



The Challenge of CO Hydrogenation to Methanol: Fundamental Limitations Imposed by Linear Scaling Relations

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Abstract

Recent developments in computational catalysis have allowed the routine reduction of the dimensionality of complex reaction networks to a few descriptors based on linear scaling relations. Despite this convenient benefit, linear scaling relations fundamentally limit the activity and selectivity of a given class of materials towards a given reaction. Here, we show an example by offering a novel description of the fundamental limits on the activity of CO hydrogenation to methanol; a reaction that offers a sustainable route to obtaining value-added chemicals from syngas. First, we show that there is a strong linear correlation between the formation energy of CO* (where * denotes an adsorbed species) and those of the transition states of a number of elementary steps along the methanol synthesis pathway on these surfaces. Using microkinetic modeling, we cast this information into activity volcano plots with the formation energies of a given transition state and CO* as independent descriptors. This analysis reveals the fundamental limits on activity imposed by the aforementioned linear scaling relations, and invites a vigorous search for novel materials that escape these linear scaling relations as a necessary condition for achieving improved activity towards methanol from CO hydrogenation. Specifically, we point out the transition states H–CO* and CH₃O–H* as key transition states to be stabilized independently of CO* for improved activity and selectivity towards methanol synthesis.

Keywords Methanol synthesis · Density functional theory · Linear scaling relations · Catalyst design · Microkinetic modeling

1 Introduction

There is a general scientific consensus that global warming is driven by anthropogenic emissions caused by our current energy infrastructure which releases the carbon

fixated in fossil fuels into the atmosphere as CO₂ [1]. To mitigate this crisis, fossil fuels must be replaced by more sustainable fuels that can be produced from CO₂ directly or indirectly (e.g. through biomass) [2, 3]. Methanol is a convenient basis fuel molecule [4–7], a liquid at ambient conditions, a hydrogen carrier [8], a feed to direct methanol fuel cells [9], a blend to gasoline in combustion engines [8], and a platform molecule for the production of gasoline, diesel, jet fuel, or higher value chemicals [10, 11]. Today, methanol is industrially produced from syngas - a mixture of predominantly CO and H₂ with 2–8 vol% of CO₂—on a Cu/ZnO/Al₂O₃ catalyst at 30–120 atm and 200–300 °C [7, 12–14]. In a descending order of molar amounts, Cu represents the active component of the catalyst, ZnO modifies and disperses Cu in porous aggregates partially covered by Zn or ZnO, while Al₂O₃ plays the role of a structural promoter [15–25]. A strong metal support interaction (SMSI) effect brings about a much-prized synergy in this catalytic system, by partially covering the Cu surface with Zn/ZnO, which strongly stabilizes crucial intermediates and transition

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states along the hydrogenation pathway (particularly of that of CO_2) [26–29]. Despite this synergistic collection of the catalyst components, turnover frequencies for methanol synthesis from syngas often do not exceed an unimpressive 10^{-2} s^{-1} [26, 30–33]. This rate is much lower than that of the intimately intertwined water–gas-shift-reaction, allowing the interconversion between CO and CO_2 to equilibrate under the industrial conditions of methanol synthesis [34].

Density functional theory (DFT) is well positioned to contribute to advancements in catalysis thanks to the ever-growing computational capabilities and increasing accuracy of exchange correlation functionals [35–38]. In the context of methanol synthesis from syngas, DFT has provided much insight into the mechanism and structure-sensitivity on transition metal catalysts [26, 29, 39–50]. Extensive calculations for the adsorption energies of reaction intermediates and the transition state energies for the various elementary steps paint a fairly complete picture of the energetics of the involved reaction networks on a given surface. By repeating this exercise on a number of structurally similar surfaces, one can elucidate trends among those surfaces for CO hydrogenation to methanol. One approach to understanding these trends and equipping them with a predictive capability is to reduce the dimensionality of the reaction network to a few descriptors through linear scaling relations between those few chosen descriptors and the remainder of the calculated energies [51]. For CO/ CO_2 hydrogenation to methanol, the descriptors have consistently been the adsorption energies of CO^* (or atomic carbon) and OH^* (or atomic oxygen). Note that these two descriptors correlate poorly with each other on the terraces and steps of transition metals [43, 52], and therefore both are needed as independent descriptors to fully characterize the reaction network. Through microkinetic modeling, the full energetics of the reaction network can be cast as a function of these two descriptors into two-dimensional volcano plots, showing regions in the descriptor space of improved activity and selectivity towards methanol, thus enabling rational catalyst design and high-throughput screening of catalytic materials.

In this work, we focus on the hydrogenation of CO, as opposed to the less plentiful component of syngas, CO_2 . It is a common industrial practice to inject CO_2 into syngas [53], but the concentration of CO_2 is limited by its tendency to deactivate the industrial Cu/ZnO/ Al_2O_3 catalyst through a combined poisoning (e.g. by water, the product of CO_2 hydrogenation) and sintering effect [54–58]. The general consensus is that CO_2 provides the active pathway to methanol formation on the industrial Cu/ZnO/ Al_2O_3 catalyst, and that it is replenished in the syngas mixture through the continuous conversion of CO to CO_2 via the water–gas-shift-reaction [29, 42, 59–62]. Crucially, this chemical equilibrium removes the H_2O produced by CO_2 hydrogenation, which otherwise would have poisoned the

surface (e.g. through high coverage of OH^* or other oxygenated species). The elimination of this poisoning/deactivation problem, and funneling the methanol synthesis rate through CO (i.e. the majority carbon source in syngas) as opposed to CO_2 necessitate finding catalysts that are active towards methanol synthesis primarily through CO hydrogenation, hence the focus of this work.

On the terraces and steps of Cu, the hydrogenation pathway of CO predominantly proceeds through the full hydrogenation of the carbon end of CO^* to methoxy (CH_3O^*), followed by the hydrogenation of the oxygen end to finally produce methanol (CH_3OH) [39]. Possible rate-determining steps include the initial hydrogenation of adsorbed CO^* to HCO^* , as well as the final hydrogenation of methoxy (CH_3O^*) to methanol [39]. The initial hydrogenation step in particular has also been suggested as rate-determining for syngas conversion to higher alcohols [52]. Here, we seek a more in-depth perspective into the reaction mechanism by first focusing on this initial hydrogenation rate-determining step. We conduct our analysis on Ag, Cu, Pt, Pd, and Rh, a suitable set of transition metals that covers a wide range of adsorption properties. Given the strong structure sensitivity of methanol synthesis on Cu and the importance of steps in the industrial catalyst [16, 26, 30–32, 63], we investigate the (111) and (211) facets of the aforementioned transition metals, to represent terraces and steps, respectively. We show that there exists a strong linear scaling relation between the energy of the initial state and that of the transition state for this elementary step. We then recast the microkinetic model to superimpose this linear scaling relation onto the two-dimensional volcano plots. We further explore other transition states along the CO hydrogenation to methanol pathway as descriptors for methanol synthesis on the (211) surfaces. This shows how this family of linear scaling fundamentally limits the activity of transition metals towards methanol synthesis from CO. We then proceed with a brief discussion of materials or strategies to escape these linear scaling relations.

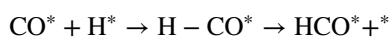
2 Methods

DFT data on the (111) surfaces are taken from our previous work [52], while DFT data on the (211) surfaces were computed anew (see Table S1) on (211) slab models identical to our previous work [43]. Briefly, all plane wave DFT calculations presented here were performed as implemented in the Quantum Espresso code [64], with the BEEF-vdW functional [65] which accounts for van der Waals dispersions in the framework of the generalized gradient approximation. The (111) surfaces were modeled with a four-layer slab in a (3×3) unit cell, with the bottom two layers fixed while the top two layers and adsorbates

were allowed to fully relax. The (211) surfaces were modeled using a (3×1) supercell structure with three metal layers, with the bottom two fixed and the upper layer and adsorbates fully relaxed. For both facets, the Brillouin zone was sampled with a $4 \times 4 \times 1$ Monkhorst–Pack mesh [66], and the energy cutoff was taken at 500 eV. Transition states were calculated with the climbing image nudged elastic band (CI-NEB) method [67], with the convergence criterion on the forces on each of the five intermediate images of 0.05 eV/Å. The harmonic approximation was used to calculate vibrational frequencies and estimate zero-point energies and entropies. All transition states have a single imaginary frequency. Steady state solutions for the rate equations were obtained using the mean-field approximation as implemented in the CatMap code [68]; we employ our previous microkinetic models for the (111) [52] and (211) [43] surfaces. Methanol, methane, ethanol, and acetaldehyde are included as possible products on the (111) surfaces, while C_2 species were not included on the less C_2 -oxygenates-selective (211) surfaces. C–O bond scission to form methane was considered through a COH^* -like intermediate on the (211) surfaces, and through $CHOH^*$ on the (111) surfaces. All microkinetic models are solved at 523 K and 20 bar, with the reaction feed containing $CO:H_2$ ratio of 1:2, and negligible amounts of products (methane, methanol, and C_2 species if applicable). Formation energies of all species are relative to gas phase energies of CO, H_2 , and H_2O .

3 Results

A common rate-determining step for CO hydrogenation to methanol is:



where * denotes an adsorbed species or a surface site, and $H-CO^*$ is the transition state for this association step, which determines the overall rate of the hydrogenation reaction. A general rate expression for this elementary step could be given as:

$$r = \nu \theta e^{-(G_{TS}-\Delta G)/kT}$$

where ν is the pre-exponential factor, θ is a generic term for the coverage of adsorbed intermediates of the initial state (CO^* and H^*), G_{TS} is the free energy of the transition state $H-CO^*$, ΔG is the free energy of the initial state consisting of CO^* and H^* , k is the Boltzmann constant, and T is the absolute temperature.

The generic coverage term could in turn be related to reactant gaseous mixture pressure p by:

$$\theta = \frac{pK}{1 + pK}$$

where K is the equilibrium constant for the adsorption elementary steps, and is given by:

$$K = e^{-\Delta G/kT}$$

Combining the above equations, and setting p to unity gives the following form of the rate expression:

$$r = \nu \frac{1}{1 + e^{\Delta G/kT}} e^{-(G_{TS}-\Delta G)/kT}$$

We then simplify this expression further by considering two limiting scenarios for ΔG : a scenario for strongly adsorbing, highly covered surfaces ($\Delta G \ll 0$), and another for weakly adsorbing, clean surfaces ($\Delta G \gg 0$).

For $\Delta G \ll 0$, the above rate expression could be simplified to:

$$r \propto e^{-(G_{TS}-\Delta G)/kT} \approx e^{-(E_{TS}-\Delta E)/kT}$$

Notice that in the expression above we refer to the zero-point energy (ZPE)-corrected total energies instead of free energies. This follows by assuming a negligible change in entropy from the initial state to the transition state, a valid assumption given that both are adsorbed states.

As for $\Delta G \gg 0$, the above rate expression could be simplified to:

$$r \propto e^{-G_{TS}/kT} = e^{\Delta S_{TS}/k} e^{-E_{TS}/kT}$$

Given that $r \propto e^{-E_a/kT}$, we find that the expressions for the activation energies for the two limiting cases become:

$$\Delta G \ll 0, E_a = E_{TS} - \Delta E \mid \Delta G \gg 0, E_a = E_{TS}$$

That is to say that the activation energy equals the transition state energy if adsorption (i.e. the initial state) is uphill, but equals the difference between the transition state and initial state if the latter is downhill compared to the gas-phase reference.

For hydrogenation/dehydrogenation elementary steps, the transition state energy has been found to scale linearly with the energy of the dehydrogenated state [39, 69]. Figure 1 shows a strong linear scaling relation ($R^2 > 0.99$) between the transition state (E_{TS}) and the initial state (ΔE) of CO^* hydrogenation to HCO^* for the close-packed (111) and the stepped (211) facets of Ag, Cu, Pt, Pd, and Rh. The transition state is significantly stabilized on the (211) facets as compared to their (111) counterparts. Notice that the slopes for the two lines are quite similar; the two lines are solely distinguished through their intercepts, with the line for the (211) facets showing on average ~ 0.30 eV stabilization for $H-CO^*$ compared to the line for (111) facets.

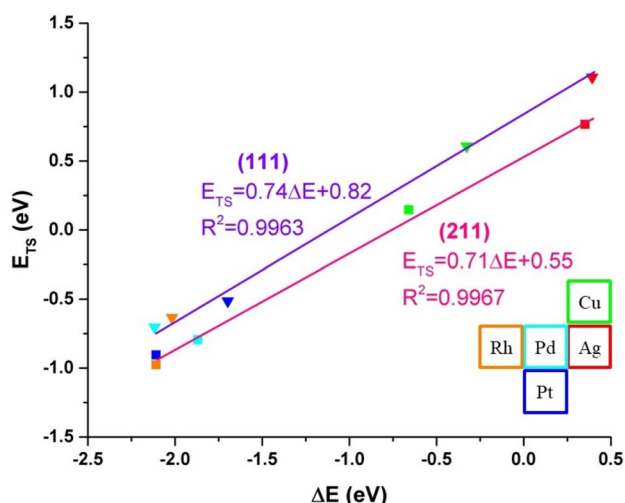


Fig. 1 Linear scaling relations between the initial and transition states of CO* hydrogenation to HCO* for the (111) and (211) facets of transition metals, represented by triangles and squares, respectively. The colors of the symbols indicate the identity of the metal according to the legend in the bottom right corner. The scaling lines for the (111) and (211) facets are in violet and pink, respectively

Plugging in the linear scaling relation into the activation energy expressions, we get:

$$\Delta E \ll 0, E_a = -(1 - \alpha)\Delta E + \beta|\Delta E \gg 0, = \alpha\Delta E + \beta$$

Notice that the limiting conditions are equally valid when expressed in terms of ZPE-corrected energies instead of free energies. Therefore, when ΔE approaches either limit, the activation energy is linearly related to the initial state, with opposite slopes for these lines at the opposite limits. These lines, if extrapolated to finite ΔE , intersect precisely at $\Delta E = 0$ and at $E_a = \beta$, as shown in Fig. 2.

To express this figure in terms of free energy, we need to add the entropy term $-TS$ to E_a (see Tables S2-S4 for details). At $T = 0K$, $E \equiv G$. We further express the free energy in terms of $-G_a$, which represents a logarithmic expression of the rate ($-G_a \sim kT \ln(r)$). This gives a volcano-like plot between the activation free energy and the ZPE-corrected energy of the initial state, with the tip of the volcano precisely at $\Delta E = 0$, as is shown in Fig. 3. This familiar volcano-type relation is a direct manifestation of the Sabatier principle, in which optimal catalysts (i.e. with the least negative $-G_a$) should not bind reaction intermediates too strongly ($\Delta E \ll 0$) or too weakly ($\Delta E \gg 0$).

The entropy term at non-zero absolute temperatures needs only be added to the $\Delta E \gg 0$ leg of the volcano, since it will largely be canceled out for ($\Delta E \ll 0$). Therefore, the $\Delta E \gg 0$ leg of the volcano is shifted downward by TS , as is shown for different temperatures in Fig. S1. To fully represent the exponent of the Arrhenius expression,

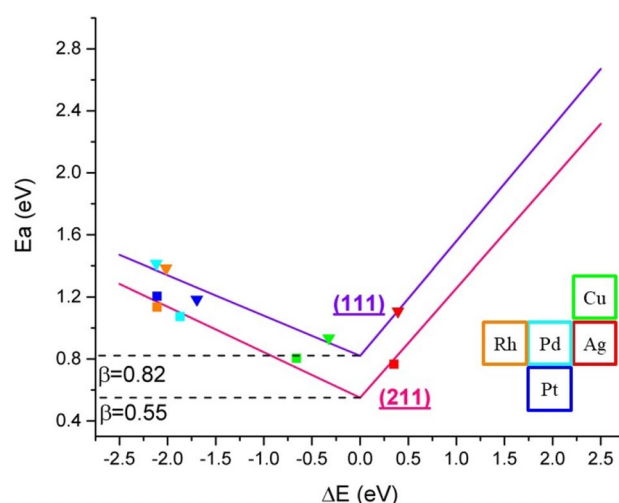


Fig. 2 The activation energy versus the initial state energy for CO* hydrogenation to HCO* on the (111) and (211) facets of transition metals, represented by triangles and squares, respectively. The colors of the symbols indicate the identity of the metal according to the legend in the bottom right corner. The scaling lines for the (111) and (211) facets are in violet and pink, respectively

we cast these volcano plots in terms of $-G_a/kT$, as is shown in Fig. 4.

Notwithstanding the confinement of our analysis to a single elementary step in the pathway to methanol, ignoring possible side products (e.g. notably methane, which we include in the microkinetic model below), we still can make the following three predictions which follow from Fig. 4:

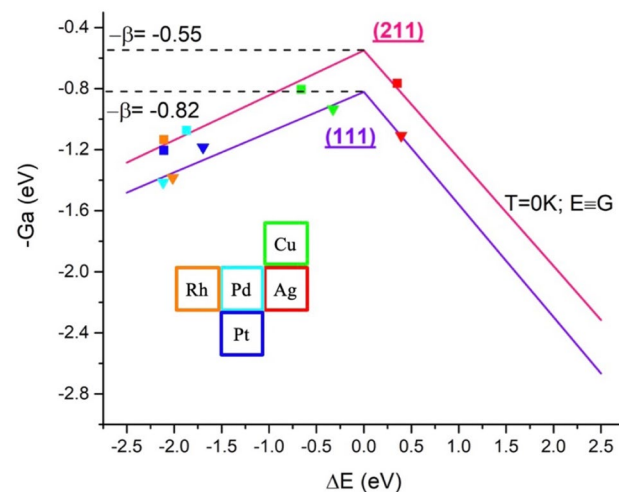


Fig. 3 The inverse of activation free energy versus the initial state energy for CO* hydrogenation to HCO* on the (111) and (211) facets of transition metals, represented by triangles and squares, respectively. The colors of the symbols indicate the identity of the metal according to the legend in the bottom left corner. The scaling lines for the (111) and (211) facets are in violet and pink, respectively

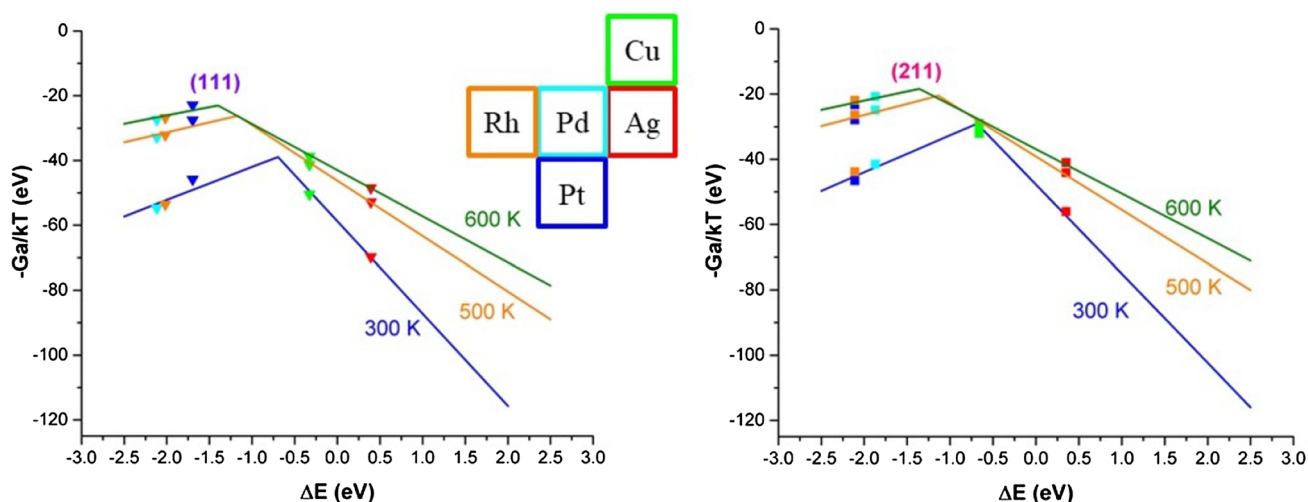


Fig. 4 $-Ga/kT$ versus the initial state energy for CO^* hydrogenation to HCO^* on the (111) and (211) facets of transition metals, represented by triangles and squares on the left and right panels, respectively. The colors of the symbols indicate the identity of the metal

1. At relevant temperatures for CO hydrogenation to methanol (e.g. 500 K), Pd, Pt, and Rh appear to be more active than Cu (this will not be the case when methanation is considered through microkinetic modeling, see below).
2. The optimal catalyst should bind the initial state stronger than Cu, but weaker than Pt or Pd.
3. The optimality is temperature-dependent, given that the tip of the volcano shifts to stronger binding as the temperature increases.

We now take a more general approach and analyze the full kinetic model of CO hydrogenation to methanol on the (111) surfaces. The microkinetic model [52] does not make any prior assumptions regarding the nature of the rate-determining elementary step(s). Furthermore, it considers pathways for forming methane and C_2 -oxygenates, thus providing a comprehensive scrutiny of competing side products. As descriptors, we choose the formation energies of CO^* (ΔE_{CO^*}) and the transition state ($\Delta E_{\text{H-CO}^*}$), with the latter replacing ΔE_{OH^*} as the corresponding descriptor in our previous work [52]. This choice enables us to superimpose the linear scaling relation between these two quantities (see Fig. 1) atop the two-dimensional volcano plots produced by the microkinetic model. This, however, comes at the expense of accuracy given that the reaction intermediates which bind through their oxygen atoms do not scale as well with $\Delta E_{\text{H-CO}^*}$ as they do with ΔE_{OH^*} , e.g. OH^* and CH_3O^* (see all (111) scaling relations in Fig. S2). This is fundamentally attributed to the fact that the hybridization between the metal d states and the adsorbate states are significantly different between those adsorbates binding to the surface through

according to the shared legend in the middle. The symbols shift with the respective temperature lines, which are in blue, orange, and green for 300, 500, and 600 K, respectively

carbon and those binding through oxygen, thus voiding the bond conservation arguments that make the realization of scaling relations possible [70].

To overcome this issue, we eliminate the linear dependence of OH^* and CH_3O^* on the descriptors, by first setting ΔE_{OH^*} to an arbitrary constant value, and then determining the value of $\Delta E_{\text{CH}_3\text{O}^*}$ according to the scaling relation between ΔE_{OH^*} and $\Delta E_{\text{CH}_3\text{O}^*}$ (see Fig. S3). This is akin to taking a cross-section of a constant value of ΔE_{OH^*} in a three-dimensional volcano in which ΔE_{OH^*} is the third descriptor (or the third dimension). We take three such cross-sections at ΔE_{OH^*} values of 0.50, 0.00, and -0.25 eV, representing weak, moderate, and strong binding of OH^* , respectively. Fig. S4–S6 show the volcano plots of the production rates of all products at these three cross sections. The main products according to the microkinetic model are methane, water, and methanol; C_2 species are produced only in trace amounts, consistent with our previous work [52]. The selectivity towards methanol versus methane is sensitive to OH^* binding: at weak binding, the catalysis is more selective to methanol, while the opposite is true at moderate and strong binding. This is intelligible, given that weak binding of OH^* (or interchangeably, weak binding of CH_3O^*) eases methanol desorption, thus steering the catalysis towards higher selectivity to methanol. On the other hand, stronger binding of OH^* (or CH_3O^*) favors C–O bond splitting, and inhibits methanol desorption, shifting the selectivity towards methane. The solutions in all three cases are qualitatively similar nevertheless, and additionally, Fig. S7 shows that the solution when both ΔE_{OH^*} and $\Delta E_{\text{CH}_3\text{O}^*}$ are allowed to scale with the two descriptors is qualitatively invariant to the three cases of Figs. S4–S6.

We now seek to analyze the volcano plot for methanol production on (111) surfaces at moderate binding of OH* ($\Delta E_{\text{OH}}=0.00$ eV) in greater detail (see Fig. 5). A clear peak for this activity volcano exists at moderate binding of CO*, and significantly stabilized H–CO*. The strong dependence of this peak on the transition state energy justifies the above analysis (Fig. 1, 2, 3, 4; Fig. S1; Table S2–S4) by showing the sensitivity of the overall rate to this particular parameter. The scaling line for the (111) facets delineates an active region that lies below the line (within moderate ΔE_{CO}) and a less active region above it, which shows the central role the initial hydrogenation of CO* to HCO* plays in the methanol synthesis chemistry.

We use the (211) data (Table S1) to construct a similar volcano plot for a reaction network that includes pathways for methane and methanol formation (we exclude C₂ species given that the (211) surfaces are known to be less selective towards higher alcohols and oxygenates [71], and given that C₂ species were hardly produced on the (111) facets anyhow). Figure 6 shows this volcano plot at a value of $\Delta E_{\text{OH}} = -0.25$ eV, chosen to be close to ΔE_{OH} on Cu(211). Similar to the (111) volcano plots, oxygenated species do not scale well with either descriptor (see Fig. S8), and therefore, $\Delta E_{\text{CH}_3\text{O}}$ is fixed via the scaling relation between the energies of OH and CH₃O. In addition, we also fix ΔE_{O} , thus making use of the correlation between the energies of O and OH on

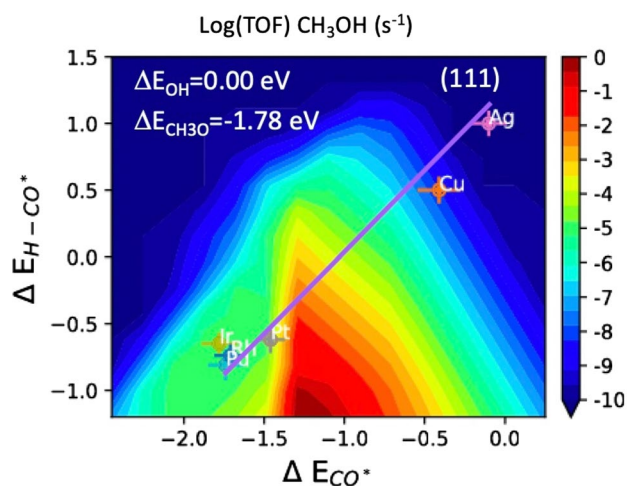


Fig. 5 Volcano plot for the rate (turnover frequency, or TOF, in s⁻¹) of methanol production via CO hydrogenation on the (111) facets of transition metals. Ir(111) was used as an extra data point for the production of this volcano plot to aid the convergence of the adsorbate-adsorbate interaction model included in the microkinetic modeling of the (111) surfaces. The TOF is plotted against the formation energies of CO* and the transition state H–CO*, allowing the superposition of the (111) linear scaling relation of Fig. 1. The error bars indicate the standard deviation of the BEEF ensemble calculations. The formation energies are relative to CO(g), H₂(g), and H₂O(g). Improved catalysis entails the stabilization of the transition state H–CO*, without further stabilizing CO*

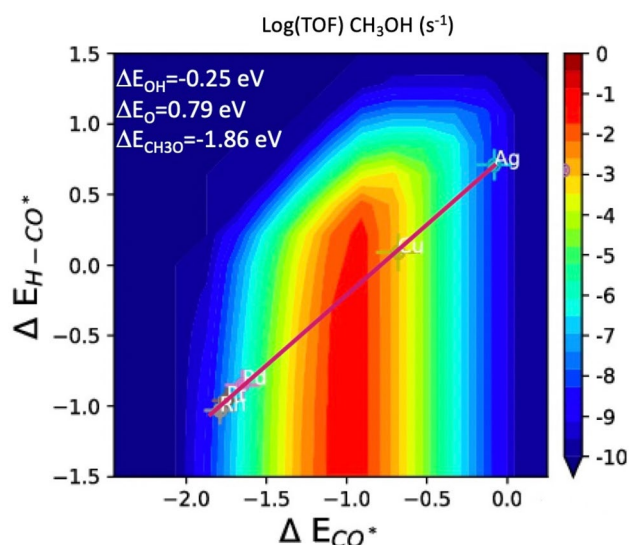


Fig. 6 Volcano plot for the rate (turnover frequency, or TOF, in s⁻¹) of methanol production via CO hydrogenation on the (211) facets of transition metals. The TOF is plotted against the formation energies of CO* and the transition state H–CO*, allowing the superposition of the (211) linear scaling relation of Fig. 1. The error bars indicate the standard deviation of the BEEF ensemble calculations. The formation energies are relative to CO(g), H₂(g), and H₂O(g). Improved catalysis entails the destabilization of CO*, without further destabilizing the transition state H–CO*

the (211) surfaces (on the (111) surfaces, this correlation is poor; see all O–OH–CH₃O scaling relations in Fig. S3). Like the (111) surfaces, the volcano plots are qualitatively invariant at different values of ΔE_{OH} (Figs. S9–S11) and also for the case where all oxygenated species are allowed to scale with the descriptors (Fig. S12). We see a clear dependence of the rate of methanol synthesis on $\Delta E_{\text{H–CO}^*}$ at the weak spectrum of this descriptor. However, below the scaling line at more stabilized $\Delta E_{\text{H–CO}^*}$, there seems to be little dependence of the methanol synthesis rate on $\Delta E_{\text{H–CO}^*}$. Unlike the (111) volcano plot, the (211) volcano plot does not offer a strong incentive to stabilize $\Delta E_{\text{H–CO}^*}$ independently of ΔE_{CO^*} . There is, however, a clear benefit if new catalysts that offer similar stability of the transition state to those on the strongly-adsorbing metals (Pt, Pd, and Rh), but significantly weaker binding of CO*, are found. Such new catalysts would offer significantly improved selectivity towards methanol at the expense of methane, as compared to the (211) facets of Pt, Pd, and Rh. Nonetheless, per the volcano plot of Fig. 6, those new catalysts will not be significantly more active than Cu(211) towards methanol synthesis.

We, therefore, investigate other transition states to serve as descriptors for the (211) surfaces. The goal is to discover whether there is a transition state that more significantly affects the rate towards methanol synthesis on the (211) surfaces than H–CO*. We recall that the final

hydrogenation step to release methanol through hydrogenation of methoxy (CH_3O) could also be rate-determining on Cu(211), along with the initial hydrogenation step of CO^* to HCO^* [39]. We therefore produce the (211) volcano plots with $\Delta E_{\text{CH}_3\text{O}-\text{H}^*}$ as an activity descriptor replacing $\Delta E_{\text{H}-\text{CO}^*}$, again at $\Delta E_{\text{OH}} = -0.25$ eV (and ΔE_{O} and $\Delta E_{\text{CH}_3\text{O}}$ fixed accordingly). Figure 7 shows this volcano plot, while Fig. S13–S14 show the corresponding (211) volcano plots employing $\Delta E_{\text{H}-\text{HCO}^*}$ and $\Delta E_{\text{H}-\text{CH}_2\text{O}^*}$ as descriptors, respectively. Notice that, like the formation energy of $\text{H}-\text{CO}^*$, the formation energies of the other transition states scale linearly with CO^* , though significant scatter exists for the cases of $\text{H}-\text{HCO}^*$ and $\text{H}-\text{CH}_2\text{O}^*$ (see correlation parameters in Figs. S13, S14 captions). These volcano plots are qualitatively similar, but because of scaling with different descriptors, the values of the calculated rates at any given descriptor value-pair would be different among the different descriptors (e.g. notice the difference in rates of Cu(211) predicted in Fig. 6 and Fig. 7). Figure 7 and Figs. S13, S14 show that there are broad regions of higher activity below the scaling lines, suggesting that the transition states $\text{H}-\text{HCO}^*$, $\text{H}-\text{CH}_2\text{O}^*$, and $\text{CH}_3\text{O}-\text{H}^*$ could be potential targets for CO^* -independent stabilization in high-throughput screening of improved methanol synthesis catalysts. Finally, we note that all these transition states scale with one another, given their strong correlation

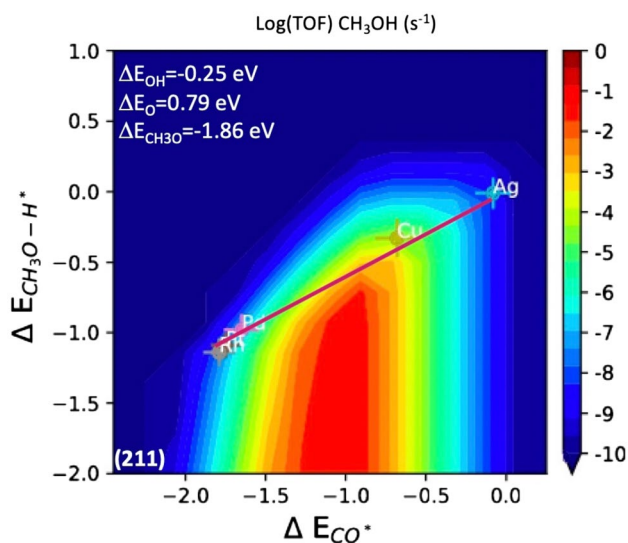


Fig. 7 Volcano plot for the rate (turnover frequency, or TOF, in s^{-1}) of methanol production via CO hydrogenation on the (211) facets of transition metals. The TOF is plotted against the formation energies of CO^* and the transition state $\text{CH}_3\text{O}-\text{H}^*$, allowing the superposition of the (211) linear scaling relation ($\Delta E_{\text{CH}_3\text{O}-\text{H}^*} = 0.66\Delta E_{\text{CO}^*} + 0.07$ eV, $R^2 = 0.9949$). The error bars indicate the standard deviation of the BEEF ensemble calculations. The formation energies are relative to $\text{CO}(\text{g})$, $\text{H}_2(\text{g})$, and $\text{H}_2\text{O}(\text{g})$. Improved catalysis entails the stabilization of the transition state $\text{CH}_3\text{O}-\text{H}^*$, without further stabilizing CO^*

with the formation energy of CO^* . While the goal is to escape these scaling relations as defined on transition metals, it is safe to assume that new materials would also follow their own scaling relations that are distinct from those on transition metals we identify here. This means that stabilizing any of these transition states likely entails the stabilization of the remaining ones, allowing them to be used interchangeably as screening criteria for new catalysts. Therefore, even if normally tools like degree of rate and selectivity control [72–74] could be used to determine which transition state is more rate-determining, the decision regarding which descriptor to use would likely be more dependent on the suitability of a given transition state to easy calculation and screening.

We would like to finish our discussion of the volcano plots with a few remarks regarding the positions of our surfaces on these energy maps. Ag appears to be the least active metal in CO hydrogenation due to its weak-binding characteristics, consistent with literature [75, 76]. Figures 6, 7 and Figs. S13, S14 show Cu(211) to fare significantly better than Cu(111) does on Fig. 5, which is consistent with the well-established structure sensitivity of methanol synthesis on Cu surfaces [16, 26, 30–32, 63]. Pd is well known to form a hydride phase under hydrogenation conditions [77, 78], and Pd-based nanoparticles have been suggested as hydrogen storage materials due to their affinity to retaining subsurface hydrogen [79–81]. A (partial) hydride phase of Pd would lie at more active regions of CO hydrogenation than metallic Pd does on Fig. 5. We calculated the values of the descriptors on a (2×2) unit cell of a PdH(111) slab model (larger unit cells affected the binding energies of CO^* and H^* by less than 0.10 eV). The bulk phase was taken from The Materials Project database [82], as material ID mp-24289. The formation energy of CO^* on PdH(111) was calculated to be -1.33 eV; that is, 0.32 eV higher (i.e. less stable) than that on Pd(111), as detailed in Table S1. At a CO^* formation energy of -1.33 eV, the scaling relation would give a formation energy value of $\text{H}-\text{CO}^*$ at -0.55 eV on PdH(111), which is close to the DFT-calculated value of -0.40 eV. Pt, Pd, and Rh were shown to have high methanol synthesis activity per the analysis of Fig. 4. Absent from Fig. 4 was any treatment of methanation, however. When a competing pathway towards methane is introduced through the microkinetic models we discussed, we predict that either facet of the strongly-adsorbing metals of Pt, Pd, and Rh will be more selective towards methane than methanol (see Figs. S15–17). Indeed, numerous reports in literature discuss the activity and selectivity of Pd, and to less extent, Pt and Rh towards methanol synthesis versus methanation [83–95], although selectivity towards methanol (vis-à-vis the competitive methane) vary widely depending on the support, presence of additives, as well as the catalyst synthesis conditions. In general, a high selectivity to methanol is attributed

to the inability of these metals to dissociate the C–O bond, a prerequisite for methane formation.

4 Discussion

Figures 5, 6 and 7, S13 and S14 show that there is room for development for CO hydrogenation catalysts, but this development is limited by the presence of linear scaling relations. Put another way, the challenge in methanol synthesis from syngas lies in stabilizing H–CO* and/or other transition states along the methanol synthesis pathway independent of CO*, as well as destabilizing CO* independently of the transition state energies on strongly adsorbing surfaces, thus breaking the strong linear scaling relations between the energies of these states. Interestingly, this is also a challenge for the electrochemical reduction of CO, for which a very similar volcano plot was recently derived [96]. This materials challenge necessitates finding new catalytic materials that do not follow the scaling relations of transition metals. This is a necessary, but insufficient, condition [43] to improve the activity and selectivity towards methanol, since the selectivity would depend on the overall production rate of the several possible products based on coupled atomic-scale factors (e.g. support effects, surface reconstruction under realistic reaction conditions).

We briefly survey the literature for inspiration on how to surmount this challenge in CO hydrogenation to methanol catalysis. Typically, breaking linear scaling relations requires the realization of active sites that are geometrically and/or electronically different from those for which the linear scaling relations under question are derived [97]. Transition metal phosphides [98] and oxides [99] have demonstrated their abilities to break linear scaling relations derived on transition metals by offering significantly different active sites for adsorption of reaction intermediates. An immediate logical step to achieve this variation in geometrical/electronic properties within the class of transition metals is offered by bimetallic catalysts. The improved activity could be attributed either to the Interpolation Principle [100], in which the adsorption properties of an alloy lie in between those of its constituent metal components, or attributed to synergistic effects between the alloy constituents, pushing the performance of the alloy beyond the simple linear interpolation of those of its individual components. Bimetallic alloys have been shown to help escape the linear scaling relations governing CO* and HCO*, given that the latter interacts with the surface through either the carbon or oxygen atom, unlike CO* which only adsorbs through carbon. This might also be true of the H–CO*, if the transition state does not completely resemble the dehydrogenated state; e.g. if CO* gets tilted enough at the transition state to allow the oxygen end to interact with the surface. If one of the two

components of the bimetallic alloy binds oxygen significantly differently than the other component binds carbon, then we may arrive at a bifunctional catalyst that potentially escapes the linear scaling relations on monometallic catalysts. This bifunctionality was suggested to preferentially stabilize HCO* compared to CO* over the stepped surfaces of several bimetallic alloys for the electrochemical reduction of CO/CO₂ [101]. A drawback was the low stability for most of the suggested alloys, especially in the aqueous environment typical of electrochemistry. In this regard, it is worth mentioning that high entropy (quinary) alloys have been recently proposed as potentially stable and active for the electrochemical CO₂/CO reduction [102].

A special case of bimetallic alloys that have proven to be quite useful in escaping scaling relations is single atom alloys (SAAs). In SAAs, a solute metal exists in very dilute concentrations in the top layer or the immediate sublayer of the host metal. A Pt or a Pd atom embedded in other transition metals were suggested to stabilize the transition state of hydrogen dissociation without affecting the adsorption energy of atomic hydrogen [103], among several other examples for industrially-relevant chemistries [104–107]. While the massively combinatorial search space for bimetallic alloys (including bulk alloys, core@shell alloys, and SAAs) offers a great potential to arriving at surfaces that stabilize H–CO* independently of CO*, and despite exciting advances in the inorganic synthesis community aiming at depositing metal layers atop nanoparticles or shape-selected nanocrystals of other metals [108–115], realizing certain alloy compositions/morphologies experimentally or preserving the structures of their unique active sites under reaction conditions (e.g. against segregation/aggregation) remains an open challenge [116–121].

5 Conclusions and Outlook

We presented a trends analysis study of CO hydrogenation to methanol on the terraces and steps of transition metals, by first investigating the rate-determining step: CO* hydrogenation to HCO*, then by studying a full microkinetic model. By plotting the rate of methanol synthesis versus the formation energies of CO* and H–CO* (or other methanol synthesis transition states) as descriptors, we show a fundamental limitation for transition metal catalysis for methanol synthesis, as imposed by linear scaling relations between the formation energy of CO* and those of the transition states along the hydrogenation pathway to methanol. The challenge in this catalysis is to find catalytic materials that are able to escape these linear scaling relations, significantly stabilizing the transition states independently of CO*, and/or destabilizing CO* independently of the transition states.

The expansive search space of materials to be explored invites clever techniques to more efficiently achieve a thorough exploration and discovery of catalytic materials that escape the unfavorable linear scaling relation of CO^* and H-CO^* , while performing as few DFT calculations as possible. In recent years, machine learning has emerged as a powerful tool in exploring materials search space, with special focus on the design and discovery of catalytic materials [122–126]. Recent studies employing machine learning rely on Bayesian statistics to train algorithms on data sets (either computed or derived from materials data repositories [127]) to rapidly predict relevant properties (e.g. descriptors) from the structures of proposed materials. Indeed, several recent reports have focused on relating the catalytic behavior to electronic or structural properties like generalized or orbital-wise coordination numbers [128–130], site-specific stabilities [131–134], or *d*-band moments [135], all of which are properties that machine learning models could be trained to predict on the fly. Machine learning models including non-linear regression techniques, neural networks, and Gaussian process regression have been recently employed to describe adsorption energies of important intermediates in methane to methanol conversion [136], CO/CO_2 electro-reduction and the hydrogen evolution reaction [102, 137], methanol electrooxidation [138], and oxygen evolution reaction [139]. Finally, we also note that machine learning surrogate models have been suggested to calculate transition states at a fraction of the computational cost required by explicit DFT (e.g. via the nudged elastic band method) [140–142], thus making another case for using machine learning to screen materials based on transition state energies as descriptors.

In the end, we would like to discuss a few kinetic pathways that we did not investigate in this study. Specifically, the water–gas shift reaction is quite active on $\text{Cu}(211)$ [34], $\text{Cu}(111)$ [42] and other surfaces studied here. On either Cu surface, the reaction mechanism was calculated to proceed through a COOH^* mechanism (while HCOO^* acted as a spectator), and water dissociation to H^* and OH^* was rate-limiting. The water–gas shift reaction is significantly faster than CO (or CO_2) hydrogenation to methanol, allowing the water–gas shift reaction to equilibrate under methanol synthesis conditions. A more complete description of the kinetics of methanol synthesis should include reaction pathways for the water–gas shift reaction, as well as CO_2 hydrogenation. Additionally, higher methanol composition in the reaction mixture—a possibility on surfaces that succeed in improving the methanol yield—could affect the overall methanol yield and selectivity. To simulate this scenario, methanol was added to the synthesis gas composition in a microkinetic model for the (211) facet of transition metals [43]. As a result, selectivity towards ethanol increased at the expense of methanol, which was attributed to higher CH_3O coverage (C-O bond scission is easier in CH_3O than in CO

and an increased rate for subsequent C–C coupling elementary steps. This observation could set an additional design constraint on the new materials we proposed. In addition to lowering the barrier for C–H bond formation, C–C bond formation and C–O bond dissociation should be simultaneously suppressed. These additional constraints—however challenging given the myriad possible pathways through which C–C coupling could take place—would ensure a robust screening and computational design approach to achieve materials that would take us a step closer to the methanol economy.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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