Methane Activation by Transition-Metal Oxides, $\text{MO}_x$ ($\text{M} = \text{Cr, Mo, W}; x = 1, 2, 3$)

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Recent experiments on the dehydrogenation—aromatization of methane (DHAM) to form benzene using a MoO$_y$/HZSM-5 catalyst stimulated us to examine methane activation by the transition-metal oxide molecules, Mo$_x$ ($\text{M} = \text{Cr, Mo, W}; x = 1, 2, 3$). The present studies use hybrid density functional theory (B3LYP). The reactivity trend is rationalized in terms of changes in the electrophilicity of Mo$_x$, the strength of the $\text{M}^-$O $\pi$ bond, and the bonding properties of Mo$_x$ to methyl or hydrogen as M and x are varied. It is found that $\sigma$-bond metathesis to the metal hydride product ($\text{H}^+\text{MO}_x\text{CH}_3$) occurs preferentially over the high oxidation state form (MO$_x$) of the heavier metals, as well as all chromium oxides (CrO$_x$). Instead, oxidative addition of MO$_x$ leading to metal metal hydride ($\text{H}^-\text{MO}_x\text{CH}_3$) is more favorable over the low oxidation state of MO$_x$ ($\text{M} = \text{Mo, W}, x = 2, 1$). In particular, it is found that WO$_2$ can undergo oxidative addition with negligible activation barrier and is predicted to be the most reactive compound of this class toward methane activation. Our finding that MO$_3$ ($\text{M} = \text{W, Mo}$) is the best oxidation state for this class of metal oxides toward methane activation suggests that the MO$_3$/HZSM-5 catalysts active in the DHAM reaction may be W and Mo oxycarbides (MO$_2$C$_2$). The formation of such intermediates may be the reason that the experiments find an induction period before the catalyst is active for the desired reaction.

1. Introduction

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1. Introduction

The efficient catalytic conversion of methane to petrochemical feedstocks and liquid fuels is a great technical challenge but quite important to society with the potential to revolutionize natural gas utilization. A very promising approach is the dehydrogenation—aromatization of methane (DHAM) to form benzene in the absence of gas-phase oxygen.$^{1-19}$ MoO$_y$/HZSM-5 is generally believed to be the best catalyst for DHAM and has been widely studied. While pure MoO$_3$ leads to no formation of benzene and HZSM-5 has very limited activity toward methane activation, the combined system MoO$_y$/HZSM-5 yields conversions as high as 10% with 80% selectivity toward benzene.$^1$ This catalyst has an induction period and appears to be poisoned by coke formation.$^1$ There is general agreement that this system forms a bifunctional catalyst with the metal responsible for methane activation to C$_2$ species and the zeolite responsible for their conversion to benzene.$^{1,2,8,20}$ Barry et al.$^{11}$ report that this system contains highly dispersed Mo monomers or dimers that are likely to play a role in the catalytic process. It is not clear, however, what is the active phase or what reaction sites, the complex composition of the catalysts, and the differing large amounts of CO$_2$. The activity of W-based catalysts are variously reported as no activity by ref 7, low activity by ref 8, and of the highest activity by ref 9. The active phase for methane activation has been suggested to be Mo$_x$ ($\text{M} = \text{Cr, Mo, W}$) by refs 6, 9, and 15, MoO$_y$C$_2$ by refs 14, 16, and 18 and Mo$_2$C by refs 4 and 12. The C—H bond activation mechanism has been proposed as

$$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}^2$$

$$\text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2^{19}$$

$$\text{CH}_4 \rightarrow \text{CH}_3^{\delta^+} - \text{H}^{\delta^- - 7}$$

$$\text{CH}_4 \rightarrow \text{CH}_3^{\delta^-} - \text{H}^{\delta + 1}$$

$$\text{CH}_4 + \text{H}^+ \rightarrow \text{CH}_3^+ \rightarrow \text{CH}_3^+ + \text{H}_2^{19}$$

The broad range of hypotheses concerning this process is largely because studies of mechanisms for reactions over oxide catalysts are complicated by the irregular structure of the active sites, the complex composition of the catalysts, and the differing reaction conditions of the catalytic processes. To gain an understanding of such complex heterogeneous systems, considerable attention has been devoted to studying the more tractable chemistry of gas-phase metal oxides.$^{20-26}$

The gas-phase metal oxides are typically generated in a plasma environment or by laser ablation of metal plus oxygen systems or of solid metal oxides; however, for even the simplest gas-phase reactions, there remain many unresolved issues regarding the reaction mechanisms and the energetics for the processes of interest. Because these gas-phase species provide the simplest model of the heterogeneous active sites, such studies can provide valuable insight into the elementary steps of more complex heterogeneous catalytic processes.
We present here the first systematic quantum chemical study of methane activation by the transition-metal oxide molecules of MO$_x$ (M = Cr, Mo, W, x = 1, 2, 3). This allows us to obtain some of the mechanistic details relevant to the catalytic processes. Our purpose is to understand (1) how the C–H is activated, (2) what is the best oxidation state for each of the metals considered, (3) which metal is the most active, and (4) what factors determine the reactivity. We expect that answers to these questions will stimulate new investigations both to validate the mechanistic understanding and to improve catalyst design.

2. Computational Details

All computations were performed using the B3LYP hybrid density functional, which includes a mixture of Hartree–Fock exchange with the Lee–Yang–Parr exchange–correlation functional including a generalized gradient approximation. B3LYP method provides good descriptions of reaction profiles, including geometries, heats of reactions, and barrier heights.

We use the Wadt and Hay core-valence (relativistic) effective core potential for the metal center (14 explicit electrons and -C, and H, we use the standard 6-31G** basis sets developed by Pople and co-workers.

All calculations were carried out with the Jaguar 4.0 program suite. Vibrational frequencies were calculated to ensure that each minimum is a true local minimum (only real frequencies) and that each transition state has only a single imaginary frequency. For each species considered, we investigated all plausible spin states.

3. Results and Discussion

Figure 1 shows the reaction scheme. We optimized two kinds of molecular complexes between CH$_4$ and MO$_x$. M1 corresponds to the pseudo-C$_{2v}$ coordination mode with two methane C–H bonds toward the metal center; while M2 is in the pseudo-C$_{3v}$-coordination mode with three methane C–H bonds in direct contact with the metal center. M1 and M2 can be further classified into the staggered or the eclipsed configurations based on the relative position of C–H bonds and M–O bonds (cf. Table 2 in Supporting Information).

We considered three kinds of transition states: T1 leading to D1 (H–MO$_{x-1}$–OCH$_3$), T2 leading to D2 (CH$_3$–MO$_{x-1}$–OH), and T3 leading to D3 (H–M(O$_x$)–CH$_3$). In the T1 transition state, methane approaches the M–O bond from the O end with H attacking the metal and the methyl group attacking the oxygen. We refer to the resulting species (D1) as the hydride product (it has a M–H bond). In the T2 transition state, methane approaches MO$_x$ with its methyl group attacking the metal. We refer to the resulting product, D2, as the carbide product (it has a M–CH$_3$ bond). These two processes correspond to [2, 1+] additions, often denoted as $\sigma$-bond metathesis. The reaction leading to product D3 is generally referred to as oxidative addition, with the metal center M formally oxidized by two units simultaneous with forming the new M–H and M–CH$_3$ bonds. D3 might also be referred to as methyl metal hydride product. As shown in Figure 1, R1, R2, and R3 are the radical products formed by homolytic cleavage of the corresponding C–M and C–O bond from D1, D2, and D3.

3.1. MO$_x$. Description. Table 1 summarizes the properties of the electronic ground state of the metal oxides. For MO$_3$, the ground state is always singlet, corresponding formally to a double bond from the M to each O. Here, the positive charge on the metal center increases from Cr (+1.12) to Mo (+1.44) to W (+1.53).

Because of the increased exchange stabilization of the singly occupied (nonbonding) d orbitals, high spin states become more and more favorable as the metal oxidation state is reduced. However, there are distinct differences, which can be understood.
We note the following trends: (1) coordination energies are from the metal side. Table 2 summarizes the binding energies. These trends suggest that the attractive interaction of CH\textsubscript{4} is electrostatic, involving donation of negative charge from the methane to the metal center. Table 3 reports the amount of charge transferred from methane to metal upon complexation. The binding energy correlates roughly with the changes in the exchange energy during the reaction, (2) the relative energy of the various spin states electronic configurations Mulliken charges

<table>
<thead>
<tr>
<th>M</th>
<th>CH\textsubscript{4}•••MO\textsubscript{x}</th>
<th>CH\textsubscript{4}•••MO\textsubscript{x}</th>
<th>CH\textsubscript{4}•••MO\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>13.5</td>
<td>10.6</td>
<td>3.7</td>
</tr>
<tr>
<td>Mo</td>
<td>12.6</td>
<td>7.5</td>
<td>3.9</td>
</tr>
<tr>
<td>W</td>
<td>15.3</td>
<td>2.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

a All energies (kcal/mol) are referred to the corresponding ground states of CH\textsubscript{4} + MO\textsubscript{x}. Binding energies become smaller as x goes from 3 to 1 and as M goes down the column from CrO\textsubscript{3} to WO\textsubscript{3} for x = 2, 1. Binding is strongest for WO\textsubscript{3}.

from the differences in the atomic ground states, which correspond to s\textsuperscript{d} for Cr and Mo but s\textsuperscript{d} for W. Accordingly, the low oxidation states WO\textsubscript{3} (x = 1, 2) have lower spin multiplicity and more s character than the respective CrO\textsubscript{3} and MoO\textsubscript{3}.

For the lower oxidation states, the positive charge on the metal center decreases slightly (<0.09) going from Cr to W. This is in contrast to the trend found for MO\textsubscript{3}. For binding, binding energies become smaller as x goes from 3 to 1 and as M goes down the column from CrO\textsubscript{3} to WO\textsubscript{3} for x = 2, 1. Binding is strongest for WO\textsubscript{3}.

3.2. CH\textsubscript{4}•••MO\textsubscript{x} Molecular Complexes. The interaction between CH\textsubscript{4} and MO\textsubscript{x} is attractive when CH\textsubscript{4} approaches MO\textsubscript{x} from the metal side. Table 2 summarizes the binding energies. We note the following trends: (1) coordination energies are nearly independent of CH\textsubscript{4} orientation; (2) the stability of the molecular complexes decreases with the oxidation state; (3) for oxidation state VI, the CH\textsubscript{4}•••MO\textsubscript{2+} bond strength is roughly the same for Cr and Mo and only slightly stronger for W; (4) for oxidation states IV and II, the CH\textsubscript{4}•••MO\textsubscript{2+} bond strength decreases from Cr to Mo and to W.

These trends suggest that the attractive interaction of CH\textsubscript{4} and MO\textsubscript{x} is electrostatic, involving donation of negative charge from the methane to the metal center. Table 3 reports the changes in Mulliken charges upon formation of the molecular complexes. The binding energy correlates roughly with the amount of charge transferred from methane to metal upon coordination. To form a strong bond for the complex, it is important to have the metal center be electrophilic and to have available vacant frontier orbitals of the correct symmetry (s for C, coordination and s + d for C\textsubscript{2z} coordination). For oxidation state VI, W possesses the highest positive charge and forms the strongest bond to CH\textsubscript{4}. For oxidation states IV and II, W has the highest s occupation, which pushes away the CH\textsubscript{4} leading to the least stable CH\textsubscript{4}•••MO\textsubscript{2+} molecular complexes.

3.3. Dissociative Products. The relative energy of the various products depends on separately measurable factors such as (1) the promotion energy to bring the metal in a reactive state and the changes in the exchange energy during the reaction, (2) the

<table>
<thead>
<tr>
<th>M</th>
<th>CH\textsubscript{4}•••MO\textsubscript{x}</th>
<th>CH\textsubscript{4}•••MO\textsubscript{x}</th>
<th>CH\textsubscript{4}•••MO\textsubscript{x}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>52.2</td>
<td>19.7</td>
<td>15.0</td>
</tr>
<tr>
<td>Mo</td>
<td>66.9</td>
<td>26.1</td>
<td>13.5</td>
</tr>
<tr>
<td>W</td>
<td>87.1</td>
<td>37.9</td>
<td>24.1</td>
</tr>
</tbody>
</table>

a These energies can be related to the strengths of the M–O σ bonds. The M–O π bond gets stronger as M varies from Cr to W and x varies from 3 to 1.

<table>
<thead>
<tr>
<th>M–O</th>
<th>OM–O</th>
<th>O= M–O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>25.0</td>
<td>32.3</td>
</tr>
<tr>
<td>Mo</td>
<td>51.0</td>
<td>51.8</td>
</tr>
<tr>
<td>W</td>
<td>66.0</td>
<td>65.0</td>
</tr>
</tbody>
</table>

The π binding energy for M–O bonds, and the bond energies for M–H/M=CH\textsubscript{3} and O/H/O–CH\textsubscript{3} in Table 4, the strength of the M–O π bond in MO\textsubscript{x} is estimated by singlet–triplet splitting for the orbitals involved in the π bond. The π bond is weakest in MO\textsubscript{3} because of the spectator oxo effect.\textsuperscript{38,39} For lower oxidation states, the π bond strength is larger and roughly constant for a given metal M (except for Cr where the loss of exchange energy upon formation of the π bond is most significant). The π bond becomes stronger for heavier metals, CrO\textsubscript{3} ≈ MoO\textsubscript{3} ≈ WO\textsubscript{3}, for each value of x. This is partly because the smaller d–d exchange stabilization for heavier elements leads to a smaller loss for bonding these orbitals.

Table 5 lists the strengths for the R–MO\textsubscript{x} and R–OMO\textsubscript{x–1} bonds, where R = CH\textsubscript{3} or O. The results can be generalized as follows: (1) The bond R–MO\textsubscript{x} is essentially covalent and similar for all oxidation states of M for a given pair of R and M. The CH\textsubscript{3}–OMO\textsubscript{x–1} and the H–OMO\textsubscript{x–1} bond strengths are about 100 and 120 kcal/mol, respectively. That is, the H–OMO\textsubscript{x–1} bond is consistently about 20 kcal/mol stronger than the corresponding CH\textsubscript{3}–OMO\textsubscript{x–1} bond. This is similar to the bond strength of CH\textsubscript{3}–OCH\textsubscript{3} (83.2 kcal/mol),\textsuperscript{40} which is 20 kcal/mol smaller than that of H–OCH\textsubscript{3}(104.2 kcal/mol).\textsuperscript{40} (2) The strength of a CH\textsubscript{3}–MO\textsubscript{x} bond is comparable to that of a H–MO\textsubscript{x} bond for a given metal, in analogy to CH\textsubscript{3}–H (104.9 kcal/mol)\textsuperscript{40} vs H–H (104.2 kcal/mol).\textsuperscript{40} (3) The R–MO\textsubscript{x} bond becomes stronger as the metal goes down the column.

Table 6 illustrates the reaction energetics for the formations of the hydride D1 (H–MO\textsubscript{x–1}–OCH\textsubscript{3}), the carbide D2 (CH\textsubscript{3}–MO\textsubscript{x–1}–OH), and the methyl metal hydride D3 (H–M(O\textsubscript{3})–CH\textsubscript{3}). Negative values indicate exothermic reaction with the product thermodynamically more stable than the reactants. As reported in Table 6, D1 is unstable for WO\textsubscript{3} and MoO\textsubscript{3}, while
the exothermicity of \( \text{D}_2 \).

In the case of Mo and W, the CH\(_3\) energies of the hydride radicals decreases, the M\(\text{MO}_x\) bond is stronger, the hydride radical formation is less exothermic. This leads to the observation that the stability of H\(\text{MO}_{1-x}\) increases as M goes down the column and x changes from 3 to 1. (3) Because the hydride bond is fairly independent from the oxidation state, the stability of the hydroxyl radical MO\(_x\)-H is determined by the strength of the M-O \(\pi\) bond. Accordingly, R\(2\) formation is most favorable over CrO\(_x\) (\(x = 3, 2, 1\)) or MO\(_3\) (M = Cr, Mo, W).

3.5. Transition States. Table 8 lists the activation energies corresponding to transition states T\(1\), T\(2\), and T\(3\) in Figure 1. The general trend can be rationalized in terms of both electrostatic and orbital interactions, see Figure 2.

With the exception of T\(3\) on Cr, the activation barriers follow the trend T\(1 > T2 > T3\). The relative heights of T\(1\) and T\(2\) appear to arise mainly from electrostatic factors (Figure 2a). In T\(1\), 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 T\(2\), the electrostatic interaction lowers the energy and no further rearrangement of charges occurs. Thus, it is reasonable that T\(2\) has a lower energy than T\(1\).

In the nucleophilic attack of CH\(_3\) on MO\(_x\) (T\(2\)), the reaction is concerted with a four-center, four-electron cyclic transition state, see Figure 2b. Consistent with this, the activation barriers for T\(2\) depend strongly on the strength of the M-O \(\pi\) bond. The general trends of the reactivity of MO\(_x\) via T\(2\) are CrO\(_3\) > MoO\(_3\) > WO\(_3\) and MoO\(_3\) > MO\(_3\) > MO. The abnormal behavior of the reactivity of MO\(_3\) in T\(2\) can be explained by considering the relative size of s and d orbitals. The d orbitals are compact for the first-row transition metal; while the d and the s orbitals are comparable in size for the third-row transition metal. The large size of d orbitals in W makes WO\(_3\) react more easily than does CrO\(_3\), even though the W-O \(\pi\) bond is stronger than the Cr-O \(\pi\) bond.

### Table 6: Relative Energies (kcal/mol) of the Hydride D\(1\) (H-MO\(_x\)-CH\(_3\)), the Carbide D\(2\) (CH\(_3\)-MO\(_x\)-H), and the Methyl Metal Hydride D\(3\) (H-CH\(_3\)-MO\(_x\)) Products\(^{\text{a}}\)

<table>
<thead>
<tr>
<th>x = 3</th>
<th>x = 2</th>
<th>x = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>-17.0</td>
<td>-9.2</td>
</tr>
<tr>
<td>Mo</td>
<td>-21.5</td>
<td>-9.4</td>
</tr>
<tr>
<td>W</td>
<td>-35.7</td>
<td>-7.5(^{\text{b}})</td>
</tr>
</tbody>
</table>

### Table 7: Relative Energies (kcal/mol) of the Hydride Radicals R\(1\) and R\(3\) (H-MO\(_x\)) and the Hydroxyl Radicals R\(2\) (MO\(_x\)-H)\(^{\text{a}}\)

<table>
<thead>
<tr>
<th>x = 3</th>
<th>x = 2</th>
<th>x = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>81.8</td>
<td>64.1</td>
</tr>
<tr>
<td>Mo</td>
<td>79.0</td>
<td>46.7</td>
</tr>
<tr>
<td>W</td>
<td>65.8</td>
<td>32.3</td>
</tr>
</tbody>
</table>

### Table 8: Activation Energies (kcal/mol) for \(\sigma\) Bond Metathesis (T\(1\) and T\(2\)) and Oxidative Addition (T\(3\)) of MO\(_x\)\(^{\text{a}}\)

<table>
<thead>
<tr>
<th>x = 3</th>
<th>x = 2</th>
<th>x = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>40.5</td>
<td>52.0</td>
</tr>
<tr>
<td>Mo</td>
<td>43.7</td>
<td>58.6</td>
</tr>
<tr>
<td>W</td>
<td>32.2</td>
<td>63.1(^{\text{b}})</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\) Positive values indicate endothermicity with respect to the corresponding ground states of CH\(_3\) + MO\(_x\). Radical mechanisms are less plausible. CrO\(_x\) is the best candidate for a radical mechanism to happen.

\(^{\text{b}}\) Indicates change of spin multiplicity during the reaction.

\(^{\text{c}}\) All energies are relative to the corresponding ground states of CH\(_3\) + MO\(_x\).
T3 is concerted with a cyclic three-center, four-electron transition state. The activation barrier for T3 is generally small because it does not require breaking the M–O π bond. The reactivity follows the trend WOₓ > MoOₓ > CrOₓ (x = 2, 1), as expected from the relative size of the d orbitals, with the exception of WOₓ. For WOₓ, the reactant ground state contains a doubly occupied s orbital (recall that the ground state of W is s²d⁴) on the metal, which prevents the methane from attaining a good transition-state geometry, leading to higher activation energy. The deciding factor for the high activation barrier of CrOₓ is the unfavorably compact d orbital. We note that CH₄ can undergo the oxidative addition on WOₓ with practically no activation barrier. In fact, even though the transition state T3 is above the energy of the molecular complex, it is below the energy level of CH₄ + WOₓ. Except for WOₓ, forming T3 requires a decrease in spin multiplicity. Thus, the barrier should correlate with the spin excitation energy, which is 19.4 (Cr) and 13.7 (Mo) kcal/mol from the ground-state triplet to the singlet of MOₓ and 22.7 (Cr) and 10.8 (Mo) kcal/mol from the ground-state quintet to the triplet of MOₓ.

Note that the data in Tables 6 and 8 indicate that the optimum spin state sometimes changes during a reaction. For strong spin–orbit coupling (e.g., W), such reactions can be allowed during the time scale of a reaction. However, for weak coupling (e.g., Cr), the actual processes may be spin-allowed (involving either an excited spin state of the reactant or of the product). Further discussion of such surface crossings is found in refs 26–29 and 41.

3.6. Discussion of DHAM Catalysis. On the basis of these findings for simple gas-phase molecules, we speculate that for the more complicated catalysts observed to activate CH₄ to form ethylene and benzene, the reactions will involve mechanism T2 or T3 or both, depending on the metal and the oxidation conditions. Although the presence of a heterogeneous support and of additional elements may affect the chemistry of the active centers, our results demonstrate that methane activation can occur with low activation barriers over metal oxides.

We expect that carbide formation is favored by high oxidation states, as well as by high positive charge and low s-orbital population on the metal center. To undergo oxidative addition requires that the metal center is in an intermediate or low oxidation state. Our finding that MOₓ (M = W, Mo) is the best oxidation state for this class of metal oxides toward methane activation suggests that the MOₓ/HZSM-5 catalysts active in the DHAM reaction may be W and Mo oxy carbides (MOₓCₓ). The formation of such intermediates may be the reason that the experiments find an induction period before the catalyst is active for the desired reaction.

4. Conclusions

We examined the activation of methane by transition-metal oxide molecules of the form MOₓ (M = Cr, Mo, W; x = 1, 2, 3) using hybrid density functional theory (B3LYP). We find that the trends in reactivity can be rationalized in terms of the electrophilicity of the MOₓ, the strength of M–O π bonds, and the binding energies of the MOₓ to methyl and hydrogen.

The main results can be summarized as follows:

(1) The molecular complex CH₄–MOₓ is stable. The binding between CH₄ and MOₓ is dominated by charge-induced dipole-moment interaction. The trends in the relative stability of CH₄–MOₓ are

\[
\text{MO}_3 > \text{MO}_2 > \text{MO}; \quad \text{CrO}_x < \text{MoO}_x < \text{WO}_x \quad \text{for} \quad x = 3
\]

and

\[
\text{CrO}_x > \text{MoO}_x > \text{WO}_x \quad \text{for} \quad x = 2, 1
\]

paralleling the trends in the electrophilicity of MOₓ.

(2) As the oxidation state decreases, the M–O π bond strength increases, leading to the π bond strengths in the order MO > MO₂ > MO₃ for a given M. The π bond becomes stronger according to the trend CrOₓ < MoOₓ < WOₓ for a given x.

(3) The bond R–MOₓ (R = H, CH₃) is essentially covalent. Its strength remains constant for a given pair of R and M against varying x. The R–MOₓ bond becomes stronger as M changes from Cr to Mo to W. While the strength of the H–MOₓ bond is comparable to that of the CH₃–MOₓ, the H–OMOₓ₋₁ bond is about 20 kcal/mol stronger than the CH₃–OMOₓ₋₁ bond. This
leads to a carbide product (CH$_3$–MO$_x$–OH) that is about 20 kcal/mol more stable than the hydride product (H–MO$_x$–OH).

(4) The activation barriers generally follow the trend T1 > T2 > T3. The σ bond metathesis to produce the hydride product (H–MO$_x$–OH) is the most favorable reaction for the high oxidation state of MO$_x$ and for the chromium oxides of CrO$_2$.

Oxidative addition of MO$_x$ leading to methyl metal hydride (H–M(O$_x$)–CH$_3$), is the most favorable reaction for the low oxidation states of MO$_x$ (M = Mo, W, x = 2,1). WO$_2$ can undergo oxidative addition with practically no activation energy and is predicted to be the most reactive species toward methane activation among the MO$_x$, see Table 9.

Acknowledgment. This work was partially supported by Chevron Corporation. The facilities of the MSC are also supported by grants from DOE-ASCII-ASAP, DOE-FE, AROMURI, NSF-MRI, NSF-CHE, NSF-CTE, 3M, Seiko-Epson, General Motors, Avery-Dennison, Kellogg’s, Asahi Kasei, Nippon Steel, and the Beckman Institute.

Supporting Information Available: Tables providing comparison between Mulliken and ESP charges, geometries and binding energies of molecular complexes, changes of Mulliken charges upon CH$_4$ and MO$_x$ interactions, and strengths of X–MO$_x$ and X–OMO$_{x-1}$ bonds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes