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Research Note

Alkane metathesis by a tungsten carbyne complex grafted on gamma alumina: Is there a direct chemical role of the support?

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Abstract

The activity in alkane metathesis of tungsten complexes grafted on gamma alumina raises many questions regarding the structure of the active site and the reaction pathways. We examine the case of a perhydrocarbyl tungsten complex on alumina from periodic density functional theory calculations. The quantum chemistry exploration of energy pathways suggests two possible mechanisms for alkane metathesis. The first mechanism occurs on the grafted complex only but is significantly activated. The second mechanism shows that hydration defects on the alumina surface can be active in alkane dehydrogenation toward alkenes, whereas the tungsten complex efficiently catalyzes the subsequent olefin metathesis step. The calculations thus underscore the role of the alumina support in the mechanism.

Keywords: Metathesis; Alkanes; Alumina; Surfaces; Tungsten; Mechanisms; Dehydrogenation; Density functional theory

1. Introduction

The valorization of alkanes represents an important challenge, especially in terms of the capability to selectively form longer or shorter alkanes chains to optimize their properties as fuel. In this respect, alkane metathesis is a reaction with significant potential applicability. Such a reaction has been approached by homogeneous and heterogeneous catalysis [1–3]. At the midpoint between these two methods, surface organometallic chemistry offers an innovative approach and has proven its efficiency in alkane metathesis with Ta, Mo, or W complexes grafted onto silica or alumina [4–12]. This chemistry is constructed with the tools of homogeneous catalysis brought to their limits, with the oxide surface considered as a ligand [13].

Besides the choice of the metal complex, the nature of the oxide support also may play a decisive role in the reactivity thus obtained. This is especially so when a surface such as γ-Al_2O_3, with its partial hydroxylation and its rich acid–base chemical properties, is used. The development of tungsten-based heterogeneous alkane metathesis catalysts from a surface organometallic chemistry approach has indeed uncovered some support effects that remain unexplained [10]. Grafting $[W(C\mathit{t}Bu)(CH_2\mathit{t}Bu)_3]$ onto SiO_2 or γ-Al_2O_3 after partial dehydroxylation at 500 °C leads to well-characterized neutral mono-siloxy $(Si_sO)W(C\mathit{t}Bu)(CH_2\mathit{t}Bu)_2$ and mono-aluminoxy $(Al_sO)W(C\mathit{t}Bu)(CH_2\mathit{t}Bu)_2$ complexes, respectively, where Si_s and Al_s represent surface silicium and aluminum atoms. The complex grafted onto alumina is active in propane metathesis (turnover number [TON] = 28), whereas that grafted onto silica is not (TON = 0) [10,13,14]. Recently, it was shown that a silica–alumina support, treated under similar conditions, yields a very similar surface complex as silica, with grafting onto the Si atom $(Si_sO)W(C\mathit{t}Bu)(CH_2\mathit{t}Bu)_2$ but, surprisingly, gives a propane metathesis reactivity similar to that on the alumina support [15]. The influence of the support thus seems especially confused. In addition, it has been proposed that, as for grafted tantalum complexes, in alkane metathesis olefin metathesis is the key homologation process, because olefins have been identified as primary products, and the ratios of products of cross-metathesis between various alkanes are in agreement with those of the corresponding olefin metathesis [5–10]. All surface tung-

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sten complexes, including those grafted on silica, are indeed active in olefin metathesis. However, the mechanism for the initial alkane dehydrogenation step to form the olefin and the differences between the oxide supports are not yet clearly understood. Thus, probing the support reactivity at a molecular level, together with that of the grafted complex, is of primary importance to improve such chemistry and can lead to a new interpretation of the numerous phenomena occurring when using alumina as a catalyst support.

Density functional theory (DFT) applied to periodic calculations has proven to be a useful tool in a comprehensive approach of γ-Al_2O_3 reactivity toward H_2O, H_2, alkane, metallic clusters, and various organometallic complexes [14,16–18]. The aim of the present work was to use a quantum mechanical approach in the DFT framework to gain insight into the role of this oxide when used as a support for perhydrocarbyl tungsten complexes in the catalysis of alkane metathesis. We compared possible mechanisms for alkane metathesis catalyzed by $[(Al_sO)W(CtBu)(CH_2tBu)_2]$, to identify and differentiate the influences of the complex and of the support, γ-Al_2O_3 [14].

2. Methods

We performed the calculations in a DFT framework with the PW91 functional using a periodic description of the system as implemented in the VASP code [19–21]. The atomic cores were described with the projected augmented wave (PAW) technique with an energy cutoff of 275 eV [22,23]. Minimum energy pathways were found using the nudged elastic band (NEB) method with eight equally spaced images along the pathway [24]. The transition state structures were fully optimized and characterized by a single negative force constant along the reaction pathway.

The surface was modeled by a four-layer slab. The influence of slab thickness has been evaluated for up to eight layers, with no significant change noted [16]. The two bottom layers of the slab were maintained in the geometry of the bulk, whereas the two upper layers were relaxed. With such an asymmetric representation of the surface, some dipole corrections may be necessary. Tests revealed only infinitesimal changes in geometries and energetic corrections below 5 $kJ\,mol^{-1}$, congruent with the large vacuum zone between the slabs ($\approx$17 Å). Thus, such corrections were not applied. Moreover, zero point energy corrections were not systematically taken into account. Indeed, testing demonstrated that these corrections never exceeded 10–15 $kJ\,mol^{-1}$ in favor of the species including fewer C–H bonds.

3. Results and discussion

The model used for the γ-alumina bulk results from a study investigating the dehydration of boehmite by determining the optimal distribution of 25% tetrahedral and 75% octahedral Al in a fcc lattice of O atoms [25]. This model is in good agreement with the measured bulk modulus and X-ray diffraction spectra. The (110) surface of γ-alumina, the most exposed surface in the particles (75%), is described here by a four-layer periodic slab of unit formula $Al_{16}O_{24}$ with cell vectors of 8.4×8.1 Å^2 [26–28]. The bare (110) surface unit cell exhibits several accessible unsaturated Al atoms, one tricoordinated from a tetrahedral Al in the bulk and three tetracoordinated from bulk octahedral atoms.

The surface can be hydrated by successive adsorption of water molecules. The simulation of IR spectra shows that the trihydrated surface unit cell with a OH coverage of 7.3 OH/nm^2 (vs 4 OH/nm^2 determined experimentally) correctly describes the diversity of OH groups present on γ-Al_2O_3 pretreated at 500 °C [26–28]. However, the hydration of alumina is not uniform, and adsorption of methane and H_2 through a combined experimental and theoretical approach has shown that dehydrated tricoordinated Al centers are present as strong Lewis acid site defects ($\sim$0.04 $site/nm^2$) and have a strong Lewis acid character [16]. The periodic description of such a low concentration of defects would require a huge unit cell. Instead, we modeled the dehydrated defects separately by the nonhydrated γ-Al_2O_3 unit cell.

The W complex is grafted on the hydroxylated alumina surface. It was shown previously by a mechanistic simulation that the grafting occurs by a σ-bond metathesis reaction involving a surface OH group on a tetrahedral Al atom and the W–CH_2tBu bond, with the formation of a neutral mono-aluminoxy complex (**1**) and the release of a neopentane molecule [14]. Further elimination involving neighboring OH groups to give a bis-aluminoxy surface complex is activated (barrier, 100 $kJ\,mol^{-1}$) from geometric constraints; however, this transformation could occur at the temperature of the alkane metathesis reaction (150 °C). Calculations have shown that this bis-aluminoxy surface complex has very similar reactivity to the mono-aluminoxy surface complex, and thus here we limit the presentation to the latter. The mono-aluminoxy complex (**1**) has been further validated by the simulation and complete interpretation of the ^{13}C NMR and IR spectra [14]. Its calculated structure, which is in excellent agreement with the EXAFS data [10], is shown in Fig. 1b with model ligands (methyl instead of neopentyl and CCH_3 instead of $CtBu$). Together, the total energy, the comparison with EXAFS, and the spectra calculations demonstrate that this structure is a realistic model of the surface organometallic site, and we explore its reactivity in the present work.

The simplest way to approach the mechanism, used up to now, is to consider that all of the elementary steps occur on the tungsten complex, with no chemistry on the alumina (Fig. 1a). This mechanism starts from propane and complex **1** (Fig. 1b) as a model of the catalyst [14]. We have studied this mechanism up to the formation of the metallacycle **4**, with the subsequent steps being the reverse of those leading to **4** with exchange of the substituents. The energy profile is given in Fig. 1c.

The activation of propane on the complex can occur by C–H/W–C σ-bond metathesis (reaction energy, $\Delta E = 9\ kJ\,mol^{-1}$; activation energy, $\Delta E^{\ddagger} = 140\ kJ\,mol^{-1}$) or by addition of a C–H bond of propane on the carbyne ligand ($\Delta E = 52\ kJ\,mol^{-1}$ and $\Delta E^{\ddagger} = 110\ kJ\,mol^{-1}$). From this second product, no pathway with reasonable barriers was found for subsequent reaction steps (β-H elimination or α-H abstraction), and thus only the product **2** of the C–H/W–C σ-bond metathesis will be

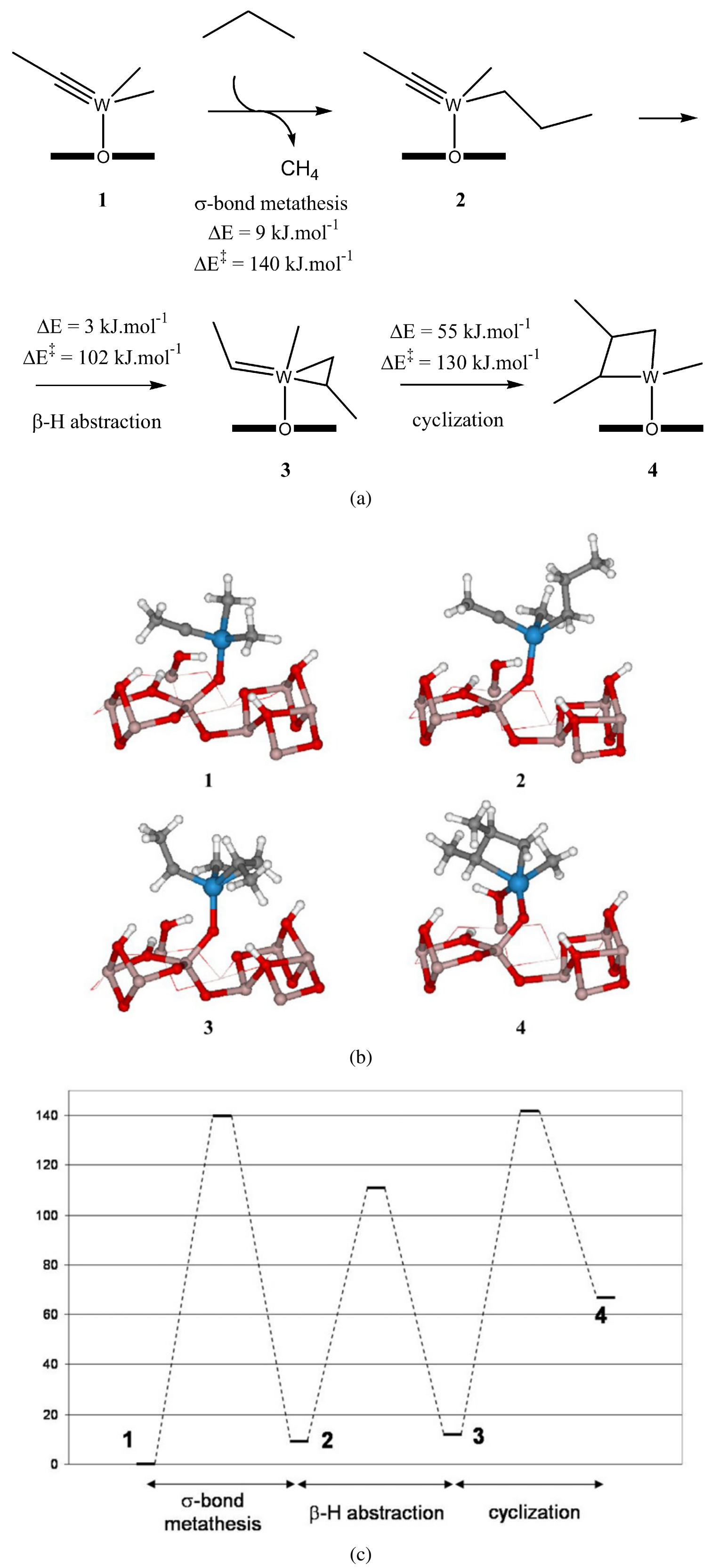


Fig. 1. A first hypothesis for alkane metathesis mechanism by propane activation on the W complex (a), associated structures (b) and energy profile (c). On all the structures, only a fraction of the atoms of the slab used in the periodic calculation is shown for clarity.

considered further. This can undergo β-H abstraction by the nucleophilic carbyne, giving a carbene **3** ($\Delta E = 3\ \mathrm{kJ\,mol^{-1}}$ and $\Delta E^{\ddagger} = 102\ \mathrm{kJ\,mol^{-1}}$) and a coordinated olefin on $\mathrm{W^{IV}}$, which also can be viewed as a metallacyclopropane of $\mathrm{W^{VI}}$, with the strong pyramidalization of the carbon atoms and the distance between the two carbon atoms (1.46 Å) in **3** favoring the latter description. Formation of metallacyclobutane, the central intermediate for the olefin metathesis reaction, can then occur, yielding the d^2 complex **4** ($\Delta E = 55$ kJ mol^{-1} and $\Delta E^{\ddagger} = 130$ kJ mol^{-1}), for which the triplet state is more stable than the singlet state ($\Delta E_{\text{T-S}} = -34$ kJ mol^{-1}).

The decoordination of the olefin from **3** is calculated to be endothermic by $\Delta E = 184$ kJ mol^{-1}, which is too high to account for the experimental detection of olefins as primary products. In addition, the activation energies in this process are rather high; the highest transition state along the pathway is 142 kJ mol^{-1} above the reactant state. The entropic effects from translational and rotational degrees of freedom in gas phase can be included to simulate the free energy at 150 °C. The free energy barrier between **1** and **2** is 200 kJ mol^{-1} (because both propane and methane are immobilized in the transition state), and the metallacyclobutane **4** is 92 kJ mol^{-1} less stable than the reactants. Thus, direct activation of the alkane on the surface tungsten complex seems difficult, at least from the energy pathways explored here.

The previous conclusion and the different reactivity for the silica and alumina (or silica–alumina) support lead us to consider other mechanisms, including direct participation of the oxide surface in the reactivity. As explained above, the γ-Al_2O_3 surface shows a small fraction of totally dehydrated and reactive tricoordinated aluminum atoms (see structure **5** in Fig. 2a) [16]. The C–H bonds of propane can react with such tricoordinated aluminum atoms to give a hydroxyl group and an alkyl-aluminum (structure **6**) on the surface by addition of C–H on a Al–O bond ($\Delta E = -127$ kJ mol^{-1} and $\Delta E^{\ddagger} \approx 25$ kJ mol^{-1}), as observed previously with methane both experimentally and theoretically [16]. Starting from this alkyl-aluminum, propene can be obtained by β-H elimination ($\Delta E = 127$ kJ mol^{-1} and $\Delta E^{\ddagger} = 140$ kJ mol^{-1}). The reaction forms an aluminum hydride and a hydroxyl group with the same characteristics as that obtained by dissociation of H_2 on such a defect site (see structure **7** in Fig. 2). The overall process (C–H addition and β-H elimination) is iso-energetic and corresponds to a dehydrogenation of propane with the stabilization of H_2 on the surface by its dissociation on strong Lewis acid sites (see the energy profile in Fig. 3c). Including entropic effects in the gas phase, the barrier to activating propane on the dehydrated defect increases to 105 kJ mol^{-1}, a reasonable value for a reaction at 150 °C, whereas the intermediate structure **6** is stabilized only by $\Delta G = -47$ kJ mol^{-1} with respect to gas-phase propane. The overall process remains thermoneutral ($\Delta G = +2$ kJ mol^{-1}), because the number of molecules in the gas phase is conserved. Zero point energy corrections stabilize the final state **7** slightly, by 15 kJ mol^{-1}.

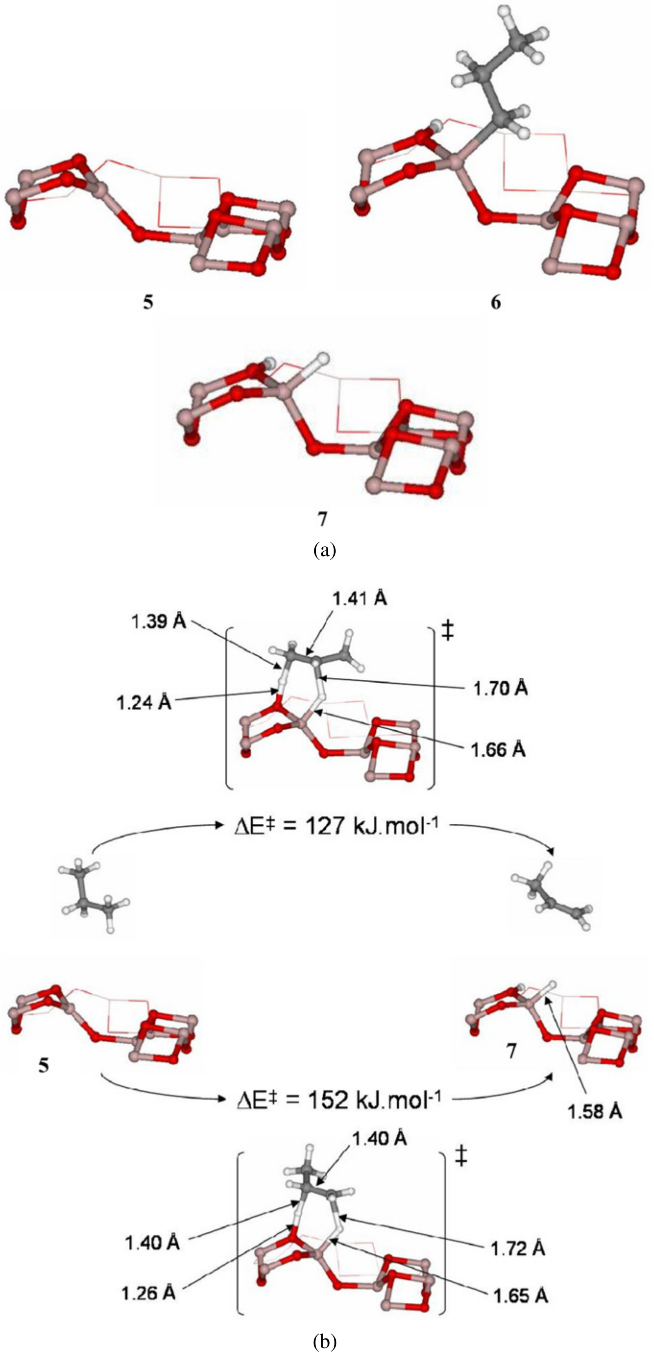
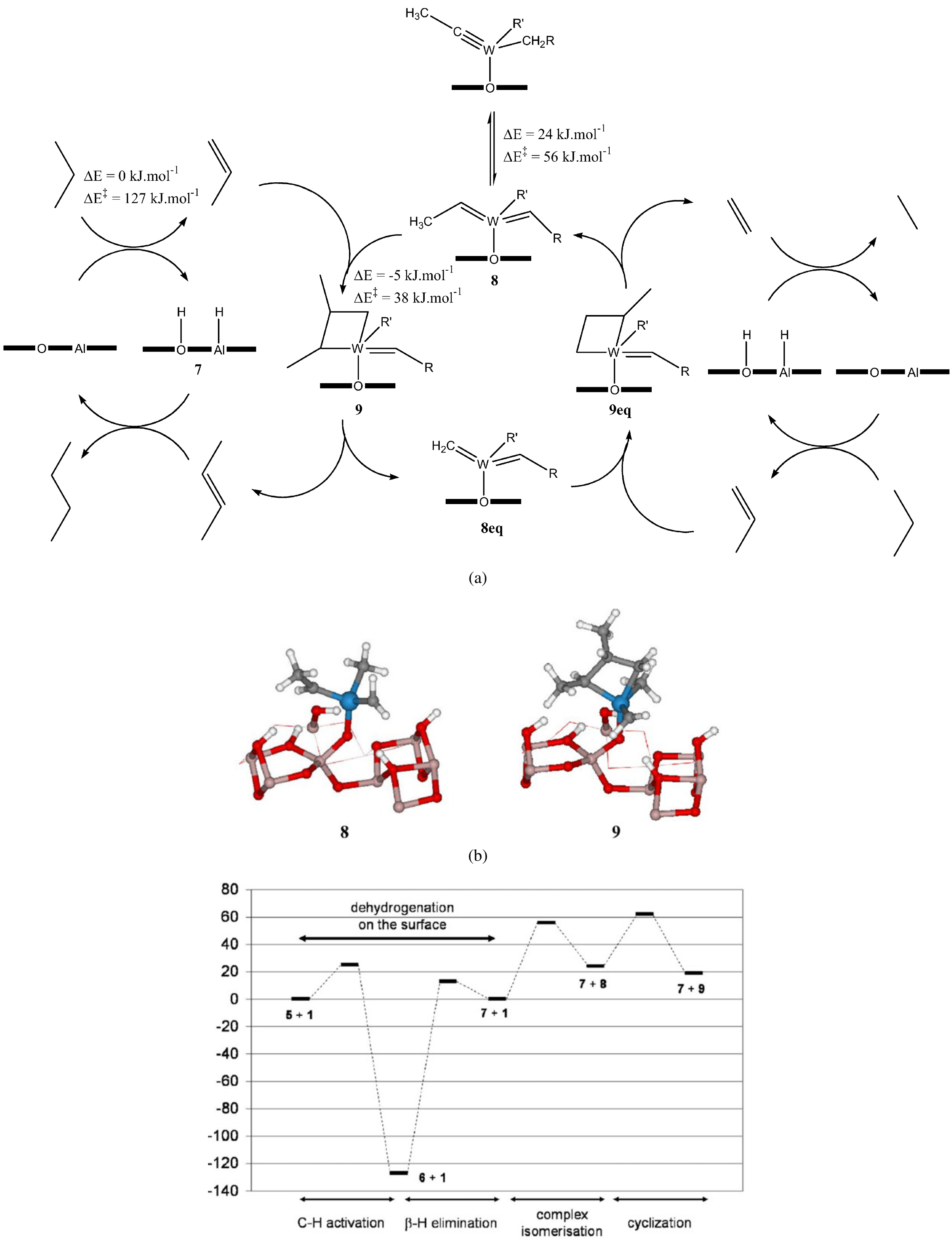


Fig. 2. Surface structures involved in the two-step dehydrogenation of propane on γ-Al_2O_3 defect sites (a). Concerted mechanism for the dehydrogenation of propane into propene on γ-Al_2O_3 defect sites (b).

Another possible route to dehydrogenated propane on such a defect site is through a concerted reaction via a six-member ring transition state. In this transition state, the two hydrogen atoms are transferred to the surface, one on an oxygen atom, the other on the Al_{III} atom. Because the transfer of the hydride on the aluminum atom is largely advanced in the transition state, this one looks like a carbocation, and the more it is substituted, the more stable it is, as can be seen from the values reported in Fig. 2b for the two isomers of the transition state, which differ by 25 kJ mol^{-1}. However, the activation barrier ($\Delta E^{\ddagger} = 127$ kJ mol^{-1}) is higher than for the stepwise process, especially if entropic effects are estimated ($\Delta G^{\ddagger} = 207$ kJ mol^{-1}). Thus, the two-step mechanism with the proton-alkyl intermediate is favored. This demonstrates the possible role of the alumina surface in generating primary products. To the best of our knowledge, such activity of γ-alumina for the propane dehydrogenation step has not yet been pointed out. Note, however,



(a)

(b)

(c)

Fig. 3. Surface assisted alkane metathesis mechanism (a), associated additional structures (b) and corresponding energy profile (c).

that this dehydrogenation reaction is stoichiometric and not catalytic, where the number of propene molecules produced is less than the number of hydration defects on the alumina support.

In parallel to the olefin formation on the alumina low coordination sites, the carbyne complex **1** can isomerize in a bis-carbene structure **8** represented in Fig. 3b ($\Delta E = 24\ \mathrm{kJ\,mol^{-1}}$ and $\Delta E^{\ddagger} = 56\ \mathrm{kJ\,mol^{-1}}$), a well known process for analogous complexes [29,30]. Thus, every element is present to produce a metallacyclobutane: propene and carbene **8**. No precursor state has been identified: the metallacycle **9** (Fig. 3b) is formed without coordination of the olefin before ring closure ($\Delta E = -5\ \text{kJ mol}^{-1}$ and $\Delta E^{\ddagger} = 38\ \text{kJ mol}^{-1}$).

The reaction energy to form the metallacycle **9**, a d^0 complex of W(VI), is 24 kJ mol^{-1} more favorable than that for forming the d^2 metallacycle of W(IV) **4** in its triplet state. This feature is a key aspect in the comparison between the two mechanisms; the transition state leading to **4** is higher than that leading to **9**, because it requires a change in the oxidation state of the tungsten atom from +VI to +IV with a spin transition. These electronic changes are not necessary in the mechanism leading to **9**.

The ring opening of **9** will form butene, which can be hydrogenated in an approximately thermoneutral process by the reverse reaction of the dehydrogenation presented above in the case of propane/propene (Fig. 2). The complete catalytic cycle is presented in Fig. 3a. This dual mechanism forms the olefin on the alumina defects and clearly explains its detection as a primary product. Olefin metathesis then occurs on the supported W complex, whereas the new alkane is regenerated by backward hydrogenation on the aluminum hydride–hydroxyl couple (**7**) previously formed on alumina. The thermoneutral nature of the hydrogenation/dehydrogenation reaction on the tricoordinated Al atom plays an important role here. The new bis-carbene **8eq** can again coordinate propene to form the metallacycle **9eq** (similar to the **8** → **9** reaction). Thus, metathesis regenerates the initial site **8** and produces ethene which can be hydrogenated on alumina.

4. Conclusion

The quantum chemistry exploration of energy pathways suggests two possible mechanisms for alkane metathesis. The first one takes place on the grafted complex only. It activates the propane by σ-bond metathesis, forms a carbene–olefin complex by β-H abstraction, and finally transforms it to a d^2 metallacycle. This mechanism presents an overall barrier of 140 kJ mol^{-1} in energy and ∼200 kJ mol^{-1} in free energy and is hence significantly activated. Moreover, the production of propene, seen as a primary product in the experiment cannot be accounted. It cannot be excluded however that the well-characterized grafted complex is not the final active site but is instead a precursor of the catalyst, which structure would still be unknown.

The second mechanism is based on the demonstrated existence of a small amount of dehydrated defects (0.04 per nm^2) on γ-alumina (pretreated at 500 °C) able to react with a C–H bond of an alkane [16]. Propane can be dehydrogenated on such defect sites, stoichiometrically forming propene, an aluminum hydride and a hydroxyl group. The maximum barrier in this process is 127–140 kJ mol^{-1}, in energy and also in free energy, and the reaction is thermoneutral. The amount of olefin formed is linked to the number of low-coordination Al sites. Olefin metathesis is then performed in a second step by the grafted tungsten–alkyl complex, in a mechanism with small barriers. The olefins thus formed (butene and ethene) can then react again with the proton-hydride site in a process that is the reverse of the initial propane activation process, to generate butane and ethane. The overall reaction cycle is catalytic, because the stoichiometric reaction is performed twice, once forward and once backward. This mechanism is appealing due to its reasonable free energy barrier, which leads to a favorable exponential term in the rate. However, the prefactor is reduced from the small number of active sites on alumina. In addition, this mechanism agrees with the initial formation of propene in the experiment.

This mechanism implying the support could naturally explain why the same complex grafted on silica is inactive in alkane metathesis. Silica does not have defect sites with strong Lewis acidity and cannot activate alkanes as alumina can. The silica–alumina support, which gives an active complex, also is interesting. The tungsten is grafted by a siloxy linkage, as on silica, and thus its activity in this case is not expected. In contrast, three-fold coordinated Al defects also should be present on silica–alumina, presumably in larger amounts than on alumina, because aluminum is mostly in a tetrahedral environment in silica–alumina bulk. Thus, the dual mechanism implying support to activate the alkane also should be possible on this support. The activation of methane on silica–alumina should be tested experimentally to confirm this hypothesis.

The dehydrated defects on γ-alumina are certainly fragile entities. They can react with traces of water or with olefins, forming oligomers. This could explain the rapid catalyst deactivation. An experiment designed to selectively remove these sites before alkane metathesis would provide proof of their participation in that reaction, as proposed herein.

Quantum simulations can provide important insight on the reaction mechanism for surface organometallic chemistry, underscoring the complementarity of the reactivity of the grafted complex and that of the oxide support itself. This intimate duality, at the molecular level, is a clear advantage, enabling the design of innovative catalysts.

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