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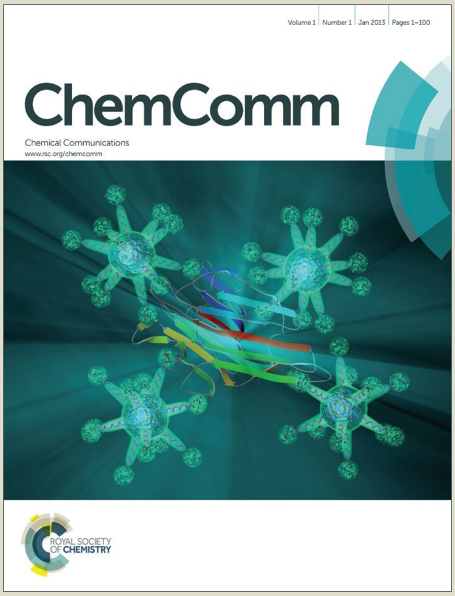

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On the role of the surface oxygen species during A-H (A = C, N, O) bond activation: a density functional theory study†

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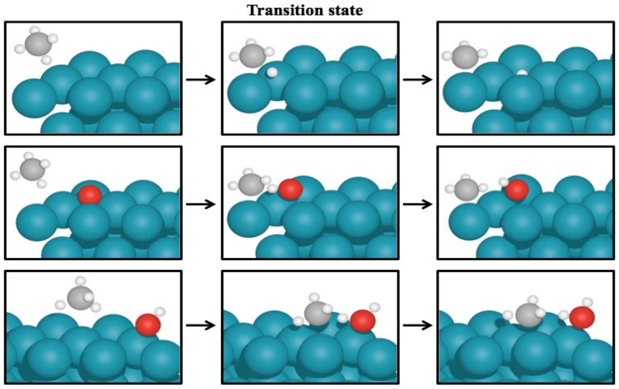
During A-H (A = C, N, O) bond cleavage on O* or OH* pre-covered (111) surfaces, the oxygen species play the role of modifying the reaction energy by changing the species involved in the initial and final states of the reaction.

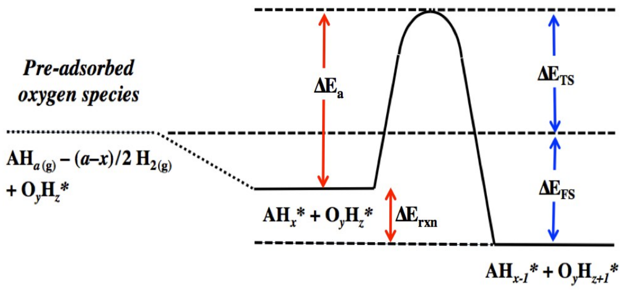
C-H bond activation plays an important role in the functionalization of hydrocarbons.[1-3] In catalytic partial oxidation of fossil fuels, oxidants are strongly involved in the reaction mechanism, creating a variety of oxygen species on the catalyst surface.[4,5] The extents to which these surface oxygen species participate in C-H bond activation, and how they affect the reaction energetics have been vividly debated in the literature.[5-7] Previous studies have shown that the reactivities as well as the coverages of the oxygen species are dependent on the nature of the transition-metal (TM) surface employed.[8-11] For example, atomic oxygen chemisorbed (O*) on gold is known to be active for C-H bond activation.[12-14] The weak binding of O* on gold makes O* highly active, thus promoting C-H bond activation.[15,16] On the other hand, O* on Pt-group metals is shown to be inert for C-H bond activation.[17,18] The comparatively strong binding of O* on Pt-group metals leads to a high O* coverage, thus poisoning the catalyst surface.[19-21]



Scheme 1 Illustrations of the direct (top row), O-assisted (middle row), and OH-assisted (bottom row) CH_4 activations on a fcc(111) transition-metal surface.

Previously, we investigated the nature of the transition states for dehydrogenation reactions by establishing the transition-state scaling (TSS) relations for AH_x (x = 1-4, 1-3, 1-2, for A = C, N, O, respectively) dehydrogenation reactions on clean TM surfaces.[22] Herein, we extend the study towards O*, and OH* pre-covered TM surfaces (see Scheme 1). This would allow for the comparison between the direct ($AH_x^* \rightarrow AH_{x-1}^* + H^*$), O-assisted ($AH_x^* + O^* \rightarrow AH_{x-1}^* + OH^*$), and OH-assisted ($AH_x^* + OH^* \rightarrow AH_{x-1}^* + H_2O_{(g)}$) AH_x dehydrogenations. Rather than using the Brønsted-Evans-Polanyi (BEP) relations (ΔE_a vs. ΔE_{rxn}),[23-25] this study is based solely on the TSS relations since they reflect the trends among different TM surfaces more clearly than the BEP relations.[22] The goal of this study is to understand the effect of the surface oxygen species during A-H bond activation on different TM surfaces (e.g. coinage vs. Pt-group metals), in terms of simple reaction energetics.

Scheme 2 illustrates a potential energy diagram showing the reference energy levels used in the TSS relations for the direct, O-assisted, and OH-assisted AH_x dehydro-genation reactions. The TSS relations are based on the transition-state energy (ΔE_{TS}) and the final-state energy (ΔE_{FS}), which are taken relative to either a clean, or O*, or OH* pre-covered, TM surface, and CH_4, NH_3, H_2O and H_2 in the gas phase. This



Scheme 2 Potential energy diagram for AH_x dehydrogenation (x = 1-4, 1-3, 1-2 for A = C, N, O, respectively). ΔE_{TS} and ΔE_{FS} are taken relative to the energies of either a clean (y = 0 and z = 0), or O* (y = 1 and z = 0) or OH* pre-covered (y = 1 and z = 1) surface, and AH_a and H_2 in gas-phase (a = 4, 3, 2 for A = C, N, O, respectively).

specific reference system is more useful here than that used in the BEP relations because: (1) the variations in ΔE_{TS} and ΔE_{FS} among TM surfaces are much larger than those in ΔE_{rxn} and ΔE_a; (2) it allows a direct comparison of ΔE_{TS}'s for series of AH_x dehydro-genation reactions, since ΔE_{TS} and ΔE_{FS} are taken relative to the gas-phase species, whereas ΔE_a and ΔE_{rxn} are taken relative to the initial states of different reactions.

Fig. 1 shows the TSS relations for $CH_{4(g)}$ activation on clean, O* pre-covered, and OH* pre-covered, Ag, Au, Cu, Pd, Pt and Rh (111) surfaces. A close inspection of the figure reveals that the O-assisted $CH_{4(g)}$ activation is more favourable than the direct $CH_{4(g)}$ activation on Ag, Au, and Cu, but not on Pd, Pt, and Rh. Similarly, the OH-assisted $CH_{4(g)}$ activation is preferred to the direct $CH_{4(g)}$ activation on Ag, Au, Cu, and Pt, but not on Pd, and Rh. In fact, the TSS relations for the O-assisted, and OH-assisted $CH_{4(g)}$ activations are quite similar, hence both oxygen species promote C-H bond cleavage on noble metals, but not on reactive ones. Similar arguments can be made for $NH_{3(g)}$ and $H_2O_{(g)}$ activation reactions as shown in Electronic Supplementary Information (ESI)[†] (see Fig. S7a and S9a). Overall, our results are in good agreement with previous experimental and theoretical studies.[10,19,26-28]

To better understand the promoting effect of the surface oxygen species during $CH_{4(g)}$ activation on noble metals, we will examine the reactions on Au(111) in more detail. $CH_{4(g)}$ dissociation on clean Au(111) ($CH_{4(g)} + * \rightarrow CH_3* + H*$) is strongly uphill in energy ($\Delta E_{FS} \approx 1.58$ eV, see Fig. 1). This is accompanied by an extremely high activation barrier of about 2.23 eV (note that for reactions involving closed-shell gas-phase reactants such as $CH_{4(g)}$, $\Delta E_{FS} \approx \Delta E_{rxn}$ and $\Delta E_{TS} \approx \Delta E_a$). On the other hand, $CH_{4(g)}$ dissociation on O* pre-covered Au(111) ($CH_{4(g)} + O* \rightarrow CH_3* + OH*$) is quite thermo-neutral (0.15 eV) whose activation barrier is only about 1.33 eV. Thus, it can be concluded that the formation of CH_3* and OH*, instead of CH_3* and H*, on Au(111) makes ΔE_{FS} ($\approx \Delta E_{rxn}$) of the O-assisted $CH_{4(g)}$ activation much lower than that of the direct $CH_{4(g)}$ activation (1.58 eV → 0.15 eV), which has an effect of lowering ΔE_{TS} ($\approx \Delta E_a$) (2.23 eV → 1.33 eV) (see orange arrows in Fig. 1). Similar arguments can be made when the TSS relation for the OH-assisted $CH_{4(g)}$ activation is compared to that for the direct $CH_{4(g)}$ activation on Au(111). We show that $NH_{3(g)}$ and $H_2O_{(g)}$ activation reactions also behave similarly in ESI[†] (see Fig. S7a and S9a).

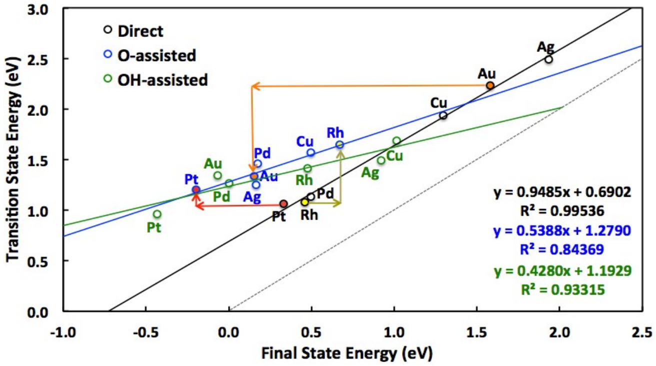


Figure 1 TSS relations for $CH_{4(g)}$ activation on clean (black), O* pre-covered (blue), and OH* pre-covered (green) fcc(111) surfaces. Black, blue, and green solid lines represent the linear regressions for the data sets of same colour. The dashed line indicates $y = x$.

Interestingly, the TSS relation for the O-assisted $CH_{4(g)}$ activation is located above that for the direct $CH_{4(g)}$ activation for a ΔE_{FS} below 1.45 eV (see Fig. 1). This weakens, or in some cases, even reverses the effect described above for some reactive metals (we will show that the difference in the slope of the TSS relation is insignificant for C-H bond activation). For example, in the case of Pt(111), ΔE_{TS} ($\approx \Delta E_a$) increases slightly from 1.06 to 1.20 eV, although ΔE_{FS} ($\approx \Delta E_{rxn}$) is decreased from 0.33 to –0.20 eV (see red arrows in Fig. 1). In the case of Rh(111), ΔE_{TS} ($\approx \Delta E_a$) increases greatly from 1.08 to 1.64 eV, because ΔE_{FS} ($\approx \Delta E_{rxn}$) is increased from 0.46 to 0.67 eV (see yellow arrows in Fig. 1). Similar arguments can be made when the TSS relation for the OH-assisted $CH_{4(g)}$ activation is compared to that for the direct $CH_{4(g)}$ activation on Pt-group metals.

High catalytic activity of gold for hydrocarbon partial oxidation reactions has been previously explained by the weak binding (or Brønsted basicity) of O* on gold.[11,10] As shown in Scheme 1, however, C-H bond activation occurs via binding of carbon to the surface, and hydrogen to O*/OH*. Hence, much better linear correlations can be obtained when ΔE_{TS}'s for the O-/OH-assisted C-H bond activation are plotted against ΔE_{FS}'s (see Fig. S1 in ESI[†]) than $\Delta E_{O/OH}$'s (see Fig. S2 in ESI[†]). This is due to the fact that ΔE_{FS} reflects the surface's ability to bind both oxygen and carbon species. Thus, ΔE_{TS}'s for the O-/OH-assisted C-H bond activation are

Table 1. R^2 values of the linear correlations shown in Fig. S1-S6 in ESI†.

	O-assisted		OH-assisted	
Reaction	ΔE_{TS} vs. ΔE_{FS}	ΔE_{TS} vs. $-\Delta E_{O}$	ΔE_{TS} vs. ΔE_{FS}	ΔE_{TS} vs. $-\Delta E_{OH}$
CH_4 activation	0.84	0.70	0.93	0.41
CH_3 activation	0.89	0.05	0.96	0.22
CH_2 activation	0.92	0.26	0.97	0.11
CH activation	0.99	0.21	1.00	0.15
NH_3 activation	0.80	0.82	0.83	0.53
NH_2 activation	0.89	0.72	0.86	0.52
NH activation	0.95	0.74	0.94	0.23
H_2O activation	0.96	0.09	N/A	N/A
OH activation	N/A	N/A	0.85	0.69

not only dependent on the binding strength of the oxygen species, but also the carbon species. Similar arguments can be made for the O-/OH-assisted N-H and O-H bond activations (see Fig. S3-S6 in ESI†), although the improvements in the linear correlations are relatively little or even absent for some N-H bond activation reactions (see Table 1).

Fig. 2 shows the difference in ΔE_{TS} between the O-/OH-assisted, and direct $CH_{4(g)}$ activations ($\Delta E_{TS}^{O\text{-}/OH\text{-}assisted} - \Delta E_{TS}^{direct}$) as a function of the difference in ΔE_{FS} ($\Delta E_{FS}^{O\text{-}/OH\text{-}assisted} - \Delta E_{FS}^{direct}$). The two linear relations shown in the figure are similar. This is not surprising given that similar TSS relations have been obtained for the O-assisted, and OH-assisted $CH_{4(g)}$ activations. The importance of this figure is that it can be used to quantitatively distinguish which surfaces prefer the O-/OH-assisted $CH_{4(g)}$ activation to the direct $CH_{4(g)}$ activation. According to the figure, O* or OH* will participate in $CH_{4(g)}$ activation when the difference in ΔE_{FS} ($\approx \Delta E_{rxn}$) is smaller than about –0.3 or –0.5 eV, respectively. For (111) surfaces whose ΔE_{FS} ($\approx \Delta E_{rxn}$) is near these boundaries, a detailed energetic study is needed to precisely determine which $CH_{4(g)}$ activation reaction is more favourable than another. For example, contrary to what Fig. 2 shows, Pt(111) slightly prefers the OH-assisted $CH_{4(g)}$ activation to the direct $CH_{4(g)}$ activation, as shown in Fig. 1.

Fig. 3 shows the combined TSS relations for the activations of C-H, N-H, and O-H bonds. A series of sequential AH_x (x = 4, 3, 2 for A = C, N, O, respectively) dehydrogenation reactions on clean, O* pre-covered, and OH* pre-covered surfaces have been investigated. As can be seen in Fig. 3a, ΔE_{TS}'s for the O-/OH-assisted CH_x dehydrogenations are generally higher than those for the direct CH_x dehydrogenations. On the other hand, as shown in Fig. 3b, ΔE_{TS}'s for the O-/OH-assisted NH_x dehydro-genations are generally lower than those for the direct NH_x dehydrogenations (the same is true for OH_x dehydrogenations, see Fig. 3c). Thus, the effect of O* and OH* on C-H bond activation is relatively small compared to that on N-H or O-H bond activation. This explains why the O-/OH-assisted $CH_{4(g)}$ activation is favourable on coinage metals (see Fig. 1), whereas the O-/OH-assisted $NH_{3(g)}$ or $H_2O_{(g)}$ activation is favourable on coinage plus some Pt-group metals (see Fig. S7a and S9a in ESI†).

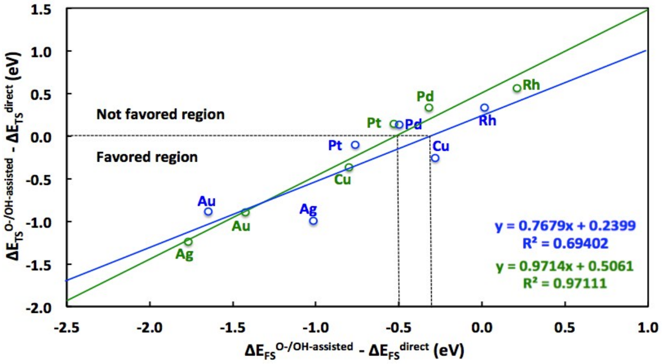


Figure 2 Difference in ΔE_{TS} between the O-(blue) or OH-(green) assisted, and the direct CH_4 activation reactions as a function of the difference in ΔE_{FS}. Blue, and green solid lines represent the linear regressions for the data sets of same colour. The dashed lines indicate the boundaries where the O-/OH-assisted CH_4 activation is favoured over the direct CH_4 activation.

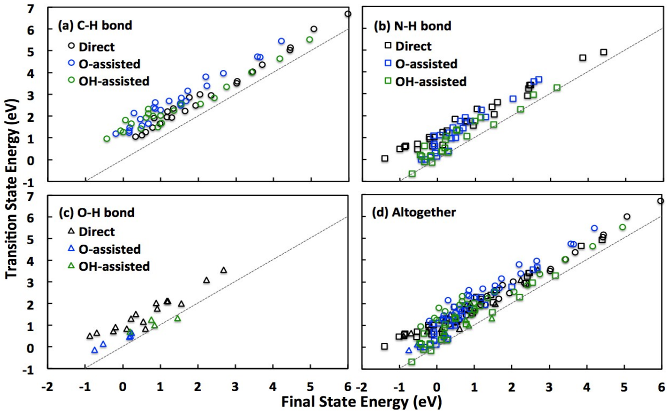


Figure 3 TSS relations for activating (a) C-H; (b) N-H; and (c) O-H bond based on (a) CH_x (x = 1-4); (b) NH_x (x = 1-3); and (c) OH_x (x = 1-2) dehydrogenations on clean (black), O* pre-covered (blue), and OH* pre-covered (green) fcc(111) surfaces. (d) TSS relation when data in (a), (b) and (c) are combined. The dashed lines indicate $y = x$. Most data shown in black are taken from the reference[22].

As shown in Fig. 3a, 3b, and 3c, the slopes of the TSS relations, if obtained separately for the direct, O-assisted, and OH-assisted A-H (A = C, N, O) bond activation reactions, are very similar (nearly one). This can be seen more clearly when we combine the three figures into one (see Fig. 3d). Therefore, the transition states for the direct, O-assisted, and OH-assisted A-H bond activations are all 'late-type', i.e., they are closer to the final states than the initial states. This is in agreement with our finding that ΔE_{TS}'s for the O-/OH-assisted $CH_{4(g)}$, $NH_{3(g)}$, and $H_2O_{(g)}$ activations are not only dependent on the binding strength of the oxygen species, but also the atom A species. Thus, the variations in ΔE_{TS} among the direct, O-assisted, and OH-assisted A-H bond activations must be explained by the variations in ΔE_{FS}, rather than by the variations in $\Delta E_{O/OH}$. For example, on noble metal surfaces, ΔE_{TS} for the O-assisted AH_x dehydrogenation is lower than that for the direct AH_x dehydrogenation because ΔE_{FS} for the former reaction ($\Delta E_{AHx-1} + \Delta E_{OH} - \Delta E_O$) is much lower than that for the latter reaction ($\Delta E_{AHx-1} + \Delta E_H$). On the other hand, on reactive metal surfaces, ΔE_{TS} for the O-assisted AH_x dehydrogenation is higher than that for the direct AH_x activation because ΔE_{FS} for the former reaction is either slightly lower or higher than that for the latter reaction. Similarly, the effect of the surface oxygen species during A-H bond activation is stronger on noble metal surfaces than on reactive ones because more energy can be gained on former surfaces when O* or OH* is reduced to OH* or $H_2O_{(g)}$, respectively. For example, $\Delta E_{OH} - \Delta E_O$ is –1.23 eV on Au(111), whereas it is –0.19 eV on Rh(111) (see Table S2 in ESI†). This large difference in $\Delta E_{OH} - \Delta E_O$ originates from the fact that ΔE_O varies more significantly than ΔE_{OH} among different metal surfaces ($\Delta E_O \approx 2\Delta E_{OH} + \alpha$).[29]

To conclude, the promoting effect of O*/OH* during A-H bond activation is high on noble metal surfaces whereas it is low or even absent on reactive ones. Only a few Pt-group metal surfaces benefited from O*/OH involvement during N-H and O-H bond activations. The effect of the surface oxygen species during A-H bond activation not only depends on the binding strength of the oxygen species, but also the atom A species. In addition, the TSS relation for the O-/OH-assisted A-H bond activation is found to be similar to that for the direct A-H bond activation. Thus, the role of the oxygen species during A-H bond activation is simply to modify the thermodynamic driving force, i.e. ΔE_{rxn}, by changing the species involved in the initial and final states of the reaction, which in turn influences ΔE_{TS}.

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Notes and references

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† Electronic Supplementary Information (ESI) available: additional data, calculation method. See DOI: 10.1039/c000000x/

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Graphical Abstract (Table of Contents)