Structure of Dimeric Molybdenum(VI) Oxide Species on γ-Alumina: A Periodic Density Functional Theory Study

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The structure and stability of dimeric Mo(VI) oxide species on γ-alumina are investigated with a periodic DFT approach. A large number of Mo dimers of various geometries, located on the (100) and (110) surfaces of γ-Al2O3, are modeled. The most stable dimeric species on the (100) plane are mixed dioxo−monooxo or double-monooxo species that are 3-, 4-, or 5-fold bonded to the surface. In most cases, the molybdenum atoms are pseudotetrahedrally coordinated. In the case of the (110) surface, the most stable dimeric Mo(VI) forms are double-monooxo species, which are 6- or 5-fold bonded to the support. The coordination of the molybdenum atoms is most frequently a distorted square pyramidal, but distorted octahedral or distorted tetrahedral geometry also happens. The energetic stability of the dimeric Mo(VI) species, relative to the corresponding monomeric Mo(VI) centers, is determined. On the minority (100) surface, the complex–surface interaction is moderate and the dimeric Mo(VI) species are more stable than the monomeric Mo(VI) forms. Therefore, the formation of Mo oligomeric species on this surface is predicted. On the majority (110), in contrast, the interaction energy is strong, which favors dispersion, and hence, the monomers are more stable than the dimers so that, even at high Mo loadings, the monomeric Mo species can be still present on γ-alumina, together with polymeric chains.

The calculated Mo=O vibrational frequencies for the Mo(VI) dimers on the (100) surface are higher than for the corresponding monomeric Mo(VI) species and only slightly shifted in the case of the majority (110) surface. Theoretical Mo−O−Mo frequencies match well the experimental values attributed to surface polymeric Mo species on alumina.

1. Introduction

Molybdena−alumina systems are applied in many catalytic processes, among others, olefin metathesis,6,7 selective oxidation reactions,6,7 dehydrogenation,8 oxidative dehydrogenation,9 and hydrodesulphurization.10 It is often postulated that the active sites are formed from highly dispersed surface Mo species, presumably single MoO3 units.1,11 On the other hand, in molybdena−alumina systems with high Mo loadings, polymerized surface molybdenum oxide species coexist with the isolated monomeric forms.12−19 Moreover, some authors reported, in contrast, the presence of surface polymerized species even for extremely low Mo loadings.20,21 Hence, the situation from experiment is not very clear. Besides the monomeric forms, dimeric and polymeric Mo species have been also proposed as the active site precursors in molybdena−alumina systems.1,19,22−24

On the basis of in situ measurements13−19,25,27,28 and theoretical investigations,25,26 much information about the structure of isolated monomeric Mo(VI) forms on γ-alumina is now available. Most likely, under dehydrated conditions, they are tetrahedrally coordinated dioxo species or five-coordinated monooxo centers. Tetrahedral monooxo Mo(VI) sites have also been proposed and are calculated to be only slightly less stable than dioxo on the alumina (100) surface. However, as the polymeric Mo(VI) species are concerned, the details related to their structure and stability are rather scarce and not unambiguously confirmed. According to the results obtained from Raman and XANES techniques, these forms probably consist of monooxo Mo(VI) centers13,14,16,18,19 that are octahedrally coordinated.13−19 Even less information is available about dimeric Mo(VI) species on γ-alumina. Various structures were suggested in the literature1,17,19,22,29 (Figure 1), but only some propositions19 (Figure 1a) are based on the results obtained under controlled dehydrated conditions. One should remember, however, that these species are expected to be in the minority on the surface, so they are not easily detectable by spectroscopic

Figure 1. Structures proposed in the literature for dimeric Mo(VI) oxide species supported on the alumina surface.1,17,19,22,29
techniques. On the other hand, such centers may be the active site precursors,\textsuperscript{1,19,22–24} hence being decisive for the catalytic activity.

Taking into account the insufficient experimental data concerning dimeric Mo(VI) species on alumina, computational chemistry methods are expected to provide more detailed information in this subject. Therefore, we have undertaken a periodic density functional theory (DFT) study on the structure and stability of possible dimeric Mo(VI) oxide forms on alumina. To the best of our knowledge, such investigations have not been reported so far. The previously developed models of the γ-alumina surfaces,\textsuperscript{30,31} successfully applied and verified many times,\textsuperscript{11,26,30–34} are employed to enable a realistic description of the molybdena–alumina system.

In our recent paper,\textsuperscript{26} we reported analogous DFT investigations of monomeric Mo(VI) oxide species on γ-alumina. Our calculations appeared to be helpful in the detailed interpretation of the experimental results concerning the molybdena–alumina system. Moreover, we obtained a large amount of valuable complementary information, not accessible at this moment by experimental techniques. It was shown that, under dehydrated conditions, the square pyramidal monooxo species is most probable on the majority (110) surface, whereas tetrahedral dioxo species and five-coordinated dioxo species should be dominant on the minority (100) facet. The latter, first time proposed, could be experimentally undetectable; however, it is predicted to be the precursor of the most active center for alkene metathesis.\textsuperscript{11,26} In the present work, we have extended our previous studies to dimeric Mo(VI) oxide species on the γ-alumina surface. The main purpose is to determine the geometry of the potential Mo(VI) dimers on the (100) and (110) γ-alumina under dehydrated conditions. The relative energies of the various proposed structures for the dimeric Mo(VI) sites are predicted, and their stability is compared with that of the previously studied\textsuperscript{26} monomeric Mo(VI) species. Finally, the theoretical Mo=O and Mo–O–Mo stretching frequencies are discussed, taking into account the available experimental data for the molybdena–alumina system.

2. Computational Methods and Models

The periodic DFT calculations have been performed using the Perdew and Wang (PW91) generalized gradient approximation exchange-correlation functional,\textsuperscript{35} implemented in the Vienna Ab Initio Simulation Package (VASP).\textsuperscript{36–38} The one-electron wave functions are developed on a basis set of plane waves. Atomic cores are described with the projector-augmented wave method (PAW).\textsuperscript{39} In all calculations, standard PAW atomic parameters were used, requiring a cutoff energy of 400 eV (fixed by the O atom) for a converged total energy. For Mo, the PAW is built with 12 e in the valence. For some selected systems studied, electron localization function (ELF) analysis\textsuperscript{40} was performed.

The previously validated models of the γ-Al\textsubscript{2}O\textsubscript{3} surface\textsuperscript{30,31} are based on the nonspinel bulk structure.\textsuperscript{41} The (110) plane is the most exposed surface on the particles (70–83%) and the (100) surface is in minority (17%), whereas the (111) plane can be neglected.\textsuperscript{30,42,43} As minor species can play an important role in catalysis, both (110) and (100) facets have been taken into account in the present study, analogous to our earlier work.\textsuperscript{26} Surfaces have been modeled by a four-layer slab. The bottom two layers are frozen in the geometry of the bulk, to reproduce the properties of extended surfaces, whereas the upper two layers have been allowed to relax. Frequency calculations on the stable geometry have been carried out by numerical differentiation of

the force matrix. All the optimized degrees of freedom were used for the frequency calculations. In most calculations, the surface unit cell dimensions (Å) are $a = 8.414$, $b = 11.180$ for the (100) plane and $a = 8.097$, $b = 16.827$ or $a = 16.194$, $b = 8.414$ for the (110) plane (unit formula = Al\textsubscript{16}O\textsubscript{48}). A 331 Monkhorst–Pack mesh has been applied for Brillouin zone sampling. To check the influence of lateral interactions between periodic images, twice bigger unit cells, $a = 16.827$, $b = 11.180$ and $a = 16.194$, $b = 16.827$, for the (100) and (110) facets, respectively, were also considered in some selected cases (unit formula = Al\textsubscript{8}O\textsubscript{36}). These tests showed that the same Mo(VI) surface structures are obtained, independent of the cell size. The differences in the corresponding Mo\textsubscript{2}O\textsubscript{6(g)} adsorption energies, to form the surface Mo dimers, are below 10 kJ mol\textsuperscript{-1}. Additionally, the two most stable structures on the (110) surface were recalculated using a six-layer slab in the smaller unit cell, with the upper three layers allowed to relax. Again, the geometry of the Mo sites is hardly changed compared to the four-layer slab model, and the Mo\textsubscript{2}O\textsubscript{6(g)} adsorption energies do not differ by more than 13 kJ mol\textsuperscript{-1}. The four-layer slabs in the smaller unit cells were hence used in standard calculations, for practical reasons. The validation of the theoretical approach in terms of the prediction of bond lengths and Mo=O stretching frequencies on known molecular compounds was done previously.\textsuperscript{26}

Dimeric Mo species on γ-alumina are modeled under dehydrated conditions, that is, under the conditions of usual thermal pretreatment of the molybdena–alumina catalysts prior to reaction ($T > 800$ K and very low vapor pressure).\textsuperscript{1–3,5} It was previously shown by means of periodic DFT calculations and thermodynamic analysis that, under such conditions, fully dehydrated molybdenum species are present on both (100) and (110) γ-alumina.\textsuperscript{11,26} Therefore, no water molecules have been added to the alumina surface containing the models of the Mo species, besides some test calculations on slightly hydrated (110) surface (see section 3.2).

The dehydrated (100) surface presents five-coordinated Al Lewis centers (Al\textsubscript{IV}), arising from octahedral Al in the bulk, whereas tetrahedral Al are located below the surface plane. The dehydrated (110) surface shows a stronger Lewis acidity and presents Al\textsubscript{III} (from octahedral Al in the bulk) and Al\textsubscript{IV} centers (from tetrahedral Al in the bulk). These various unsaturated sites have been used to attach the dimeric Mo species. All models will consider Mo atoms in the +VI oxidation state.

Surface deformation energies have been calculated as the energy difference between the alumina part frozen in the geometry of the Mo/Al\textsubscript{2}O\textsubscript{3} system and the free alumina surface in its relaxed geometry:

$$E_{\text{def}}(\text{Al}_{2}\text{O}_{3}) = E(\text{Al}_{2}\text{O}_{3}\text{frozen}) - E(\text{Al}_{2}\text{O}_{3}\text{relaxed})$$

Deformation energies for the surface Mo dimers and monomers have been calculated in a similar way:

$$E_{\text{def}}(\text{MoO}_{6}) = E(\text{MoO}_{6}\text{frozen}) - E(\text{MoO}_{6}\text{relaxed})$$

$$E_{\text{def}}(\text{MoO}_{3}) = E(\text{MoO}_{3}\text{frozen}) - E(\text{MoO}_{3}\text{relaxed})$$

Interaction energies for the dimers and monomers, respectively, are defined as the difference between the energy of the whole system and the energies of the respective fragments frozen in the geometry they have in the Mo/Al\textsubscript{2}O\textsubscript{3} system.
whereas the adsorption energies of Mo2O6(g), to form the dimers and monomers, respectively, are calculated as

$$E_{\text{ads}, \text{d}} = E(\text{system}) - E(\text{Al}_2\text{O}_3)_{\text{frozen}} - E(\text{Mo}_2\text{O}_6)_{\text{frozen}}$$

$$E_{\text{ads}, \text{m}} = E(\text{system}) - E(\text{Al}_2\text{O}_3)_{\text{relaxed}} - E(\text{Mo}_2\text{O}_6)_{\text{frozen}}$$

Notice that the monomer adsorption energy is doubled and that the same reference is used as for the dimer, for comparison purposes (the “*” refers to that specific choice).

3. Results and Discussion

3.1. Structures and Relative Stabilities of Dimeric Mo Species on (100) γ-Alumina. The various optimized structures of dimeric Mo(VI) oxide species supported on the (100) surface of γ-alumina are shown in Figure 2, in order of increasing energy. The respective deformation, interaction, and adsorption energies are presented in Figure 3. The selected atomic distances are shown in Table 1.

Most of the molybdenum atoms are connected via one or two oxygen linkages to aluminum atoms with distorted octahedral coordination (previously AlV on the bare surface). Additionally, dative bonds from an oxygen lone pair on the surface toward the Mo Lewis acid center are formed, further stabilizing the dimeric Mo structures. The molybdenum atoms possess one or two oxo ligands with Mo–O distances in the range of 1.70–1.72 Å (Table 1), similar to that of the gas-phase dimer (1.71 Å). In one case only (100_d10), a slightly elongated Mo–O bond is found (1.73 Å). The Mo–O bond lengths in the Mo–O–Mo bridges show a stronger variation (1.85–2.10 Å) around the gas-phase dimer distance (1.94 Å), and usually, these Mo–O bonds in a given Mo dimer have different lengths. This is related to the geometric constraints imposed by the alumina surface on the conformation of the dimer. The almost fully symmetrical 100_d5 structure (Figure 2) with the Mo–O distances close to those calculated for the gas-phase Mo2O6 dimer (Table 1) is an exception. Indeed, the Mo2O6 deformation energy is significantly lower in this case (180 kJ mol$^{-1}$) compared with other dimeric Mo sites (Figure 3). In the case of 100_d5 and 100_d7, the distance between the molybdenum atoms (2.99 and 3.14 Å, respectively) is not significantly longer than the corresponding value calculated for the gas-phase Mo2O6 dimer (2.88 Å). However, both formal electron counting and the performed topological ELF analysis do not indicate the formation of the metallic Mo–Mo bond, either for the mentioned surface Mo dimers or in the case of the gas-phase dimer. For the remaining Mo(VI) species, the Mo–Mo distance is strongly increased, being in the range of 3.31–3.73 Å (Table 1).

Interestingly, the most stable species on the (100) surface (100_d1) are built from one dioxo and one monooxo fragment. This is somewhat consistent with our recent results for the dehydrated monomeric Mo(VI) centers on γ-alumina, indicating that the dioxo species are most stable on the (100) surface, although the energy of the monooxo species is only slightly higher (by 13 kJ mol$^{-1}$). Indeed, in the present study, we have found that the double-monooxo Mo(VI) dimers (100_d3 and 100_d4) are less stable than 100_d1 by only 22–23 kJ mol$^{-1}$.

On the other hand, the only double-dioxo species (100_d9) is highly unstable because it only allows forming two bonds between the Mo dimer and alumina. This is reflected in the relatively low value of the interaction energy (–607 kJ mol$^{-1}$, Figure 3).

Considering further the geometry of the Mo(VI) dimeric species, it should be noted that both molybdenum atoms in the most stable form, 100_d1, are pseudotetrahedrally coordinated. The same situation takes place in the case of the 100_d4 species that resemble the calculated Mo(VI) dimers on titania. In several other structures, at least one molybdenum atom possesses a distorted tetrahedral coordination. Our recent calculations for

Figure 2. Optimized structures and relative energies for the dimeric Mo(VI) oxide species supported on (100) γ-alumina.
Dimeric Molybdenum(VI) Oxide Species on γ-Alumina

The most stable dimeric structure, 100_d1, is only 3-fold coordinated to the surface, which is, however, in accordance with the previous findings for Mo(VI) monomers, where the species 2-fold bonded to the (100) surface are most stable, whereas the 3-fold coordinated monomers have higher energy. Other dimeric Mo(VI) species, characterized by relatively low energy, are 4-fold (100_d2, 100_d4) and 5-fold (100_d3, 100_d5) bonded to the support. A 6-fold coordinated structure has been optimized as well (100_d6); however, its energy is highest among the species 100_d1–100_d6 (+47 kJ mol⁻¹). Generally, the calculated interaction energies (Figure 3) increase with the number of bonds formed between the Mo dimer and the surface (100_d5 is the main exception). However, more interaction points with the surface also induce a more severe deformation of the dimer, at the expense of the deformation energy cost. The overall balance is negative, and the three-coordinated 100_d1 system results in the best interaction–deformation compromise. One of the two Mo=O–Mo bridges in the gas-phase dimer is open upon grafting. The 100_d5 system keeps the dimer gas-phase structure, but in this case, the interaction with the alumina support occurs through high coordinated atoms (five-coordinated Mo and three-coordinated O) and the resulting interaction energy is moderate. This is a low interaction–low deformation grafting mode that is significantly less stable than 100_d1 (+37 kJ mol⁻¹).

The presence of the remaining four Mo(VI) dimeric species, especially the very unstable 100_d9 and 100_d10, is not probable in the real molybdena–alumina system. The mixed monooxo and dioxo structure, 100_d7, 3-fold bonded to the surface, is quite similar to the most stable 100_d1. However, it is seen (Figure 2) that the alumina surface is more distorted in the case of 100_d7 compared with 100_d1, which is confirmed by the difference in the corresponding Al₂O₃ deformation energies (Figure 3). Although the MoO₃ deformation energy is slightly lower for 100_d7, the tendency in the interaction energies is just opposite, but exactly in the same range (Table S1, Supporting Information); hence, the stability of the 100_d7 system is lower than that of 100_d1. The two most unstable species from our ensemble have quite unusual geometries. As was mentioned above, 100_d9 forms only two bonds with the surface, which seems to be a too small number for providing the necessary stabilization of the dimeric structure. On the other hand, one of the molybdenum atoms in 100_d10 is as high as 4-fold coordinated to the surface. Consequently, a strong distortion of the alumina surface takes place, which is confirmed by the Al₂O₃ deformation energy, being clearly highest among the values calculated for the dimers on the (100) surface (Figure 3). This significant energy loss is not compensated by the increase of the interaction energy. In fact, we did not find previously any Mo(VI) monomeric species that would be 4-fold bonded to the (100) surface. Taking into account its high relative energy, 100_d10 may be excluded as a real species on γ-alumina. Overall, the stability of the dimer on the (100) surface stems from a subtle balance between establishing bonds between the dimer and the support, on the one hand, and perturbing bonds in the dimer or on the alumina surface, on the other hand.

![Figure 3. Energy analysis for the dimeric and monomeric Mo(VI) species on (100) γ-Al₂O₃.](image)

**TABLE 1: Selected Atomic Distances (Å) Calculated for the Dimeric Mo Oxide Species Supported on the γ-Alumina Surface. The Corresponding Values Obtained for Mo₂O₆ in the Gas Phase Are Also Shown.**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Mo=O1 (Mo=O1')</th>
<th>Mo=O2 (Mo=O2')</th>
<th>Mo=O3</th>
<th>Mo=O3</th>
<th>Mo=O3</th>
<th>Mo=O3</th>
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<tr>
<td>100_d1</td>
<td>1.71 (1.72)</td>
<td>1.71</td>
<td>1.88</td>
<td>1.92</td>
<td>3.73</td>
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<tr>
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<td>1.72</td>
<td>1.97</td>
<td>1.85</td>
<td>3.50</td>
<td></td>
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<tr>
<td>100_d3</td>
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<td>1.88</td>
<td>1.95</td>
<td>3.58</td>
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</tr>
<tr>
<td>100_d4</td>
<td>1.70</td>
<td>1.71</td>
<td>1.88</td>
<td>1.94</td>
<td>3.57</td>
<td></td>
</tr>
<tr>
<td>100_d5</td>
<td>1.70</td>
<td>1.70</td>
<td>1.93</td>
<td>1.94</td>
<td>3.29</td>
<td></td>
</tr>
<tr>
<td>100_d6</td>
<td>1.71</td>
<td>1.71</td>
<td>1.86</td>
<td>1.96</td>
<td>3.31</td>
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<tr>
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<td>1.71 (1.71)</td>
<td>1.88</td>
<td>2.00</td>
<td>3.14</td>
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<tr>
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<td>1.71 (1.72)</td>
<td>2.08</td>
<td>2.10</td>
<td>3.70</td>
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</tr>
<tr>
<td>100_d9</td>
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<td>1.72 (1.71)</td>
<td>1.97</td>
<td>1.86</td>
<td>3.61</td>
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</tr>
<tr>
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<td>1.94</td>
<td>1.89</td>
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<td>2.00</td>
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<td>1.94</td>
<td>1.88</td>
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</tr>
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<td>1.85</td>
<td>3.41</td>
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<td>2.00</td>
<td>1.90</td>
<td>3.20</td>
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<td>1.95</td>
<td>1.87</td>
<td>3.47</td>
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<td>1.99</td>
<td>3.16</td>
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<td>110_d8</td>
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<td>1.71</td>
<td>1.99</td>
<td>1.89</td>
<td>3.05</td>
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<tr>
<td>110_d9</td>
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<td>1.70</td>
<td>2.26</td>
<td>1.95</td>
<td>3.95</td>
<td></td>
</tr>
<tr>
<td>110_d10</td>
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<td>2.00</td>
<td>1.83</td>
<td>3.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo₂O₆(g)</td>
<td>1.71</td>
<td>1.71</td>
<td>1.94</td>
<td>1.94</td>
<td>2.88</td>
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</tr>
</tbody>
</table>

Mo(VI) monomers confirmed their strong preference to adopt the pseudotetrahedral geometry on the (100) surface of γ-alumina. The presence of the remaining four Mo(VI) dimeric species, especially the very unstable 100_d9 and 100_d10, is not probable in the real molybdena–alumina system. The mixed monooxo and dioxo structure, 100_d7, 3-fold bonded to the surface, is quite similar to the most stable 100_d1. However, it is seen (Figure 2) that the alumina surface is more distorted in the case of 100_d7 compared with 100_d1, which is confirmed by the difference in the corresponding Al₂O₃ deformation energies (Figure 3). Although the MoO₃ deformation energy is slightly lower for 100_d7, the tendency in the interaction energies is just opposite, but exactly in the same range (Table S1, Supporting Information); hence, the stability of the 100_d7 system is lower than that of 100_d1. The two most unstable species from our ensemble have quite unusual geometries. As was mentioned above, 100_d9 forms only two bonds with the surface, which seems to be a too small number for providing the necessary stabilization of the dimeric structure. On the other hand, one of the molybdenum atoms in 100_d10 is as high as 4-fold coordinated to the surface. Consequently, a strong distortion of the alumina surface takes place, which is confirmed by the Al₂O₃ deformation energy, being clearly highest among the values calculated for the dimers on the (100) surface (Figure 3). This significant energy loss is not compensated by the increase of the interaction energy. In fact, we did not find previously any Mo(VI) monomeric species that would be 4-fold bonded to the (100) surface. Taking into account its high relative energy, 100_d10 may be excluded as a real species on γ-alumina. Overall, the stability of the dimer on the (100) surface stems from a subtle balance between establishing bonds between the dimer and the support, on the one hand, and perturbing bonds in the dimer or on the alumina surface, on the other hand.
The most stable species, \textbf{110\_d1}–\textbf{110\_d4}, do not correspond to any prototype structures proposed earlier for the Mo dimers on alumina (Figure 1a–d).\textsuperscript{17,19,22,29} On the other hand, \textbf{110\_d5} is quite similar to the structure in panel b (Figure 1), whereas \textbf{110\_d6} matches almost exactly the proposed structure in panel a. Finally, \textbf{110\_d9} is very close to the structure in panel d; however, the existence of such a double-dioxo dimeric Mo(VI) species is unlikely on the (100) \gamma-alumina, taking into account its high relative energy. The calculations show that the most stable structures of the Mo dimers on the (100) alumina surface are not symmetric, contrary to all earlier proposed models.

**3.2. Structures and Relative Stabilities of Dimeric Mo Species on (110) \gamma-Alumina.** The optimized structures of dimeric Mo(VI) oxide species on the (110) \gamma-alumina surface and their relative energies are presented in Figure 4, whereas the corresponding deformation, interaction, and adsorption energies are shown in Figure 5. The molybdenum atoms are connected via oxygen bridges to octahedral or tetrahedral Al centers (previously, Al\textsubscript{IV} and Al\textsubscript{III} on the bare surface, respectively). Similar to the (100) plane, the Mo atoms interact also with surface oxygen atoms, forming Mo–O–O dative bonds. The calculated Mo–O bond lengths are slightly shorter, on average, compared with the dimeric Mo(VI) species on the (100) surface. For most of the structures, they are in the range of 1.70–1.71 Å, and only in the case of \textbf{110\_d6} or \textbf{110\_d10} were slightly longer Mo–O distances (1.72 Å) obtained. The Mo–O bonds in the Mo–O–Mo bridges are not equivalent within a given structure, and their lengths range between 1.83 and 2.26 Å. In the case of the most stable species \textbf{110\_d1}–\textbf{110\_d3}, this range is narrower (1.84–2.05 Å). The Mo–Mo distance for \textbf{110\_d2} (2.99 Å) is close to that of the Mo\textsubscript{2}O\textsubscript{6} dimer in the gas phase. Again, the ELF analysis excludes the formation of a Mo–Mo bond. Slightly longer Mo–Mo distances (3.05–3.20 Å) are calculated for \textbf{110\_d1, 110\_d5, 110\_d7,} and \textbf{110\_d8} species, whereas for other Mo species shown in Figure 4, they are in the range of 3.38–3.95 Å (Table 1).

The geometries of the dimeric Mo(VI) oxide species attached to the (110) \gamma-alumina surface are quite different compared with the (100) plane (Figures 2 and 4). First of all, the most stable species \textbf{110\_d1} shows a double-monooxo functionality and is 6-fold bonded to the surface. This structure can be regarded as built from two surface monomeric Mo(VI) monooxo species: one having the square pyramidal geometry (on the right) and one the tetrahedral (on the left).\textsuperscript{26} The right-side molybdenum atom (Mo2) exhibits a distorted square pyramidal coordination, and this fragment of the dimer structure corresponds to the most stable monomeric Mo(VI) species on the (110) \gamma-alumina.\textsuperscript{26} The geometry of the left-side fragment of \textbf{110\_d1} is no more tetrahedral. Instead, it can be regarded as square pyramidal, but the oxo ligand O1 is here not in the top of the pyramid, but in the basis. Alternatively, we can consider the Mo1 coordination as distorted octahedral because the distance between Mo1 and O4 atoms is only 2.49 Å. Hence, O4 can be regarded as the sixth ligand of Mo1. It can be noticed that the \textbf{110\_d1} species match well the structure shown in Figure 1a.

The next two Mo dimers, \textbf{110\_d2} and \textbf{110\_d3}, are also double-monooxo species, multifold coordinated to the surface. Their energies are only slightly higher than in the case of \textbf{110\_d1}; hence, they can exist in the real molybdena–alumina system. \textbf{110\_d3} is somewhat similar to \textbf{110\_d1}, but both molybdenum atoms are here definitively five-coordinated, forming the distorted square pyramidal geometry. The oxo ligand O1 defines the top of the pyramid, and the oxo ligand O2 is placed in the pyramid basis. The geometry of \textbf{110\_d2} is quite different. The molybdenum on the right (Mo2) is tetrahedrally coordinated, whereas the left-side fragment of the dimer shows a distorted octahedral geometry.

The next structures presented in Figure 4 have clearly higher energy than \textbf{110\_d1}–\textbf{110\_d3}, and their existence in the real system is less probable. The molybdenum atoms in \textbf{110\_d4} have square pyramidal (Mo1) and tetrahedral (Mo2) coordination. In the case of \textbf{110\_d5}, both the right-side and the left-side fragments of the dimer have a distorted square pyramidal geometry with the oxo ligands in the pyramid tops. \textbf{110\_d6} is the first structure in this sequence that possesses two molybdenum atoms tetrahedrally coordinated and is a mixed dioxo–monoxo species. It is only 3-fold bonded to the surface, which could explain its relatively high energy compared with the \textbf{110\_1}–\textbf{110\_5} species that are 6- or 5-fold coordinated to the alumina support and, therefore, better stabilized. However,
the interaction energy calculated for 110_d6 is not the lowest among the 110_d1−110_d6 systems (Figure 5), and only a balance of all the energy components explains the lower stability of 110_d6.

Dimer−surface interaction energies are much stronger on the (110) surface compared with (100) (ca. +400 kJ mol$^{-1}$) (Figures 3 and 5). This simply results from the more unsaturated character of that alumina surface with three- and four-coordinated Al atoms before interaction. As a result, both fragments are much more distorted, at the cost of extra deformation energy. The stability of the Mo species on the (110) plane can result from a very strong interaction between the dimer and the support (110_d1, 110_d3), accompanied, however, by significant distortion of the surface and the Mo dimer, or from weak deformation connected with relatively low interaction energy (110_d2).

We showed recently that monomeric Mo species on the partially hydrated (110) γ-alumina surface are dioxo species, whereas the fully dehydrated structures are monoxo Mo species. To examine how partial hydration can influence the geometry of the dimeric Mo species, 110_d1h1 and 110_d1h2 structures have been calculated (Figure 6). The Mo atom close to the OH group shows one less aluminoxi bridge and one more oxo ligand involved in hydrogen bonding with the OH, compared with 110_d1. Consequently, this Mo=O bond is significantly elongated, especially for 110_d1h1, where one surface hydrogen is placed very close to the Mo site (Figure 6). In the case of the 110_d1h2, this hydrogen is located a bit further and the formation of the hydrogen bond forces the Mo−O−Mo double bridge open, hence forming a tetrahedrally coordinated dioxo molybdenum atom.

The calculated energy of dehydration of 110_d1h1 and 110_d1h2, to form 110_d1, is −21 and 86 kJ mol$^{-1}$, respectively. Therefore, 110_d1h1 is clearly an unstable species at the operating temperature. Dehydration of 110_d1h2, although endothermic, is much easier than in the case of the monomeric Mo species (dehydration energy = c.a. 200 kJ mol$^{-1}$). On the basis of the calculated Gibbs free energy of dehydration, we can predict that, above T ≈ 500 K, the fully dehydrated 110_d1 form becomes more stable than 110_d1h2. This threshold temperature for dehydrated conditions is even lower under a water vapor pressure < 1 atm. Hence, as long as the models presented in Figure 6 are considered, it can be concluded that slightly hydrated Mo dimers are not stable at higher temperatures, even if there are traces of moisture in the system.

3.3. Relative Stabilities of Monomeric and Dimeric Mo Species on γ-Alumina. The determination of the energetic preference for the monomeric versus dimeric Mo(VI) species can be useful in predicting whether Mo oligomer chains grow on the surface. In Figure 7, the relative stabilities of various monomeric Mo(VI) species, investigated previously, and the presently studied most stable dimeric Mo(VI) forms are compared. The energy differences are calculated on the basis of the Mo$_2$O$_6$$_{ads}$ adsorption energies, consistently defined for both the Mo dimers and monomers (Figures 3 and 5). The notation for the monomeric species is taken from ref 26.
Three different monomeric Mo(VI) species on the dehydrated (100) γ-alumina surface are considered here. The most stable monomer, 100_3, is a dioxo structure with a distorted tetrahedral geometry. The five-coordinated dioxo species, 100_4, is less stable than 100_3 by only 2 kJ mol⁻¹, and it was shown to be a potential precursor for olefin metathesis active sites in molybdena–alumina systems. Finally, the pseudotetrahedral 100_5 structure is the only monomeric Mo(VI) species on the (100) γ-alumina surface with the monooxo functionality. Its energy is higher by 13 kJ mol⁻¹ compared with 100_3. On (100) Al₂O₃, the dimeric Mo(VI) form, 100_d1, is always more stable than the monomeric Mo(VI) species (Figures 3 and 7). Therefore, the growth of the Mo oligomer chains can be expected on the (100) γ-alumina surface. The formation of the Mo–O–Mo linkage in the dimer is hence more stabilizing than the formation of two Al–O–Mo links on the monomers.

A clear difference for this relative monomer/dimer stability is seen between the (100) and (110) alumina surfaces. In the latter case, the most stable Mo(VI) monomer, 110_6, is a five-coordinated monooxo species with a distorted square pyramidal geometry. It is more stable than the most energetically favored dimeric Mo(VI) form (110_d1) (Figures 5 and 7). Hence, it can be predicted that, up to high molybdenum loadings, the monomeric Mo species are still present on the (110) surface, which is the major termination of γ-alumina. Other kinds of the possible Mo(VI) monomeric species, that is, the pseudotetrahedral monooxo 110_5 and 110_4 forms, are significantly less stable than 110_6, by 74 and 99 kJ mol⁻¹, respectively. Consequently, 110_5 is of similar stability to 110_d1, whereas 110_4 is even less stable than the dimeric species (Figures 5 and 7). Obviously, both 110_5 and 110_4 are much less probable than 110_6. Nevertheless, the formation of dimeric and, further, also polymeric Mo(VI) structures, even at lower Mo loadings, is still not excluded, taking into account that not all locations on the (110) surface favor the formation of the very stable 110_6 monomers. Moreover, the average energy of the surface monomeric species is expected to increase with a decrease of the average distance between them, corresponding with the increase of the molybdenum loading. To support this prediction, two monomeric Mo(VI) species of the 110_6 type, localized close to each other on the support, have been optimized (110_mm, Figure 8). They are still more stable than the 110_d1 dimer; however, the energy difference is reduced by 42 kJ mol⁻¹ compared with the more distant 110_6 species (Figure 7). This is caused by the fact that the left-side species in Figure 8 cannot fully adopt the favorable 110_6 geometry because of the surface constraints, in contrast to the right-side monomer.

MoO₃ dimerization in the gas phase is much more exothermic than any corresponding reaction on the alumina surface considered here (Figure 7). The interaction with the surface causes a strong distortion of the MoO₃ geometry and perturbation of the Mo–O–Mo bonds. The deformation of MoO₃ geometry in the monomeric surface species is much less significant. This is clearly seen from the energy decomposition analysis presented in Figures 3 and 5, where the deformation and interaction energies for the monomers are doubled, just enabling the direct comparison between the dimers and monomers. In each case, the MoO₃ deformation energies are much higher than the deformation energies for MoO₃. Moreover, the interaction energies for the dimers are lower (less negative), on average, than for the monomers. Although the Al₂O₃ deformation energies are, on average, slightly lower for dimers, the energy balance indicates that the surface strongly decreases the relative stability of the dimers compared to the gas phase, which results in less exothermic or even endothermic dimerization.

Considering the energy components for the 110_d1 dimer and 100_3 monomer (Figure 3 and Table S1 in the Supporting Information), the latter is stabilized by higher interaction energy (by 110 kJ mol⁻¹) and lower MoO₃/Mo₂O₆ deformation energy (by 230 kJ mol⁻¹), whereas the Al₂O₃ deformation causes a slight destabilization (by 29 kJ mol⁻¹). The total energy gain (311 kJ mol⁻¹) is still lower than the absolute value of the gas-phase dimerization energy (434 kJ mol⁻¹); therefore, the surface Mo dimer is more stable than the monomer, by 123 kJ mol⁻¹. In the case of the 110_d1/110_6 pair, the interaction energies are comparable, but both the Al₂O₃ and the MoO₃/Mo₂O₆ deformation energies strongly favor the surface monomeric species (Figure 5 and Table S1 in the Supporting Information). The total energy gain (574 kJ mol⁻¹) is higher than the dimerization effect in the gas phase; hence, the surface monomer is more stable than the dimer, by 140 kJ mol⁻¹.
TABLE 2: Calculated Mo=O and Mo—O—Mo Stretching Frequencies (cm⁻¹) for the Dimeric Mo Oxide Species Supported on the γ-Alumina Surface

<table>
<thead>
<tr>
<th>Structure</th>
<th>ν(Mo=O)</th>
<th>ν(100)</th>
<th>ν(101)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 d1</td>
<td>1012, 1005, 983</td>
<td>830, 813</td>
<td>402</td>
</tr>
<tr>
<td>100 d2</td>
<td>1005, 994, 971</td>
<td>851, 813, 801, 788, 783</td>
<td>467, 459, 442</td>
</tr>
<tr>
<td>100 d3</td>
<td>1019, 1000</td>
<td>877, 804, 753, 693</td>
<td>468, 454</td>
</tr>
<tr>
<td>100 d4</td>
<td>1022, 1000</td>
<td>891, 838, 764</td>
<td>469</td>
</tr>
<tr>
<td>100 d5</td>
<td>1025, 1014</td>
<td>746, 697, 650</td>
<td>666, 661, 659, 636</td>
</tr>
<tr>
<td>100 d6</td>
<td>1007, 996</td>
<td>816, 748, 710, 685</td>
<td>554, 548, 544, 538</td>
</tr>
<tr>
<td>110 d1</td>
<td>1019, 1003</td>
<td>773</td>
<td>635, 620, 581, 561, 540</td>
</tr>
<tr>
<td>110 d2</td>
<td>1016, 1003</td>
<td>868, 770, 750, 731</td>
<td>502, 480, 472</td>
</tr>
<tr>
<td>110 d3</td>
<td>1021, 990</td>
<td>882, 750, 635, 630</td>
<td>551, 530, 526</td>
</tr>
<tr>
<td>expθ</td>
<td>1012—985</td>
<td>870—840</td>
<td>590—580</td>
</tr>
</tbody>
</table>

a Strongly coupled with ν(Mo=O—Al). b Both symmetric and asymmetric components of the vibration are present. c Experimental data for dehydrated MoO₃/Al₂O₃ systems with various Mo loadings, refs 13–19, 25, 27, and 28.

SCHEME 1

Thus, the above results confirm the significant role of the surface that facilitates dispersion of the molybdenum species, which is often decisive for the catalytic activity of the molybdena–alumina system.1,11,19

3.4. Vibrational Frequencies. The calculated Mo=O and Mo—O—Mo stretching frequencies for the most stable dimeric Mo(VI) oxide species on γ-alumina are listed in Table 2. The obtained Mo=O frequencies are well consistent with experimental data for dehydrated molybdena–alumina systems13–19,25,27,28 (Table 2), taking into account that the calculated values are slightly overestimated.20 In the case of the (100) γ-alumina surface, the Mo=O frequencies are shifted to higher wavenumbers by approximately 30 cm⁻¹ compared to the previously calculated values for the monomeric Mo(VI) species.20 However, if the major (110) plane is considered, the Mo=O vibrational frequencies for the dimers are in the same range or only slightly higher (by some cm⁻¹) than for the monomers. These results are in general agreement with reported Raman spectroscopy data, indicating approximately a 10–15 cm⁻¹ shift to higher wavenumbers as the molybdenum loading on alumina is increased.13–17,19

The calculated Mo—O—Mo stretching modes are always strongly coupled with the support vibrations. The coupling with the Mo—O—Al modes is observed as well. The calculated frequencies of the best separated asymmetric and symmetric Mo—O—Mo vibrations (Scheme 1) are given in Table 2. The asymmetric vibrations have been calculated in a wide range of frequency values, and sometimes, the frequencies corresponding to the asymmetric and symmetric Mo—O—Mo stretching modes overlap each other (100 d5). Because the dimer structures are not symmetric upon interaction with alumina, some modes denoted in Table 2 show mixed asymmetric and symmetric components.

For most of the considered structures, the obtained Mo—O—Mo frequencies are satisfactorily consistent with the experimental data (~870–840 cm⁻¹) assigned usually to the Mo—O—Mo stretching mode of the surface polymeric species under dehydrated conditions.13,14,16,17,19 According to our calculations, these bands correspond to the asymmetric Mo—O—Mo stretch, in agreement with the literature,13,14,17 or to the mixed mode (110 d2). The band at ~840 cm⁻¹ was also observed at very low molybdenum content (1 wt % MoO₃/Al₂O₃)13 and assigned to isolated surface Mo species. Hence, one cannot exclude that the experimental bands at ~870–840 cm⁻¹ are also related to Mo—O—Al bonds, especially at low surface coverage. Indeed, we have obtained some theoretical Mo—O—Al stretching modes in the similar range, often strongly coupled with the Mo—O—Mo vibrations (Table 2).

Bands at 590–580 cm⁻¹ were also reported for MoO₃/Al₂O₃ systems14–17 and were attributed to the Mo—O—Mo stretching vibration.15,16 Among the Mo dimeric species on the minority (100) surface, only 100 d5 and 100 d6 exhibit the Mo—O—Mo modes with the frequency values not very far from this range. However, the results obtained for the most stable Mo dimer on the majority (110) plane (110 d1) match perfectly to this experimental data, whereas the frequencies calculated for 110 d3 are in satisfactory agreement. On this basis, the bands at 590–580 cm⁻¹ may be assigned to the symmetric Mo—O—Mo stretch.17 Besides, we have obtained other frequencies of the Mo—O—Mo vibrations, which are probably not detected experimentally because of their low intensities.17

To summarize, the results of the performed vibrational frequency calculations are well consistent with the available experimental data concerning the Mo=O and Mo—O—Mo stretching modes. In addition, it seems very difficult or impossible to distinguish by Raman spectroscopy the surface Mo(VI) dimeric species from the monomeric species, based on the Mo=O frequencies, as well as to distinguish the dimers from the polymeric species, based on the Mo=O and Mo—O—Mo stretches.

4. Conclusions

A DFT approach with a periodic slab model has been used for the first time to investigate dimeric Mo(VI) oxide species on γ-alumina. Many possible dimeric Mo centers of various geometries and differentially located on the (100) and (110) surfaces have been modeled. It is shown that the most stable dimeric species on the (100) and (110) facets are quite different. In the first case, they are mixed dioxo—monooxo or double- monooxo species that are 3-, 4-, or, at most, 5-fold bonded to the surface. Most of the molybdenum atoms are pseudotetrahedrally coordinated. In the second case, the most stable dimeric Mo(VI) forms are double- monooxo species, which are 6- or 5-fold bonded to the surface. The coordination of the molybdenum atoms on the (110) face is most frequently distorted square pyramidal, but distorted octahedral or distorted tetrahedral geometry is also possible.

The energetic stability of the dimeric species, relative to the corresponding monomeric Mo(VI) centers, also differs on both investigated facets of γ-alumina. On the (100) surface, the dimeric Mo(VI) species are more stable than the monomeric Mo(VI) forms. Therefore, the formation of Mo oligomeric species on this surface can be predicted on the basis of our results. On the other hand, monomeric Mo(VI) species on the (110) γ-alumina are clearly more stable than the Mo(VI) dimers investigated. This suggests that, even at high Mo loadings, the monomeric Mo species can be still present on γ-alumina, together with polymeric chains. Energy decomposition analysis confirms that the surface facilitates dispersion of the molybdenum species. It shows that the dimer/surface adsorption is a compromise between a destabilizing deformation of the dimer with respect to its gas-phase structure, together with a deformation of the surface, and of its stabilizing interaction with the
support. The deformation is necessary to optimize the complex/surface interaction. The (110) surface shows a stronger interaction, and strong deformation energy terms, whereas these values are weaker on the less unsaturated (100) alumina surface.

The calculated Mo=O vibrational frequencies for Mo(VI) dimers on the (100) surface are higher than those for the corresponding monomeric Mo(VI) species and only slightly shifted in the case of the majority (110) surface, in a general accordance with the reported Raman spectroscopy results. It is also shown that many theoretical Mo—O—Mo frequencies match well the experimental values attributed to surface polymeric Mo species on alumina. Nevertheless, it appears to be a very challenging task to distinguish the surface Mo(VI) dimeric species from the monomers, on the one hand, and from the polymeric species, on the other hand, by Raman spectroscopy.

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Supporting Information Available: Table containing the deformation, interaction, and adsorption energies for the dimeric and monomeric Mo(VI) species. Optimized structures and relative energies for the less stable dimeric Mo(VI) oxide species on (110) γ-alumina, not included in Figure 4, are also presented. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes