

A DFT-study on the acidity of Mo–O–Al-clusters

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Abstract

Supported molybdenum oxide on e.g. alumina is a useful catalyst for metathesis of olefins. However, the presence of acid sites will influence the selectivity of the metathesis reaction, since they may catalyze double bond isomerisation of olefins. The acidity of supported molybdenum oxide on alumina was modelled using neutral clusters. DFT calculations showed that the strength of acidity of the sites decreases and the activation energy for double bond isomerisation increases with a decrease in the formal oxidation state of the molybdenum oxide.

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1. Introduction

Metathesis is of industrial importance for the upgrade of low value olefins to higher value olefins, such as propene or C₉–C₁₂-olefins. A heterogeneous catalyst for this reaction is from an industrial point of view preferred due to the ease of separation of catalyst from the product stream. Metathesis of olefins can be catalyzed by supported molybdenum oxide [1–3] or Co/MoO₃/Al₂O₃ [4]. However, the selectivity of the metathesis reaction can be negatively affected by the double bond isomerisation catalyzed by acid sites typically present in alumina supported molybdenum catalysts [2,5–7].

Acidity is a complex measure, which should however be related to the base of interest. Hence, it is of interest to correlate the strength of the acid sites with the rate of olefin activation, which may lead to double bond isomerisation. The rate of a reaction is dependent on the activation energy, thus information on the structure and stability of the transition state is required.

The molybdenum based metathesis catalyst may be reduced before the metathesis reaction [1,8] or during the metathesis reaction by the hydrocarbon reactants and products [3,9]. Reduction of supported molybdenum will alter its acidic properties [7,10,11] and thus the rate of double bond isomerisation. Hence,

a study into the effect of the acidity of a molybdenum based metathesis catalyst should take into account the variation in the oxidation state of molybdenum.

Kazansky and Senchenya [12] proposed that the surface intermediates of high temperature catalytic conversions of hydrocarbons on acid sites are not simple ionic structures as usually supposed. Instead, the carbenium ionic properties of the hydrocarbon are the characteristics of the transition state. In solids, the solvation in liquids, e.g. water, is replaced by the interaction of the adsorbed carbenium ion with basic surface oxygen of the solid. Therefore, depending on the basicity of the surface oxygen, proton transfer to adsorbed olefins results in the formation of more or less covalent surface alkoxides rather than carbenium ions [13]. Boronat et al. [14] showed using molecular modelling calculations that the formation of a covalent alkoxide for isobutylene depends on the position and local geometry of the Brønsted site.

In this study the acidity of the support as determined by the deprotonation energy is correlated with the activation energy of the alkoxide formation as proposed by van Santen [15]. The formation of secondary alkoxide species is investigated, since the formation of a secondary alkoxide species on acidic sites has a lower activation energy than the formation of a primary alkoxide species [16,17]. Furthermore, DFT was used to gain understanding on the influence of the formal oxidation state of molybdenum oxide on the acidic characteristics of Mo–Al-clusters.

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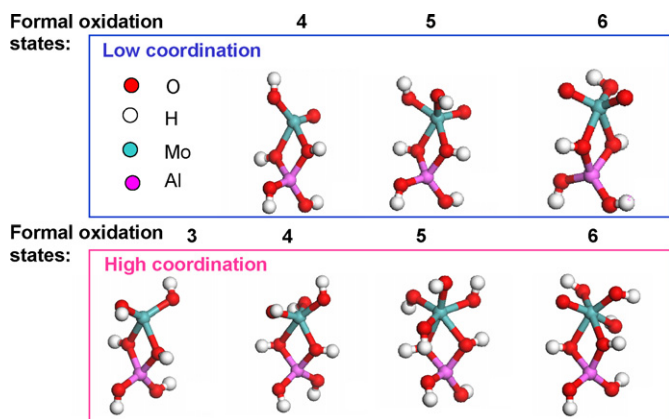


Fig. 1. Neutral Mo–O–Al-clusters with different formal oxidation states for Mo.

2. Methodology

The calculations were done employing DFT-GGA (general-gradient approximation) implemented within the DMol³ code [18,19] in the program Materials Studio (Accelrys Inc.). All electrons were included in the calculations. A double numerical base set with d-functions (DND) was employed. Geometry optimization calculations were done with auto-multiplicity, which was shown to give the minimum energy. All calculations were performed in the gaseous phase using the GGA-BLYP functional.

Stable intermediates were characterized as local minima by ensuring the absence of imaginary frequencies in the vibrational analysis, which also enabled correction of the electronic energies for zero-point vibrations. The energy convergence tolerance was set to 2.0×10^{-5} Ha, the basis set cut-off radius was 5.5 Å, the maximum force 0.004 Ha/Å, and the maximum displacement 0.005 Å. The minimum electronic energies, E_{elec} , are static energies at 0 K in vacuum.

The deprotonation energy of Mo–O–Al-clusters and heat of adsorption of propene on these clusters were determined. The structures of these clusters were based on the structure of a low coordination Mo–O–Al-cluster with Mo in the formal oxidation state of +6 as suggested by Ramani et al. [20] (see Fig. 1). The formal oxidation state of the molybdenum in the neutral Mo–O–Al-cluster was changed by varying the number of ligands on the molybdenum. The formal oxidation state of molybdenum in the neutral Mo–O–Al-clusters was calculated by assigning a formal charge of -2 to =O-ligands and -1 to OH-ligands. These clusters may mimic the behaviour of molybdenum oxide supported on γ -Al₂O₃. The calculated values for the deprotonation energy, the heat of adsorption propene will not accurately reflect the values for the deprotonation energy and the heat of adsorption of propene on actual surfaces, but the trends as a function of the formal oxidation state are thought to be similar to those obtained on heterogeneous surfaces.

The acidity of the neutral Mo–O–Al-clusters was characterised by the deprotonation energy, as determined by removal of a proton from a hydroxyl group solely attached to molybdenum. This should therefore represent the acidity of a molybdenum–oxygen species on an alumina surface. The depro-

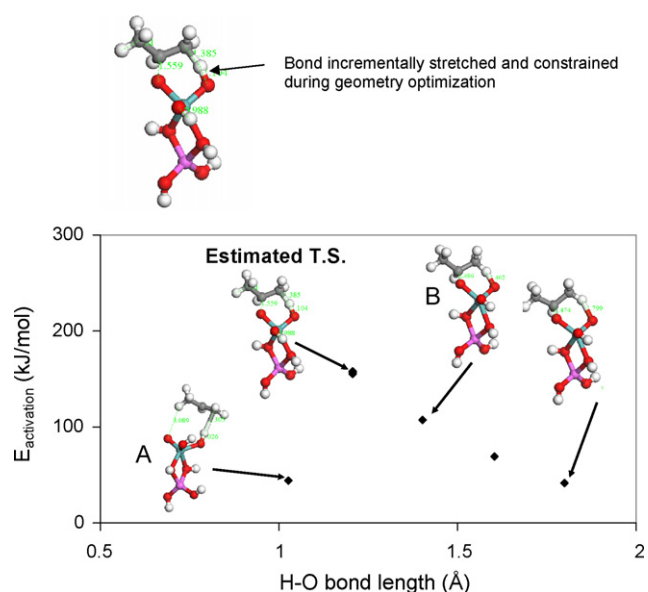


Fig. 2. Estimation of activation energy by incremental stretching of H–O bond lengths restricting the interaction between propoxide group and bridging hydroxyl groups during geometry optimizations.

tonation energy is then calculated by

$$\Delta E_{\text{rxn}}^{0\text{K}} = (E + \text{ZPE})_{\text{anion}} - (E + \text{ZPE})_{\text{neutral}} \quad (1)$$

The adsorption energy of propene was calculated by optimizing the propoxide cluster. Propene adsorption on these clusters involved hydrogen transfer resulting in a bond between the secondary carbon atom and an oxygen atom solely attached to the molybdenum. The movement of the propoxide group was restricted in the geometry optimization step to minimize the interaction with bridging hydroxyl-groups between Mo and Al to obtain a better resemblance of the expected interaction of an adsorbed olefin on a heterogeneous surface. The heat of adsorption of propene was calculated by

$$\Delta E_{\text{rxn}}^{0\text{K}} = (E + \text{ZPE})_{\text{propoxide}} - (E + \text{ZPE})_{\text{propene}} - (E + \text{ZPE})_{\text{cluster}} \quad (2)$$

The activation energy for the transformation of a secondary propoxide species to physisorbed propene was investigated, since this seems to be the most demanding step in the double bond isomerization of olefins over acids [16]. The activation energy for double bond isomerisation was estimated by finding the transition state. A bond was created between the primary carbon atom in adsorbed propene and the hydrogen (H(acid)) from a hydroxyl group solely attached to molybdenum. The H(acid)–O bond was incrementally stretched (see Fig. 2). For each incremental change in the O–H bond length, the constrained structures were optimised and the energy was calculated. The estimated activation energy is taken as the obtained highest difference between the calculated energy for the cluster with the stretched H(acid)–O bond and the energy of the stable alkoxide species.

Table 1

Energy difference between neutral, high coordination Mo–O–Al-clusters and neutral, low coordination Mo–O–Al-clusters at 0 K (energy difference defined as $\Delta E = E_{\text{high coordination cluster}} - (E_{\text{low coordination cluster}} + E_{\text{H}_2\text{O}})$)

Formal oxidation state	ΔE (kJ/mol)
6+	52
5+	36
4+	4

Structures with a short and a longer H(acid)-bond and a shorter H(acid)-bond than the estimated transition state species were used as starting structures to perform a transition state search (e.g. structures A and B in Fig. 2). The transition state search resulted in clusters with 2–4 imaginary frequencies. The imaginary frequency that corresponds to the reaction coordinate was used to search for a maximum in the reaction coordinate. The energy was minimised in the other directions. The transition state optimisation yielded a transition state with only one imaginary frequency indicating that true transition states were found.

3. Results and discussion

3.1. Characterization of clusters

The proposed, neutral Mo–O–Al-clusters (see Fig. 1) were based on a proposed low coordination structure with molybdenum in the formal oxidation state +6 [20]. The low coordination cluster can be transformed into a high coordination cluster by reaction with water. Thus, the transformation of low coordination clusters into high coordination clusters can be expected to depend on the relative stability of the clusters at a given temperature and the water partial pressure. Table 1 shows the relative stability of the high coordination cluster relative to the low coordination cluster at 0 K. Tokarz-Sobieraj et al. [21] reported that the recombination of surface hydroxyl groups yielding water on MoO₃ was energetically favourable with a difference in stability between a hydroxylated surface and a dehydroxylated surface starting from a terminal oxygen O(1) site of 54.9 kJ/mol, which compares favourably with the value reported here for the Mo–O–Al-cluster with molybdenum in the formal oxidation state of +6 of 52 kJ/mol. The low coordination Mo–O–Al-cluster is thermodynamically favoured in comparison to the high coordination Mo–O–Al-cluster. The high coordination state becomes even less favoured with an increase in the formal oxidation state of molybdenum in the cluster. The Gibbs free energy for the transformation of a low coordination Mo–O–Al-cluster into the high coordination Mo–O–Al-clusters increases with an increase in the temperature indicating the high coordination Mo–O–Al-clusters becomes even less thermodynamically unfavourable at higher temperatures. Water is typically avoided in molybdenum oxide catalyzed metathesis [4], since it poisons the catalyst. It can thus be deduced from our calculations that the low coordination state will be favoured, if the presence of significant amounts of water is avoided.

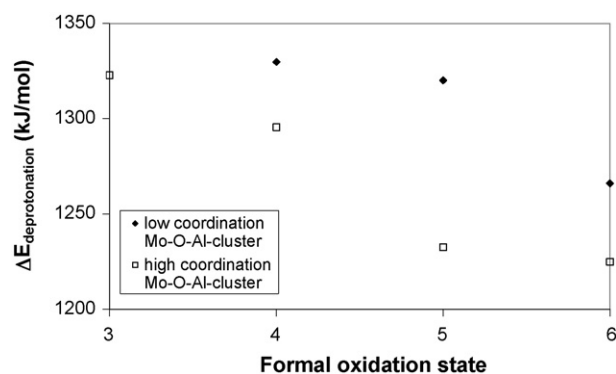


Fig. 3. Deprotonation energy of neutral, Mo–O–Al-clusters for the removal of a proton from a hydroxyl group solely attached to molybdenum as a function of the formal oxidation state of molybdenum in the cluster.

3.2. Deprotonation energy of Mo–O–Al-clusters

Acidity of the neutral Mo–O–Al-clusters was characterised using the deprotonation energy for the removal of a proton from a hydroxyl group solely attached to molybdenum as a function of the formal oxidation state of molybdenum (see Fig. 3). These clusters were used to estimate the acidity of surface molybdenum supported on alumina. The deprotonation energy increases with decreasing formal oxidation state indicating a decrease in the strength of the acid site, since it becomes energetically more costly to remove a proton. It may therefore be concluded that the strength of the acid sites on the Mo–O–Al-cluster decreases with a decrease in the formal oxidation state of the molybdenum. This concurs with the reported decrease in acidity with increasing degree of reduction [10,11,22] (after an initial increase due to generation of additional hydroxyl groups [21]). The deprotonation energy for high coordination Mo–O–Al-clusters is consistently lower than the deprotonation energy for the low coordination Mo–O–Al-cluster. This might be attributed to the larger number of oxygen atoms that can delocalise the resulting negative charge on the Mo–O–Al-cluster.

Based on deprotonation energy calculations neutral Mo–O–Al-clusters are more acidic than Al–O–Al-clusters with both aluminium atoms having a tetrahedral coordination, for which a deprotonation energy of 1499 kJ/mol was obtained. Handzlik and Ogonowski [23] obtained a deprotonation energy for an identical Al–O–Al-cluster of 1390 kJ/mol and deprotonation energies for larger alumina clusters containing 9 and 24 aluminium atoms in octahedral and tetrahedral coordination of between 1200 and 1470 kJ/mol. A deprotonation energy of 1327 kJ/mol was reported for an Al(OH)₃·H₂O cluster [15].

Neutral Mo–O–Al-clusters are less acidic than neutral Si–O–Al-clusters. A deprotonation energy of 1228 kJ/mol was calculated for the removal of a proton from the hydroxyl group between the Si and Al atoms in a Si–O–Al-cluster. A similar deprotonation energy of 1264 J/mol was obtained for a Si–O–Al–O–Si cluster [15]. The deprotonation energy depends on the geometric arrangement of the acid site and deprotonation energies between 1175 and 1181 kJ/mol in chabazite [24] and between 1290 and 1378 kJ/mol in faujasite [25] has been reported.

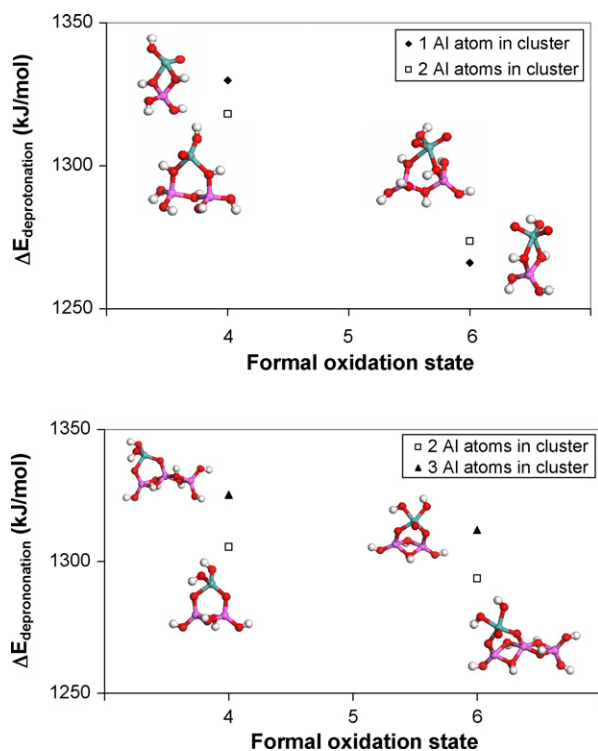


Fig. 4. Influence of number of aluminium atoms in the neutral Mo–O–Al-cluster on the deprotonation energy. Top: clusters proposed by Ramani et al. [20]. Bottom: clusters proposed by Handzlik [26].

It can thus be concluded that the acidity follows the order: zeolites (Si–Al–O-clusters) > Mo–Al–O-clusters \sim Al(OH)₃·H₂O clusters > Al–Al–O-clusters.

A monomeric molybdenum species on an alumina support is in close contact with more than one aluminium atom as presented in the Mo–O–Al-clusters shown above. A limited number of clusters were created with more than one aluminium atom based on clusters proposed by Ramani et al. [20] and Handzlik [26] to verify whether the trend of the deprotonation energy as a function of the formal oxidation of the transition metal remains the same with an increase in the number of aluminium atoms in the cluster (see Fig. 4). The deprotonation energy for clusters with molybdenum in the formal oxidation state of +6 was always lower than that for clusters with molybdenum in the formal oxidation state +4. This was independent of the number of aluminium atoms in the neutral Mo–O–Al-cluster and the configuration of the aluminium atoms within the cluster. Hence, clusters containing only one aluminium atom can be used to study the acidity characteristics as a function of the formal oxidation state. In general, the deprotonation energy increases with an increase in the number of aluminium atoms in the cluster (with exception of the cluster with molybdenum in the formal oxidation state of +4 containing a single aluminium atom). The change in the deprotonation energy can be related to the electrostatic stabilisation of the resulting anion.

Neutral Mo–O–Al-clusters may represent monomeric molybdenum species supported on alumina. These are typically present at low molybdenum loading, whereas polymeric molybdenum species will be present at high molybdenum load-

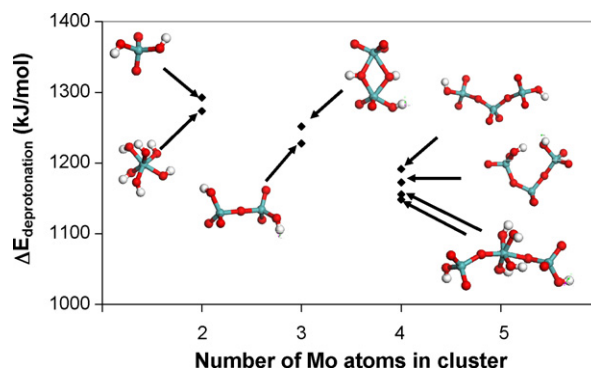


Fig. 5. Influence of number of molybdenum atoms in a neutral Mo_xO_y-cluster and its geometry on the deprotonation energy.

ings increase [27–29]. The presence of polymeric molybdenum species will alter the acidic properties of the material. Hence, the deprotonation energy of (Mo–O)_x-clusters was determined with molybdenum in the formal oxidation state of +6 (see Fig. 5). The deprotonation energy decreases with an increase in the number of molybdenum atoms in the +6 formal oxidation state in a cluster without aluminium, which is attributed to improved delocalisation of the remaining negative charge after deprotonation. Furthermore, the calculated deprotonation energy is dependent on the chosen structure and the position of the removed proton. Li and Dixon [30] obtained a lower deprotonation energy between 1093 and 1143 kJ/mol (depending on the chosen calculation parameters) for Mo₆O₁₉H₂ indicating again the importance of delocalization of the resulting negative charge over a larger entity.

3.3. Adsorption of propene

The adsorption of propene on a neutral Mo–O–Al-cluster may yield a prop-2-oxide intermediate on the cluster. The heat of adsorption of propene yielding the prop-2-oxide on the cluster was modelled with constrained configurations representing feasible intermediates upon adsorption on heterogeneous surfaces. Table 2 shows the heat of adsorption of propene as a function of the formal oxidation state of molybdenum in the cluster and its coordination state. The heat of adsorption of propene is neither a strong function of the formal oxidation state of molybdenum nor of the coordination state of the molybdenum in the cluster.

3.4. Olefin reactions over neutral Mo–O–Al-clusters

The presence of acid sites in supported molybdenum on alumina can be expected. The selectivity in metathesis of olefins

Table 2
Heat of adsorption of propene (kJ/mol) yielding 2-propoxide species on a neutral, Mo–O–Al-cluster as a function of the formal oxidation state of molybdenum in the cluster

	Formal oxidation state of molybdenum			
	6+	5+	4+	3+
High coordination	–43.4	–49.4	–54.8	–49
Low coordination	–50.8	–52.5	–50.0	n/a

can be altered, if side reactions, such as double bond isomerisation can take place. Hence, the extent to which these reactions may take place is of interest.

The interaction of an olefin with a high coordination Mo–O–Al-cluster may lead to the formation of an alcohol and the cluster in the low coordination state, analogue to the dehydroxylation of high coordination clusters yielding water and the corresponding low coordination cluster (see Table 1). This reaction is feasible for molybdenum in the formal oxidation state of +4, +5 and +6 but is more favoured with molybdenum in a higher formal oxidation state.

Double bond isomerisation can occur, if the adsorbed olefin is present as an alkoxide or an alkyl species. Neutral, high coordination Mo–O–Al-clusters with molybdenum formal oxidation states of +5, +4 and +3, do not contain basic oxygen atoms. Thus, the formation of an alkoxide species in a concerted mechanism is not possible for these clusters. The alternative pathway to form an alkoxide species on these high coordination clusters would involve ions and result in high activation energies. Hence, double bond isomerisation via an alkoxide species over a high coordination Mo–O–Al-cluster is kinetically inhibited. Alkoxide species can be formed with low coordination Mo–O–Al-clusters. The reversal of the reaction pathway may lead to the formation of double bond isomers. The cleavage of the C–O bond of the alkoxide, to obtain the desorbed olefin, is the step requiring the highest activation energy [16]. The rate of reaction for this particular step should therefore be an appropriate measure for comparison of the influence on the formal oxidation state on the rate of double bond isomerisation rather than the heat of adsorption of an olefin. The activation energy was determined by incrementally increasing the H(acid)–O-bond, which in the optimised structure lead to a decrease in the C–O bond length (see Fig. 6). With increasing H–O bond length, the energy passes a maximum. The position of the maximum is found at different H–O bond lengths for the various formal oxidation states.

The maximum energy observed corresponds to the estimated activation energy for olefin desorption, which was the lowest for the cluster with molybdenum in the highest formal oxidation state. The maximum energy is not obtained at the same H–O bond length for the various formal oxidation states. An alternative way of looking at the change is to view the change in the relative energy as a function of the change in the C–O bond length relative to the C–O bond length in the stable propoxide–Mo–O–Al-cluster. An increase in the C–O bond length of up to 10% leads to an increase in the relative energy. A further increase in the C–O-bond length leads to a decrease in the energy. The Mulliken charge on the protonated organic moiety (C₃H₇) of the transition states varied between +0.55 and +0.60 indicating significant proton transfer in the transition state structure.

The activation energy may be correlated to the deprotonation energy [15]. This correlation is only valid when the reaction pathway is the same for all Mo–O–Al-clusters and Mo–O–Mo-cluster (Al atom replaced with a Mo atom). The Mo–O–Al-cluster and Mo–O–Mo-cluster had similar deprotonation and activation energies. The optimised activation energy correlates with the deprotonation energy when reaction proceeds over the

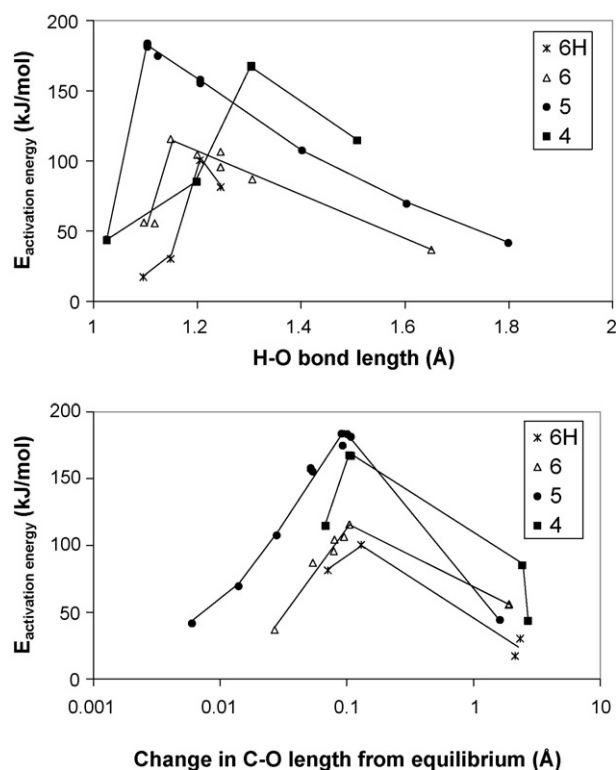


Fig. 6. Change in the energy of the cluster relative to the energy of the stable propoxide–Mo–O–Al-cluster upon stretching the H–O bond length (6H: high coordination cluster; 4–6 low coordination clusters). Top: change in energy as a function of the H–O bond length. Bottom: change in energy as a function of the change in the C–O bond length from its value in the equilibrium propoxide cluster.

alkoxide (see Fig. 7). Thus, the rate of double bond isomerisation may thus be correlated to the strength of the acid site, if the reaction proceeds via an alkoxide intermediate.

An alternative reaction pathway for double bond isomerisation was considered, i.e. via the formation of an alkyl species. The reaction cannot proceed, if the molybdenum in the Mo–O–Al-cluster has more than four ligands. Hence, only the reaction of an alkyl species over a low coordination Mo–O–Al-cluster with molybdenum in the formal oxidation state of +4 and over a high coordination Mo–O–Al-cluster with molybdenum in the formal oxidation state of +3 was considered. The

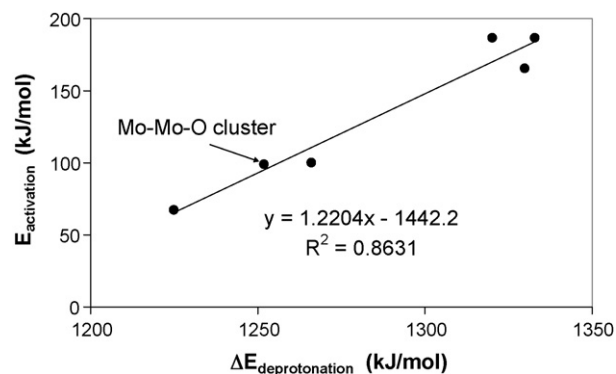


Fig. 7. Correlation between the deprotonation energy and the activation energy (optimised) for olefin desorption.

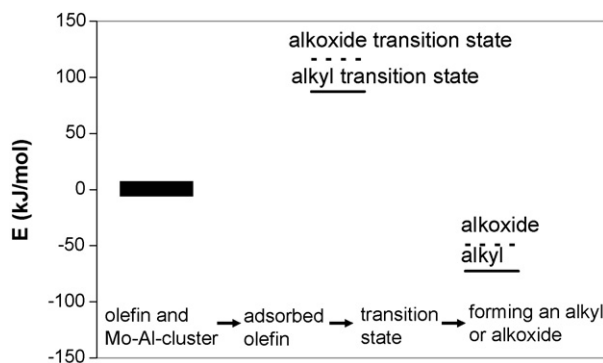


Fig. 8. Reaction pathway analysis for the adsorption/desorption of an olefin yielding an alkyl or an alkoxide species on the cluster over a neutral, low coordination Mo–O–Al-cluster with molybdenum in the +4 formal oxidation state.

Mo–O–Al-cluster with molybdenum in the +4 formal oxidation state containing the alkyl species are more stable than the cluster containing the alkoxide species (see Fig. 8), i.e. the adsorption of an olefin on these clusters will preferentially lead to the formation of an alkyl species. The obtained activation energy for the desorption pathway of the alkyl species is similar to that of the alkoxide species on the low coordination Mo–O–Al-cluster with molybdenum in the formal oxidation state of +4.

The neutral, high coordination Mo–O–Al-cluster with molybdenum in the formal oxidation state of +3 can catalyse double bond isomerisation, via the formation of an alkyl, in the absence of a basic oxygen. An activation energy of 197 kJ/mol was obtained to cleave the Mo–C bond to obtain the desorbed olefin. The high activation energy indicates that the reaction pathway is still kinetically inhibited.

4. Conclusions

The neutral clusters containing molybdenum have a higher strength of acidity than Al–O–Al-cluster. This may indicate that molybdenum modified alumina supports may have significantly stronger acid sites than alumina. Neutral, high coordination Mo–O–Al-clusters have a lower deprotonation energy, and thus higher acidity, than neutral, low coordination Mo–O–Al-clusters. However, high coordination Mo–O–Al-clusters are less likely to catalyze double bond isomerisation, since the reaction pathway for double bond isomerisation involves steps with high energy barriers (for the formation of an alkoxide intermediate or the desorption of an alkyl species).

An increase in the number of molybdenum atoms in a cluster increases the strength on the acid sites. Thus, an increase in the strength of the acid sites may be expected with an increase in the molybdenum loading in the catalysts if the oxidation state remains identical. An increase in the double bond isomerisation with an increase in the molybdenum loading in the catalyst during the metathesis reaction can thus be expected and a high molybdenum loading may not be advantageous for the metathesis selectivity.

The strength of the acid sites decreases with a decrease in the formal oxidation state of the molybdenum in the neutral, Mo–O–Al-clusters. It is estimated that the activation energy for double bond isomerisation increases with a decrease in the formal oxidation state of the molybdenum in the Mo–O–Al-cluster. Therefore, pre-reducing a metathesis catalyst may be beneficial to decrease the rate of double bond isomerisation.

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