The Reactivity of All-Metal Aromatic Complexes: A Theoretical Investigation on the Methane Activation Reaction

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The recent finding of all-metal aromaticity enlightens us to explore the reactivity of all-metal aromatic complexes. The methane activation reaction was chosen for this purpose. The whole catalysis process of all-metal aromatics was investigated by theoretical calculation. The results reveal that the reaction barriers with all-metal aromatic complexes are far lower than that without any catalysts. All-metal aromatic complexes are predicted to have potential to be used as catalysts for the first time.

1. Introduction

Recently, the aromaticity concept has been expanded into all-metal complexes by the surprising finding of aluminide clusters Al_4^{2-}.[1] Since then, a series of metallic clusters (Ga_4^{2-}, In_4^{2-},[2] XAl_3^-,[3] Hg_4^{6-},[4] and so on) with aromaticity have been reported. The properties of these all-metal aromatic complexes have also been investigated widely, such as the geometric structure,[1,5] molecular orbitals,[1,6] electron density,[7] resonance energy,[2,8] ring current, and magnetism.[5,9] All-metal aromatic compounds have also been used to build other molecules or clusters with special characteristics.[4,10] However, until now, no papers have considered the catalytic ability of such special aromatic complexes. Investigating the reactivity of all-metal aromatic complexes is thought to be challenging work in the future.[1b]

There is abundant methane in nature, and the need for the oxides of methane is increasing constantly. How to activate methane to corresponding oxides such as methanol is a useful and challenging research subject in modern chemistry. The high dissociation energy (105.0 kcal/mol[11]) of the C−H bond calls for effective catalysts. Many molecules with excellent active ability for methane have been reported, such as cytochrome P450 (rate-limiting barrier of 22−28 kcal/mol),[12] methane monooxygenase hydroxylase component (MMOH) (rate-limiting barrier of 18−25 kcal/mol),[13] hydrated iron(IV) oxo species (rate-limiting barrier of 23 kcal/mol),[14] MO^+(M = Fe, Mn, Cu, Co; step-limiting barrier of 25−55 kcal/mol),[15] MO (rate-limiting barrier of 45−70 kcal/mol),[16] chromyl chloride,[17] bipyrimidine−$PtCl_2$ or $PtCl_2(NH_3)_2$ (rate-limiting barrier of 34−44 kcal/mol),[18] N-heterocyclic carbene Pd(II) complexes,[19] and gold complexes.[20] Among these catalysts, only cytochrome P450 and MMOH convert methane to the corresponding oxide by the adsorbed oxygen molecules, and this process is highly effective because the catalyst is easily cycled.[21]

In our former works on all-metal aromatic complexes, we had investigated the interactions between all-metal aromatic systems and some small molecules.[22] The electron clouds of

these small molecules are greatly changed by the all-metal aromatic systems.[22a,d] Enlightened by these ideas, we guessed that all-metal aromatic complexes could have potential catalyzing probability in some reactions. The present paper will mainly explore the reactivity of all-metal aromatic complexes by theoretical investigation of the methane activation reaction, which addresses two challenges of current chemistry research: the reactivity of all-metal aromatic complexes and the activation of methane.

2. Computational Methods

Previous studies on all-metal aromatic systems,[23a,b] oxides of metal clusters[12c,15a,16] and other methane oxidation reactions[12a,b,13b,c,15a,16] using the B3LYP method obtained satisfying results. For some of these systems, calculations at the B3LYP method are even sufficiently accurate compared with these results obtained at CCSD(T) and QCISD methods.[8,23c,d] Hence, for this work, all the geometries were fully optimized with the *Gaussian 03* program[24] at the B3LYP/6-311++G** level of theory. Energy calculations as well as zero-point energy (ZPE) corrections have been performed at the same level of theory. All energies reported in this work are corrected by ZPE.

3. Results and Discussions

Two all-metal aromatic complexes, Al_4^{2-} and Al_4Ca, were chosen for our purposes. It has been known that the isolated Al_4^{2-} is not an electronically stable species,[1,2] whereas the neutral all-metal aromatic complexes such Al_4Li_2 and Al_4Ca are electronically stable.[1,2,22] Hence, we mainly investigated the reactivity of Al_4Ca. Our previous study has shown that, on the surface of Al_4Ca, the most energetically favorable absorption orientation of O_2 is that from the upside of the Al_4 plane, and such absorption brings the most stable oxygenous complex Al_4-CaO_2 (Figure 1) among all these isomers with one O_2 on the surface of Al_4Ca.[22d] Hence, Al_4CaO_2 was chosen for this study.

A total of four reaction pathways with catalyst as well as one pathway without catalyst were investigated in this work (Figure 1). Generally, the oxidation of methane includes two

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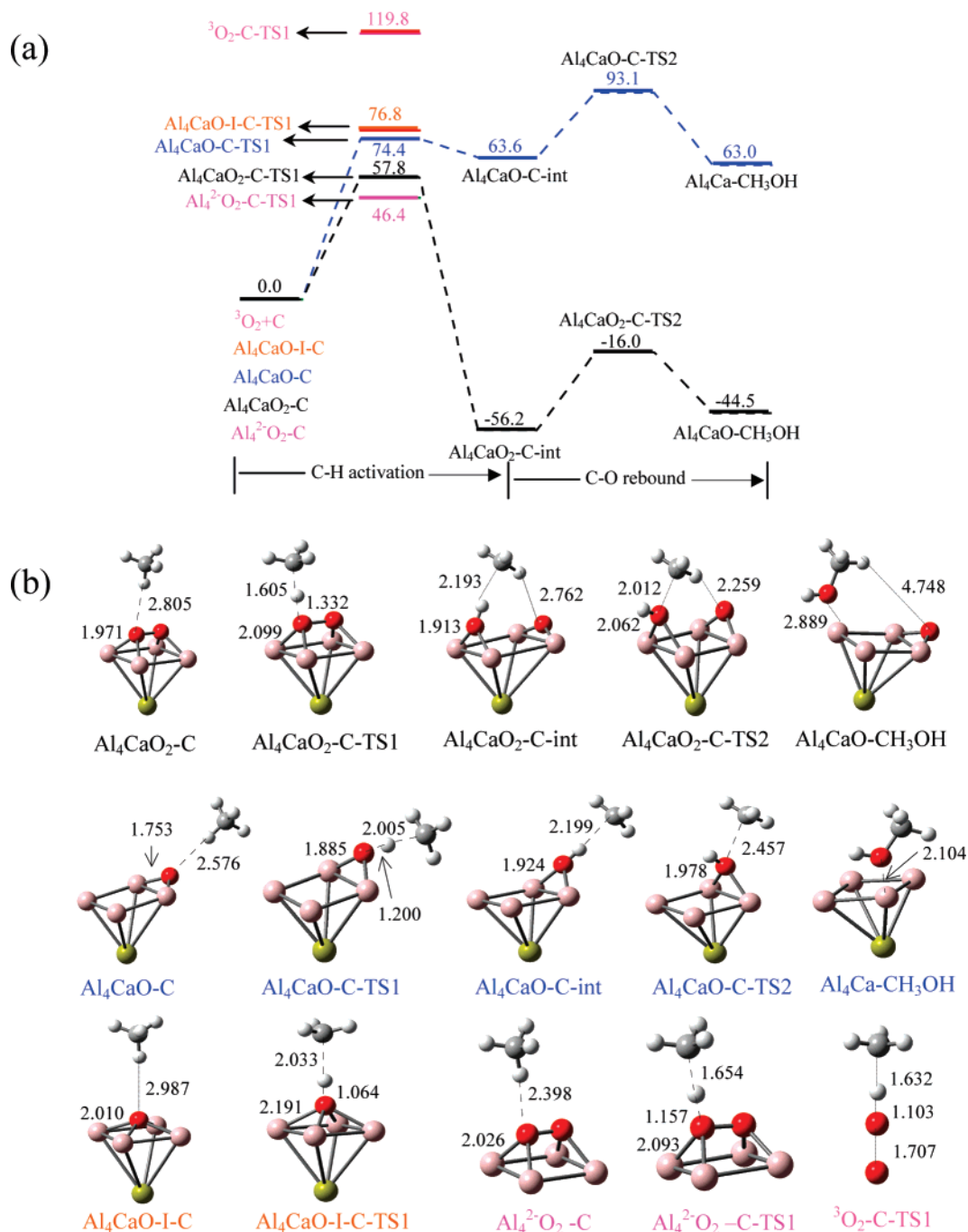
Figure 1. (a) Relative energies (free energies in kcal/mol) of the reaction pathways of methane oxidation with all-metal aromatic complexes and without any catalyst. (b) The corresponding optimized structures in the reactions. The values shown in the structure mean bond length in Å.

steps: C−H activation and C−O rebound.[12a,b] Such two-step processes of methane oxidation activated by Al_4CaO_2 are investigated. Furthermore, the barrier of C−H activation is higher than that of C−O rebound.[12a,b] Hence, for some of the compared reaction pathways, only the C−H activation step is investigated.

Unlike the activation processes with Cytochrome P450 as catalyst, after O_2 binds with the catalyst, the reduction step and the protonation step must be undergone to make the oxygen active.[21] As a result, the first oxygen atom of O_2 is converted into H_2O, and the second oxygen atom is used as an oxidant for the oxidation reaction.[21] When an all-metal aromatic complex is used as catalyst, it is found that the first oxygen atom of O_2 is more active than the second one, and it is easier to utilize the first oxygen atom of O_2 as the oxidant for the oxidation of methane (Figure 1).

As we know, the dissociation energy of the C−H bond is very high (105.0 kcal/mol[11]). The calculated results of the methane oxidation without any catalyst indicate that there exists a very high barrier (119.8 kcal/mol) in the C−H activation step. This is mainly because the energy gap between the highest occupied molecular orbitals (HOMO) of O_2 and the lowest unoccupied molecular orbitals (LUMO) of CH_4 is very large (199.5 kcal/mol) and the effective overlap between these orbits is almost zero (Figure 2).

The electron rearrangement of O_2 induced by its interaction with all-metal aromatic complexes increases the effective overlap between the LUMO of CH_4 and the HOMO of $Al_4{}^{2-}O_2$ or Al_4CaO_2 greatly. Furthermore, the orbital energy gaps are reduced by 107.0 kcal/mol for Al_4CaO_2 and 120.8 kcal/mol for $Al_4{}^{2-}O_2$. As a result, Al_4Ca and $Al_4{}^{2-}$ show great catalytic ability for the activation of CH_4. The barrier of C−H activation
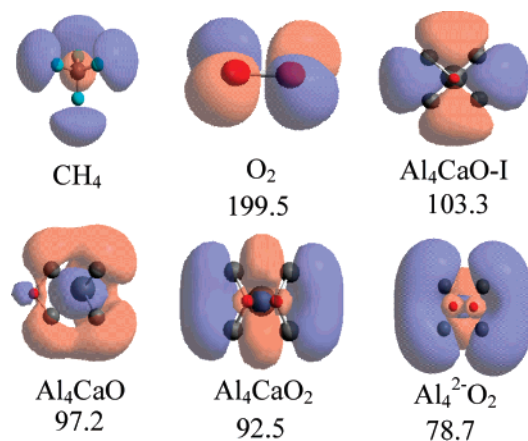
Figure 2. The lowest unoccupied molecular orbitals (LUMO) of CH_4 and the highest occupied molecular orbitals (HOMO) of O_2, Al_4CaO^--I, Al_4CaO, Al_4CaO_2, and $Al_4^{2-}O_2$. The values shown mean the energy gaps (in kcal/mol) between the LUMO of CH_4 and the HOMO of O_2 or all-metal aromatic systems.
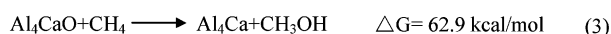
is reduced by 62.0 kcal/mol when Al_4Ca is used as catalyst and reduced by 73.4 kcal/mol when Al_4^{2-} is used as catalyst.

As we known, Al_4^{2-} is not an electronically stable species, whereas Al_4Ca is.[1,2,22] Hence, though Al_4^{2-} shows better catalytic ability than Al_4Ca, for the oxidation process with Al_4^{2-} as catalyst, only the rate-limiting step is investigated. A complete catalytic process of Al_4Ca was investigated. The transition state $Al_4CaO_2-C-TS1$ possesses an imaginary frequency (1293i cm^{-1}) assigned to the single proton transfer from CH_4 to Al_4CaO_2, and the structure of this hydrogen abstraction transition state corresponds to an almost collinear arrangement of the O−H−C bonds. In comparison with what is observed in the catalytic process of Cytochrome P450, the O−H bonds in $Al_4CaO_2-C-TS1$ are about 0.2 Å longer.[12a,b] $Al_4CaO_2-C-TS1$ leads to an intermediate $Al_4CaO_2-C-int$, where a methyl points to the hydroxyl group, analogous to the finding of Shaik et al. for CH_4 hydroxylation by Cytochrome P450[12a,b] and Basch et al. for CH_4 hydroxylation by a model of the MMOH enzyme.[13c] Unlike what Cytochrome P450 does, for which the transition process from the reactant to the first intermediate is energetically unfavorable,[12a,b] the corresponding catalytic process of Al_4CaO_2 is highly exothermic.

Following the C−H activation, a process named C−O rebound, similar to that of Cytochrome P450, happens. In this process, a proton rotation process takes place on the hydroxyl group, and the methyl migrates toward the oxygen atom of the hydroxyl group at the same time. However, the barrier of C−O rebound with Al_4Ca as catalyst is higher than that with Cytochrome P450 or MMOH as catalyst. Anyway, the barrier of C−O rebound is lower than that of C−H activation for Al_4Ca, Cytochrome P450, and MMOH. The C−O rebound process brings the final product CH_3OH that first exists as part of the cluster $Al_4CaO-CH_3OH$ and then may leave the cluster by adsorbing a little heat (about 1.5 kcal/mol). The whole energy change from Al_4CaO_2-C to $Al_4CaO-CH_3OH$ is −44.6 kcal/mol (Figure 1), which is much closer to the process catalyzed by Cytochrome P450 (−42.4 kcal/mol). The difference between these two energy changes is a result of the difference in the binding forms of the reactants and the products between Al_4Ca and Cytochrome P450.

Al_4CaO is generated as another product of the reaction between CH_4 and Al_4CaO_2. It may also react with CH_4 via a process of C−H activation and C−O rebound. Furthermore, the barrier of C−H activation step with Al_4CaO is 45.4 kcal/mol

SCHEME 1: The Gibbs Free Energy Changes in the Catalytic Processes

$Al_4Ca+O_2 \longrightarrow Al_4CaO_2$	$\triangle G$= -59.7 kcal/mol	(1)
$Al_4CaO_2+CH_4 \longrightarrow Al_4CaO+CH_3OH$	$\triangle G$= -44.6 kcal/mol	(2)
$Al_4CaO+CH_4 \longrightarrow Al_4Ca+CH_3OH$	$\triangle G$= 62.9 kcal/mol	(3)
or $Al_4CaO+H\cdot \longrightarrow Al_4CaOH\cdot$	$\triangle G$= -33.4 kcal/mol	(3')
$Al_4CaOH\cdot+H\cdot \longrightarrow Al_4Ca+H_2O$	$\triangle G$= -25.3 kcal/mol	(4')

lower than that without any catalyst. However, though the difference of the HOMO−LUMO energy gaps between Al_4CaO_2 and Al_4CaO are small (4.7 kcal/mol), compared with the reaction process with Al_4CaO_2, the barrier of the C−H activation with Al_4CaO is 16.6 kcal/mol higher. This is mainly because the effective orbital overlap between the HOMO of Al_4CaO and the LUMO of CH_4 is much small than that between Al_4CaO_2 and CH_4. Hence, to utilize the second oxygen atom and recycle the catalyst Al_4Ca, a higher reaction temperature may be necessary. Alternatively, if the high-temperature reaction is not allowed, a process in which two hydrogen atoms react with the second oxygen atom and lose a water molecule may be a favorable way (Scheme 1).

4. Conclusions

In conclusion, the catalytic ability of all-metal aromatic complexes was investigated for the first time. Al_4Ca and Al_4^{2-} were used as catalysts to activate the oxidation process from methane to methanol. The barrier of the rate-limiting step (C−H activation step) catalyzed by Al_4Ca is 57.8 kcal/mol and that catalyzed by Al_4^{2-} is 46.4 kcal/mol, which is 62.0 and 73.4 kcal/mol lower than the process without any catalyst. This value is lower than that of some efficient inorganic catalyst of methane oxidation, such as Mo_3O_9 (free energy step-limiting barrier of 63.4 kcal/mol),[16a] FeO (step-limiting barrier of 72.6 kcal/mol).[16c] The biggest difference between Al_4Ca and Mo_3O_9/FeO is that Al_4Ca can activate an oxygen molecule directly. To some extent, the catalytic process of an all-metal aromatic complex is similar to that of Cytochrome P450. However, the rate-limiting barrier catalyzed by Al_4Ca and Al_4^{2-} is higher than that catalyzed by Cytochrome P450.

It is worth noting that the present paper mainly focuses on the reaction process between methane and the most stable isomers with the O_2 adsorption on the surface of Al_4Ca. The reactivity of other oxides of Al_4Ca is not considered and needs further research. However, the purpose of this work is not limited to the catalyzing process of Al_4CaO_2 itself. The aim of this work is to provide an incentive for the future development of research on the potential catalytic ability of all-metal aromatic complexes both in theory and in experiment.

Supporting Information Available: The Z-MATRIX of calculated results. This material is available free of charge via the Internet at http://pubs.acs.org.

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