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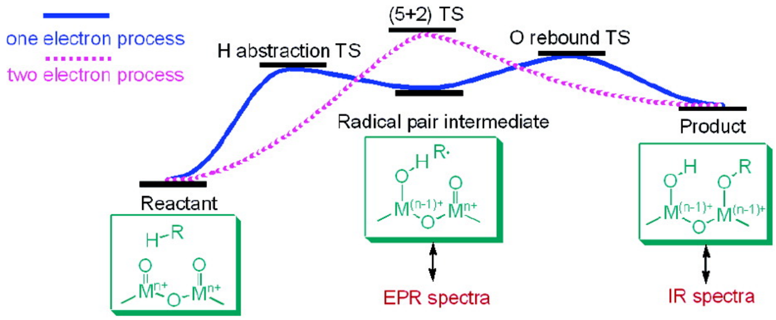

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Mechanisms of Methane Activation and Transformation on Molybdenum Oxide Based Catalysts

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Abstract: We present a comprehensive survey of different C—H activation pathways over various kinds of active sites of terminal oxygens [═O] and bridge oxygens [—O—] by using Mo_3O_9 model systems. This allows us to provide some insights into fundamental issues concerning C—H activation by metal oxo species involved in many heterogeneous, homogeneous, and enzymatic processes. We show that H abstraction is the most feasible reaction pathway for the activation of a C—H bond on molybdenum oxides; and that [═O] is more active than [—O—]. Our calculations also suggest that (2+2) can be an alternative if M═O bond possesses a high polarity, while (5+2) can provide another effective pathway if two M═O bonds are in close proximity. Implications for the related heterogeneous, homogeneous, and enzymatic processes are discussed.

Introduction

Methane is the principal component in natural gas. While abundant in nature, its largest reserves are in remote locations. Exploitation of such resources is impeded by the high cost of gas transportation. An obvious solution is the on-site conversion of methane to methanol or other efficiently transportable liquid material.[1−10] The available conversion methods are indirect (eqs 1,2), involving the production of syn-gas (carbon monoxide and hydrogen) as the first step (eq 1), which is energy intensive and thus uneconomical.[7−11]

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3\ H_2(g) \qquad \Delta G^\circ = +33.9\ \text{kcal mol}^{-1} \quad (1)$$

$$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(l)\Delta G^\circ = -7.0\ \text{kcal mol}^{-1} \quad (2)$$

Developing efficient strategies for the direct conversion of methane to methanol or other liquid fuels or chemicals has far-reaching significance.

Direct conversion of methane to oxygenates such as methanol is a fundamental and practical challenge in modern chemistry. The key issues are (1) to surmount the chemical inertness of methane as demonstrated by the high C−H bond strength (D_e = 104.8 kcal/mol), high ionization potential (12.5 eV), low proton affinity (4.4 eV), and low acidity ($pK_a = 48$) of the molecule and (2) to conquer the propensity for full oxidation in the presence of oxygen driven by thermodynamics.[7−11]

$$CH_4(g) + {}^1/_2\ O_2(g) \rightarrow CH_3OH(l) \qquad \Delta G^\circ = -27.7\ \text{kcal mol}^{-1} \quad (3)$$

$$CH_4(g) + O_2(g) \rightarrow CH_2O(g) + H_2O(l) \qquad \Delta G^\circ = -69.1\ \text{kcal mol}^{-1} \quad (4)$$

$$CH_4(g) + 3/2\ O_2(g) \rightarrow CO(g) + 2\ H_2O(l) \qquad \Delta G^\circ = -134.0\ \text{kcal mol}^{-1} \quad (5)$$

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \qquad \Delta G^\circ = -195.5\ \text{kcal mol}^{-1} \quad (6)$$

Contrasting eqs 3,4 with eqs 5,6, one can therefore view the partial oxidation of methane to the desired oxygenates, rather than to unwanted carbon oxides, as a kinetically controlled problem, where design of an efficient catalytic system of both good activity and good selectivity depends critically on the knowledge of the reaction mechanism.

Although a number of works concerning the mechanisms of alkane oxidations by transition metal oxides were reported, the detailed mechanism of C—H bond activation on these catalysts remains elusive.[10,12−16] Specially, what is the active site on the catalysts: terminal oxygens [═O], bridge oxygens [—O—], or other surface oxygen species? Which process is more favor-

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able: heterolytic cleavage or homolytic cleavage of the C−H bond? Whether the initial oxidation involves two-electron transfer or single-electron transfer? In this contribution, we aim to provide insights into these questions through density functional theory (DFT) calculations.

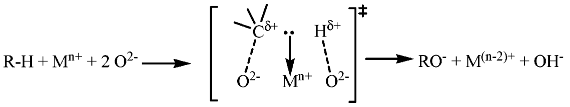
Experimental studies in recent years have yielded some interesting and seemingly contradictory results. Lunsford et al.[17] reported that MoO_3 supported on silica was a catalyst for the selective oxidation of methane to methanol and formaldehyde when N_2O is the oxidant. The O^- ions coordinated to Mo^{VI} at the surfaces were claimed to be the active species, capable of abstracting hydrogen atom from methane. Methyl radicals thus formed reacted rapidly with the surfaces to form methoxide complexes, which would then decompose to HCHO, or react with water to form CH_3OH.[17] Barbaux et al.[18] investigated the properties of surface oxygen species generated by different oxidants on the MoO_x systems. They found that O^- generated by O_2 oxidant led to the formation of CO_x, while O^{2-} generated by N_2O oxidant gave higher selective oxidation to HCHO.[18] Smith and Ozkan examined the partial oxidation of methane to formaldehyde over MoO_3/SiO_2.[19] Emphasis was laid on the surface species formed on the supports and their effects on reactivity and selectivity. They found that low weight loadings led to the formation of silicomolybdic species with terminal Mo=O sites, while higher weight loadings gave rise to the formation of polymolybdate species with Mo−O−Mo bridges, the former having a better selectivity for HCHO than the latter.[19,20] Interestingly, some other experiments seem to support the opposite view, in which it was concluded that the bridge [−O−] was responsible for the selective oxidation, while the terminal [=O] was related to the full oxidation.[21]

Heterolytic C−H bond cleavage (eq 7) is usually considered to happen at an acid−base pair. Therefore, it is not unusual to see activity for C−H activation is correlated with the acidity/basicity of the catalysts.[21,22]

$$R{-}H + M^{n+} + O^{2-} \leftrightarrow R^{-}M^{n+} + OH^{-} \qquad (7)$$

Here, a proton is abstracted by the basic site O^{2-} of the surface, while the remaining methyl anion CH_3^- is linked to the surface cation M^{n+}.[22] The key issues for this process are that there is no change of the valence state of the metal center and that methane is reversibly activated as suggested by the experimental measurement of the extent of CH_4/CD_4 isotopic equilibration.[22] Moro-oka, however, concluded that no such strong acid−base pairs existed on most metal oxide catalysts such that heterolytic cleavage would be less preferable on most metal oxide surfaces.[23] In fact, there is no direct experimental evidence for the heterolytic cleavage of the C−H bond in the rate-determining step on metal oxide catalysts.[23] Reversible activation might be the first step of the irreversible conversion of methane or simply a side reaction.[22]

In the homolytic cleavage mechanism, whether the initial oxidation step involves two-electron (2e) transfer or single-electron (1e) transfer is still an open question. Haber postulated that,[24,25] in the activation of a C−H bond on the oxide surfaces, the proton would attach to the surface oxygen to form hydroxyl (OH), while the alkyl cation would attach to the surface oxygen to make alkoxy (OR). Two electrons originally localized in the C−H bond would be injected into the conductive band of the solid (eq 8).[24]



(8)

IR spectra detected only the presence of hydroxyl and alkoxy groups on the oxide surfaces.[26] This was used as the experimental support to the Haber's mechanism.[24,25]

On the other hand, by means of kinetic and thermochemical analysis, Sinev suggested that a single electron transfer process involving the free radical formation was likely to be the most favorable process.[27] EPR (electron paramagnetic resonance) spectra showed that when *n*-pentane flowed through the tungstated zirconia catalyst, W^{5+} centers and organic radicals formed (eq 9).[28] This experiment has be thought of as lending a direct support to the radical mechanism.[17,28]

$$R{-}H + M^{n+} + O^{2-} \rightarrow R^{\bullet} + M^{(n-1)+} + OH^{-} \qquad (9)$$

In this contribution, we present a comprehensive survey of different C−H activation pathways over various kinds of active sites of terminal [=O] and bridge [−O−]. This allows us to provide some insights into fundamental issues concerning C−H activation by metal oxo species. We show that H abstraction is the most feasible reaction pathway for the activation of a C−H bond on molybdenum oxides and that terminal [=O] is more active than bridge [−O−]. The H abstraction leads to the formation of a radical pair, which can be detected by EPR experiments, while the radical pair undergoes a rapid rebound process, leading to the formation of stable hydroxyl and alkoxy species, detected by the IR experiment. Thus, the seemingly conflicting results between IR and EPR experiments are reconciled in our mechanism.

Mo_3O_9 Model Systems and Computational Details. In this report, we choose Mo_3O_9 as a model compound to provide various kinds of terminal [=O] and bridge [−O−] active sites (Figure 1).

Gas-phase chemistry of metal oxo species has been studied in detail, which has been related to heterogeneous catalytic systems.[29−32] It has been shown that Mo_3O_9 is one of the primary products of MoO_3 vaporization such that $Mo_3O_9^+$ has been generated to study gas-phase reaction with small alcohols by using Fourier transform ion cyclotron resonance (FTICR).[31]

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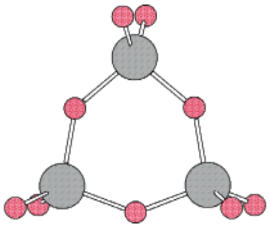

Figure 1. Mo_3O_9 cluster model, which provides various kinds of terminal [=O] and bridge [−O−] active sites such as Mo=O, O=Mo=O, Mo−O−Mo, and O=Mo−O−Mo=O, etc. Key: gray circle, Mo; red circle, O.

Theoretically, Mo_3O_9 fulfills the requirements of stoichiometry principle, neutrality principle, and coordination principle, and it has been concluded as a good model of choice.[33] In fact, Goddard's group has used this model to investigate the (amm)-oxidation mechanism of propylene.[34,35]

Such a model is also consistent with the experimental observation that metal oxide cluster itself can serve as an active component in heterogeneous, homogeneous, and enzymatic catalysis.[36,37] On a series of supported metal oxide catalysts for the oxidative dehydrogenation of low alkanes, Bell, Iglesia, and co-workers found that the active phase was the oligemer of small oxide clusters, rather than crystalline metal oxides.[37−39] Wang et al. reported that small molybdenum oxide clusters encapsulated inside SBA-15 exhibited excellent catalytic performance for the partial oxidation of methane to formaldehyde with oxygen.[40] In homogeneous systems, transition metal oxygen anion clusters have been frequently employed to catalyze the selective oxidation of alkanes.[36] Simple metal oxo compounds and oxometal halides such as CrO_2Cl_2, OsO_4, and MnO_4^- have been applied extensively in organic synthesis to insert oxygen to a C−H bond or an olefin double bond.[41−44] In biological systems, metalloenzymes such as cytochromes P_{450} exhibit high activity and selectivity to catalytically hydroxylate C−H bonds by using high valent, highly reactive $(\text{porphyrin}^{+\bullet})Fe^{IV}{=}O$ units formed in situ during the process of O_2 activation.[44−47] All these reactions bear a common feature in that they are operative on the high valent transition metal oxides with either [=O] or [−O−] as the active sites. Thus we believe that a systematic study of methane activation and transformation on the Mo_3O_9 model system may provide a mechanistic understanding of molybdenum oxide based catalytic systems. These results, after the solvent effects being properly taken into account, may also shed some light on the understanding of the related homogeneous and enzymatic processes.

In this contribution, we considered eight possible mechanisms of the C−H bond activation (Figure 2). We have (2+2), which leads to the carbide or hydride formation. This (2+2) pathway might be considered as C−H bond heterolytic cleavage over an acid−base pair, as no valence change occurs on the metal center. Figure 2 also illustrates the (3+2) and (5+2) pathways. Both of them lead to the formation of hydroxyl and alkoxy directly. These pathways are correlated with homolytic cleavage of a C−H bond of a 2e process. Mo is formally reduced from VI to IV in (3+2); whereas each Mo is formally reduced from VI to V in (5+2). The oxenoid insertion process is also a 2e process, which directly leads to the formation of alcohol. H abstraction is a 1e process, which involves radical formation with the metal center being reduced formally by one unit. We considered H abstraction by both terminal oxygen and bridge oxygen. We also considered H abstraction via anti mode and syn mode (cf. Figure 2).

The quantum calculations were performed using hybrid density functional theory at the level of B3LYP.[48−52] Full geometry optimizations and analytical frequency calculations are performed with basis sets of double-ζ quality (6-31G)[53] for the main group elements. The final energies are calculated with polarization functions being included (6-31G**).[54] Hay's effective core potential[55] (Lanl2dz denoted in Gaussian 98)[56] was used for Mo, which includes the relativistic effects. Energies reported here are enthalpies at the temperature 873 K, which corresponds to the experimental temperature where the activation energy was measured.

Geometry optimizations were also performed for some testing cases with the 6-31G** basis set. No sensible changes were found for the optimized geometries as compared to those from the 6-31G basis set, leading to small variation (generally less than 0.5 kcal/mol) of the relative energy using either geometry (See Table S1 in the supplement material). Full geometry optimizations of the Mo_3O_9 cluster along the reaction pathways are suspect to overestimation of the relaxation effect as compared to the more restricted situation of MoO_3 solids.

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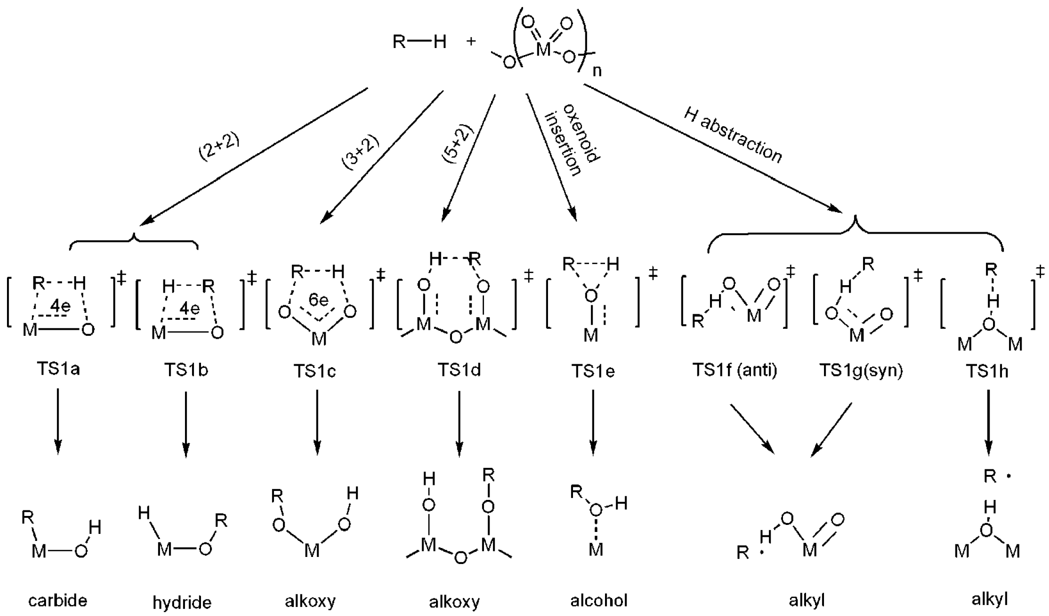

Figure 2. Possible mechanisms for the activation of C−H bond in alkanes.

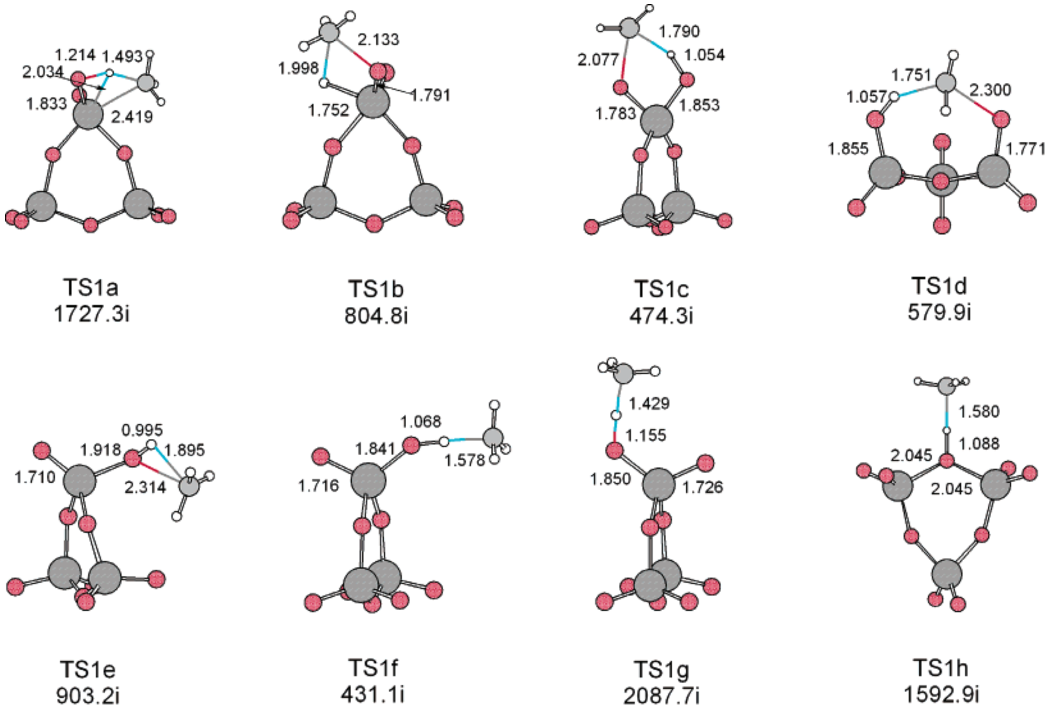

Figure 3. Optimized TS structures for CH_3−H activation by Mo_3O_9 (bond length in Å; imaginary frequency in cm^{-1}).

Testing calculations were performed with a partially optimized Mo_3O_9 geometry (i.e., only the parts directly involved in the C−H bond activation were optimized, while the other parts were kept fixed in the geometry of the free substrate). Our calculations show that the differences are generally less than 1.5 kcal/mol between partially optimized and fully optimized Mo_3O_9 clusters for the estimation of the activation barriers (see Table S2 in the Supporting Information).

Results and Discussions

C−H Bond Activation: Figure 3 and Table 1 summarize the optimized geometry and the calculated energetic of the transition state of each pathway. Altogether, we have located eight transition states. The calculated barriers range from 45.0 to 87.4 kcal/mol. As the initial reactants involved closed-shell singlet Mo_3O_9 and CH_4, we only explore the singlet potential energy surfaces for the C−H activation step, although open-shell singlets have to be considered for the hydrogen abstraction pathways. It is not uncommon in the catalysis community that thermo or photoexcited Mo^{V}−$O^{\bullet}$ was supposed as the active center,[57,58] and it is well-documented in the gas-phase ion chemistry that two states of different multiplicities determine the minimum-energy pathway of a reaction,[32] we find here that triplet Mo_3O_9 lies 60.4 kcal/mol above. Thus we do not expect

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Table 1. Calculated Energetics for CH_4 Activation by Mo_3O_9 (873 K)

				TS			product		
pathway	activation mode	active site	attribution of reaction	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol/K)	$\Delta G^{\ddagger}$ (kcal/mol)	ΔH_r (kcal/mol)	ΔS_r (cal/mol/K)	ΔG_r (kcal/mol)
TS1a	(2+2)	$Mo=O$	acid−base/2e	50.1	−35.0	80.7	23.0	−30.1	49.3
TS1b	(2+2)	$Mo=O$	acid−base/2e	86.9	−29.8	112.9	30.3	−37.3	62.8
TS1c	(3+2)	di-oxo	redox/2e	68.6	−32.7	97.1	30.2	−25.6	52.6
TS1d	(5+2)	dual $Mo=O$	redox/2e	63.2	−38.9	97.1	20.8	−23.9	41.7
TS1e	oxenoid insert	oxo	redox/2e	69.4	−27.6	93.4	26.5	−30.0	52.7
TS1f	H abstraction (anti)	oxo	redox/1e	45.0	−21.1	63.4	44.7	−14.9	57.7
TS1g	H abstraction (syn)	oxo	redox/1e	49.7	−22.8	69.6	44.7	−14.9	57.7
TS1h	H abstraction	μ-oxo	redox/1e	63.6	−16.2	77.7	62.3	−15.0	75.4
	expt[a]			41.1,[a] 42.1,[b] 45.2[c]					

[a] Reference 65. [b] Reference 17. [c] Reference 64.

that triplet Mo_3O_9 potential energy surface will interfere significantly with the singlet Mo_3O_9 potential energy surface for the lowest reaction pathway of 45.0 kcal/mol.

TS1a and TS1b belong to the (2+2) addition. The active site for both of them is $Mo=O$. The difference between them is the orientation of the C−H bond. In the TS1a transition state, methane approaches the $Mo=O$ bond from the O end, with H attacking the metal and the methyl group attacking the oxygen. We refer it as the hydride formation pathway as a Mo−H bond is going to form. In the TS1b transition state, methane approaches the $Mo=O$ bond with its methyl group attacking the metal. We refer it as the carbide formation pathway as a $Mo-CH_3$ bond is going to form. In the viewpoint of energetics, while the (2+2) process for carbide formation is a competitive pathway with an activation barrier of 50.1 kcal/mol, the (2+2) process for hydride formation must be ruled out for a too high reaction barrier (87.4 kcal/mol). Electrostatic factors were claimed to be the main reason for this 37.3 kcal/mol difference between TS1a and TS1b.[59] In TS1b the interaction between the dipoles associated with the C−H and M−O bonds tends to raise the energy. To contrast this effect, the C−H bond polarizes toward the product charge distribution, forming a negatively charged hydrogen. In TS1a, the electrostatic interaction lowers the energy, and no further rearrangement of charges occurs.[59] Furthermore, the product of the carbide pathway is 7.3 kcal/mol more stable than that of the hydride pathway because oxygen has a higher binding ability to the hydrogen atom than to the methyl group.[59]

TS1c and TS1d correspond to (3+2) and (5+2). The former involves two terminal oxygens connected to the same metal center, using the ($O=Mo=O$) unit as the active site, while the latter involves two $Mo=O$ connected by a bridge [O], using the ($O=Mo-O-Mo=O$) unit as the active site. Both (3+2) and (5+2) pathways lead to the reduction of the metal centers with the simultaneous formation of hydroxyl and alkoxy, having some resemblance to the Haber model.[24,25] But the barriers (68.6 kcal/mol for (3+2) and 63.2 kcal/mol for (5+2)) are generally too high, disfavoring Haber's 2e mechanism.[24,25] Thus we see that TS1c is 5.4 kcal/mol more stable than TS1d and that the product of (3+2) is 9.4 kcal/mol more stable than that of (5+2). In the pioneer work of Goddard on the hydrocarbon oxidation by high-valent group 6 oxides, it was concluded that the second oxo group plays a central role in stabilizing critical intermediates.[60,61] The same reasoning can be applied to understand why (5+2) is preferable over (3+2). There is an extra (spectator) oxo on each Mo in the (5+2) pathway, while no such spectator oxo remains on the metal center in the (3+2) pathway. It should be pointed out that the distance between two reacting terminal oxygens is 5.37 Å in Mo_3O_9, which is much longer than the distance (3.70 Å)[62] between two nearest neighbor terminal oxygens in α-MoO_3. In terms of (5+2), a shorter [═O]···[O═] distance will obviously lead to a lower activation barrier. Thus it can be anticipated that (5+2) will become an important C−H activation pathway for certain oxides when there are terminal oxygens within suitable distance.

Oxenoid insertion is also a 2e process. It is usually proposed to account for the C−H bond activation by electrophilic oxygen species.[63] Using a terminal oxygen, we do locate an oxenoid insertion TS (TS1e). But the high barrier (69.4 kcal/mol) found here suggests that the electrophilicity of the terminal oxo in Mo_3O_9 is relatively weak. Oxenoid insertion using a bridge oxygen would lead Mo_3O_9 to fall apart; thus the Mo_3O_9 model is not applicable for the modeling of this process. Based on Mulliken population analysis, our calculations show that charge on the bridge [−O−] is around −0.77 as opposed to −0.39 on the terminal [═O]. Thus we anticipate that [−O−] is less electrophilic than [═O] such that oxenoid insertion by a bridge oxygen would be less favorable.

TS1f, TS1g, and TS1h are for the H abstractions, which are 1e processes, leading to the formation of radicals. We find that H abstraction pathways are generally more favorable than the 2e processes. And we also find that H abstraction by terminal oxygens (barriers 45.0/49.7 kcal/mol) is favored over that by bridge oxygen (barrier 63.6 kcal/mol). The H abstraction mechanism by terminal oxygen involves only one $Mo=O$, leaving the other $Mo=O$ in the same metal center as spectator oxo.[60,61] Thus the preference for the 1e processes can be readily attributed to the spectator oxo effects. The spectator oxo effect is less profound in the case of H abstraction by bridge oxygen. Hence TS1h using [−O−] is 17.6 kcal/mol higher in energy than TS1f using [═O]. TS1f and TS1g are different in terms of how CH_4 approaches to the terminal oxygen. We find that the anti mode (TS1f) is 4.7 kcal/mol more favorable than the syn mode (TS1g), while the spectator $Mo=O$ bond length is 1.715 Å in TS1f as compared to 1.726 Å in TS1g. Thus our calculations show that the most favorable pathway is the anti H abstraction. This one-electron transfer process leads to the

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formation of a radical pair, the Mo^{5+} center, and a methyl radical, consistent with Sinev's proposal[26] and the EPR observation.[27] Considering the large singlet−triplet gap 60.4 kcal/mol as indicated by the Mo_3O_9 model, the previous proposal involving an initial excitation from closed-shell $Mo^{6+}{=}O^{2-}$ to open-shell $Mo^{5+}{-}O^{-}$ for MoO_x to enter the radical reactions may seem unnecessary.[57,58]

The calculated activation energy (45.0 kcal/mol) is in good agreement with the experimental value (45.2 kcal/mol) reported by Spencer and Pereira for methane partial oxidation to oxygenates on the MoO_3/SiO_2 catalysts at 873 K using O_2 as oxidant.[64] There exist some other experimental data to which comparison of our calculated number should be made.[17,65] Using N_2O as oxidant, Lunsford and co-workers found a linear Arrhenius plot of the rate for conversion of CH_4 to methanol and formaldehyde over a temperature range of 848−892 K, giving an activation energy of 42.1 kcal/mol.[17] Under a similar experimental situation as that of Lunsford, Khan and Somorjia were able to specify rate equations for the formation of both methanol and formaldehyde.[65] For methanol formation, an activation energy of 41.1 kcal/mol was obtained; for formaldehyde formation, two distinct activation energies (82.2 and 40.1 kcal/mol) were obtained for temperatures below and above 838 K, respectively.[65] We have also performed similar calculations for hydrogen abstraction from the methylene group in propane by the Mo_3O_9 model. We found an activation barrier of 32.3 kcal/mol,[66] while Bell and Iglesia reported an experimental value of 28.0 kcal/mol for the MoO_x/ZrO_2 system.[67] The general agreement between theory and experiment lends credit to the Mo_3O_9 system as a model of molybdenum oxide based catalysts.

Formation of Methoxy Species: The fate and the lifetime of the methyl radical decide the final reaction products. The radical pair formed in the H abstraction step can decompose to free the methyl radical into the gas phase. This process is entropy-driven. Free methyl radical can either couple with another methyl radical to form C_2 compound[3,4,10,68] or combine with O_2 to undergo total oxidation.[10,68,69] The other pathway is that the methyl radical will rebound with the surface oxygen to give methoxy species, which then dehydrogenate to form formaldehyde or hydrolyze to form methanol or undergo total oxidation.[70,71] As methyl radicals suffer from deep oxidation either in the gas phase or on the surface in the presence of oxygen, it is thus not surprising that experimentally it is observed that methanol and formaldehyde yields increase with decreasing oxygen concentration.[10]

Figure 4 illustrates the possible pathways for methyl radical rebound with the surface oxygen. As both Mo_3O_9H and CH_3 are radical species, spin-floppy can easily occur. Thus we consider energetics for closed-shell singlet, open-shell singlet, and open-shell triplet (Table 2). As shown in Figure 4, the methyl radical is ready to react with terminal [═O], bridge [─O─], and hydroxyl [─OH] oxygens. Although there is a marked difference in reactivity among these three types of oxygens, the calculated barriers range from 8.6 to 19.8 kcal/mol such that all rebound processes would be considered as facile at high temperature of 873 K for C─H activation. We find the oxo [═O] species is most active with activation barriers ranging from 8.6 to 11.2 kcal/mol. Bridge [─O─], on the other hand, is least active both from a thermodynamic point of view and from a kinetic point of view. The barrier for methyl rebound with a bridge [─O─] is predicted to be 18.2 kcal/mol. Methyl can also rebound to hydroxyl [─OH], leading to a direct formation of methanol. We find that the activity of hydroxyl [─OH] is between [═O] and [─O─], whose barrier is around 13.6 kcal/mol.

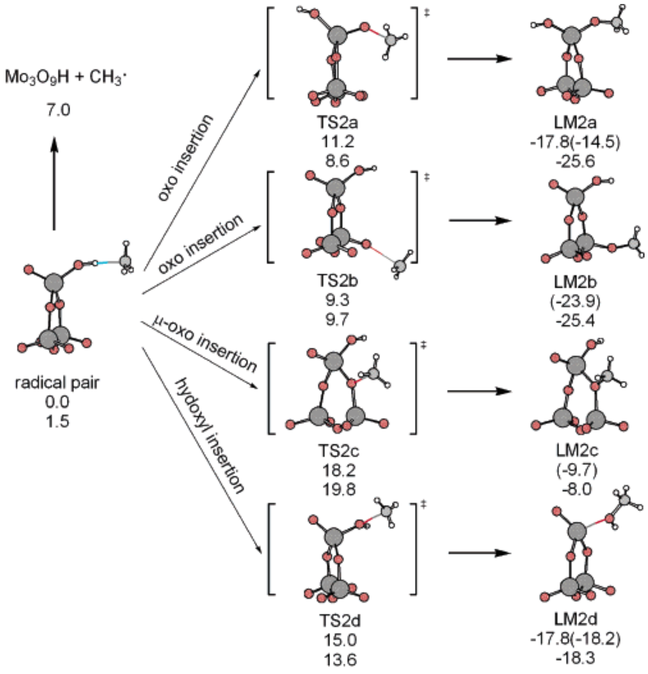

Figure 4. Calculated enthalpies in kcal/mol at 873 K for the oxygen insertion pathways. Key: First entry lists the singlet energy and the second entry lists the triplet energy (closed-shell singlet energies are in parentheses).

Thus the most favorable pathway is for methyl to recombine with a nearby oxo. We find this rebound step is a fast process with a small barrier of 8.6 kcal/mol such that H abstraction followed by a fast oxygen atom insertion leads to the formation of stable hydroxyl and alkoxy species. The presence of only hydroxyl and alkoxy species on the surfaces detected by IR spectra[35] was used to support the 2e mechanism. Our calculations show that 2e processes both are with high energy barriers (68.6 for (3+2) and 63.2 for (5+2)). On the other hand, our calculations favor the 1e process. The H abstraction leads to the formation of a radical pair, which can be detected by EPR experiments,[28] while the radical pair undergoes a rapid rebound process, leading to the formation of stable hydroxyl and alkoxy species, detected by the IR experiment.[26] Thus, the seemingly conflicting results between IR[26] and EPR[28] experiments are reconciled in our mechanism.

Not surprisingly, the distribution of the final products for methane oxidation depends critically on the rebound pathway. If methyl radical can rebound quickly with the surface oxygens, the main primary products would be methanol and formaldehyde. Experimentally, it was observed that a large amount of surface [─OH] would facilitate the formation of methanol.[72]

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Table 2. Calculated Energetics for $CH_3^{\bullet}$ Rebound at 873 K (Closed-Shell Singlet Energies Are in Parentheses)

			TS			product		
pathway	insertion moiety	spin state	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol/K)	$\Delta G^{\ddagger}$ (kcal/mol)	ΔH_r (kcal/mol)	ΔS_r (cal/mol/K)	ΔG_r (kcal/mol)
TS2a	Mo═O	singlet	55.9	−22.6	75.6	26.9 (30.2)	−25.2 (−25.6)	48.9 (52.6)
		triplet	53.3	−18.0	69.1	19.1	−24.3	40.4
TS2b	Mo═O	singlet	54.0	−12.4	64.8	(20.8)	(−23.9)	(41.7)
		triplet	54.4	−12.8	65.6	19.3	−20.5	37.3
TS2c	Mo—O—Mo	singlet	62.9	−24.4	84.2	(35.0)	(−27.2)	(58.7)
		triplet	64.5	−23.2	84.7	36.7	−22.7	56.5
TS2d	Mo—O—H	singlet	59.7	−22.1	79.0	26.9 (26.5)	−28.9 (−30.0)	52.2 (52.7)
		triplet	58.3	−18.9	74.9	26.4	−25.3	48.5

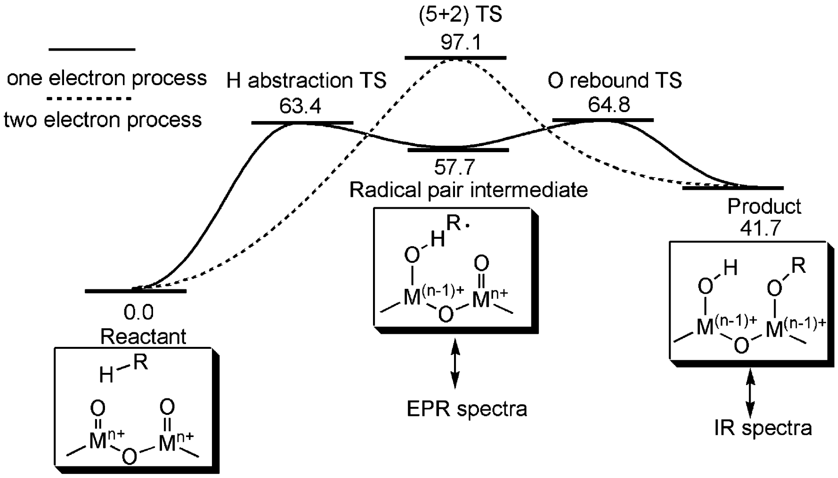

Figure 5. H abstraction/O rebound mechanism versus (5+2) mechanism. ΔG in kcal/mol at 873 K are reported.

However, a strongly bounded formaldehyde species would be in danger of deep oxidation.

On the other hand, if lattice oxygen bounds tightly with the lattice metal, the pathway for methyl radical rebound would be disfavored, leading to the gas-phase reaction for methyl coupling to C_2 as an important pathway (OCM, oxidative coupling of methane).[3,4] Since the total oxidation for methyl to bind with O_2 is an inevitable pathway, DHAM (dehydrogenation−aromatization of methane)[73] in the absence of gas-phase oxygen would be another route worthy of pursuing to make higher-value-added chemicals.

Implications in Homogeneous and Enzymatic Processes: Chromyl chloride CrO_2Cl_2 and permanganate MnO_4^- are simple metal oxo compounds that have been used for many decades in academic research to oxofunctionalize organic residues. These compounds contain M═O and O═M═O which may undergo (2+2) or (3+2) in C—H oxidation. However, Mayer and co-workers provided strong evidence that oxidation of hydrocarbons by these high-valent metal oxo compounds involves H abstraction, which may be considered as a proton-coupled electron transfer (PCET).[41−44] In terms of PCET, the metal center is the electron acceptor, whereas oxygen is the proton acceptor. Thus the activity of H abstraction shall be correlated not only with the reducibility of the metal center but also with the basicity of the oxygen atom such that formation of a strong MO−H bond is the driving force of these reactions.

There also exist many biochemical processes where one or more hydrogen atom transfer steps appear to be involved. The P450 cytochromes and the soluble methane mono-oxygenase (sMMO) are two representatives.[2,44] While the active center for the former would be a terminal oxo [═O], the active center for the latter involves a bridge oxo diion core [—O—]. An understanding of these systems would be of great significance for the design of a synthetic model that catalyzes the selective oxidation of methane with an efficiency and specificity similar to those of the native enzyme.

Conclusions

We present a comprehensive survey of different C—H activation pathways over various kinds of active sites of terminal [═O] and bridge [—O—] by using Mo_3O_9 model systems. We consider eight possible mechanisms of the C—H bond activation on metal oxides. We find that the H abstraction mechanism is the most feasible reaction pathway, which can account for most experimental observations:

1. The calculated activation energies are 45.0 kcal/mol for CH_4 activation, in good agreement with the experimental values (41.1,[65] 42.1,[17] 45.2 [64] kcal/mol).

2. The one-electron oxidation process leads to a Mo^{5+} center and an alkyl radical, in accord with the EPR experiment.[28]

3. H abstraction followed by fast oxygen atom insertion leads to the formation of stable hydroxyl and alkoxy species, which can nicely explain the IR observation.[26]

Figure 5 represents a comparison between the H abstraction/O rebound mechanism and the (5+2) mechanism. To take both enthalpy and entropy effects into account, the energies reported in this figure are ΔG at 873 K. Our calculations lend support to the proposal that the H abstraction/O rebound mechanism is

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omnipresent in various areas of chemistry involving gas-phase and matrix-isolated species, organic synthesis, homogeneous/heterogeneous catalysis, and metalloenzymes.[44] Our calculations also infer that (2+2) can be an alternative if the M═O bond possesses a high polarity, while (5+2) can provide another effective pathway if two M═O bonds are in close proximity.

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Supporting Information Available: Tables of comparison data. This material is available free of charge via the Internet at http://pubs.acs.org.

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