub> with an energy barrier of 3.6 kcal/mol. The other methyl group could be eliminated in the same way via A-TS1-2-H<sub>2</sub> with an energy barrier of 13.3 kcal/mol. Similar as before, ethylene could insert into the M-C bond via A-TS0-3-H<sub>2</sub> with an energy barrier almost the same as that without hydrogen (5.8 kcal/mol), from which the  $\beta$ -H eliminate could occur via A-TS3'-4-H<sub>2</sub> after endergonic conformation change from A3-H<sub>2</sub> to A3'-H<sub>2</sub> to bring the propyl group close to the methyl group, this time overall energy barrier reduced to 12.2 kcal/mol. This pathway is exactly the same as when hydrogen is absent, in which hydrogen function as a ligand and does not participate into the reaction. The energy barrier is reduced from 14.4 kcal/mol to 12.2 kcal/mol upon introduction of hydrogen. A third possible route would be a combination of the two developments, in which elimination from hydrogen occur after ethylene insertion to release first methane and then propane. However, this reduction via A-TS3-8-H<sub>2</sub> has an exceptionally high energy barrier of 33.4 kcal/mol, hence unlikely to happen. It is also possible that after ethylene insertion, another ethylene is adsorbed onto the available site of the metal center to give A5-H<sub>2</sub>, from which another insertion occurs via A-TS5-6-H<sub>2</sub> to form two alkyl chain. A  $\beta$ -H eliminate via A-TS6'-7-H<sub>2</sub> would produce the active center, but a conformation change bringing two propyl group close to each other is required, which is sterically unfavorable, as is showed in the high energy barrier (20.7 kcal/mol required to change from A6-H<sub>2</sub> to A6'-H<sub>2</sub>).

Judging from energy profile present in Figure 6, two pathways are energetically more favorable among these possible developments: elimination from the hydrogen molecule adsorbed onto the metal center, and ethylene insertion followed by conformation change and  $\beta$ -H elimination, namely the same pathway without hydrogen. Either way, the imposition of hydrogen reduced the energy barrier to form the active center (3.6 kcal/mol, 13.3 kcal/mol; or 5.8 kcal/mol, 12.2 kcal/mol; compared to 5.9 kcal/mol, 14.4 kcal/mol without hydrogen), the only difference would be whether hydrogen participate into the reaction, or function as a second ligand. From the calculations we tested, this reduction of energy barrier is the only compartment to demonstrate an unquestionable easing effect, hence we propose that the formation of active center is a key factor regarding catalyst activity, thus coincide with the assumption raised by Jiang *et al.* in 2016<sup>[6]</sup> that hydrogen might play an important role in the generation of active centers. In this case, hydrogen reduces the energy barrier

to generate active centers on the catalyst, hence more active centers are available for reaction, leading to the significant increase of catalyst activity.

## Conclusion

Herein we investigated the effect of hydrogen posed over Cr-PNP catalyzed ethylene oligomerization process using DFT calculation. Multiple pathways were tested and compared. The introduction of hydrogen modified the energy barriers during the oligomerization, but the exact effect is debatable and unclear. However, hydrogen do reduce the energy barrier to form the active center on the catalyst, enabling proliferation of active centers. Hence, we propose that hydrogen promotes catalyst activity by easing the formation of active centers on the catalyst.

## Experimental Sector

Computation details: All DFT calculations were accomplished with Gaussian 09<sup>[19]</sup> program package using B3LYP functional. 6-31G\* basis set were used for all atoms except for Cr, which was described with LANL2DZ (ECP) basis set<sup>[20]</sup>. The Gaussian View 6.0 program was used to build the structures. Monovalent cations with quartet spin states were considered in theoretical models for the DFT study<sup>[21]</sup>. Vibrational frequencies were checked for all minima and transition states. Intrinsic reaction coordinate calculations were carried out to verify connections between transition states and different conformations. The model chosen was Cr/Me<sub>2</sub>PN(C<sub>5</sub>H<sub>9</sub>)PMe<sub>2</sub> with a cyclopentyl group attached to N, and the formation of active cationic Cr(I) specie includes reduction implication of cocatalyst from Cr(III). The Gibbs free energy collected under default conditions, and the solvent used in the calculation is methylcyclohexane.

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