Prevalence of Bimolecular Routes in the Activation of Diatomic Molecules with Strong Chemical Bonds (O₂, NO, CO, N₂) on Catalytic Surfaces

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CONSPICUOUS: Dissociation of the strong bonds in O₂, NO, CO, and N₂ often involves large activation barriers on low-index planes of metal particles used as catalysts. These kinetic hurdles reflect the noble nature of some metals (O₂ activation on Au), the high coverages of co-reactants (O₂ activation during CO oxidation on Pt), or the strength of the chemical bonds (NO on Pt, CO and N₂ on Ru). High barriers for direct dissociations from density functional theory (DFT) have led to a consensus that “defects,” consisting of low-coordination exposed atoms, are required to cleave such bonds, as calculated by theory and experiments for model surfaces at low coverages. Such sites, however, bind intermediates strongly, rendering them unreactive at the high coverages prevalent during catalysis. Such site requirements are also at odds with turnover rates that often depend weakly on cluster size or are actually higher on larger clusters, even though defects, such as corners and edges, are most abundant on small clusters. This Account illustrates how these apparent inconsistencies are resolved through activations of strong bonds assisted by co-adsorbates on crowded low-index surfaces.

Catalytic oxidations occur on Au clusters at low temperatures in spite of large activation barriers for O₂ dissociation on Au(111) surfaces, leading to proposals that O₂ activation requires low-coordination Au atoms or Au-support interfaces. When H₂O is present, however, O₂ dissociation proceeds with low barriers on Au(111) because chemisorbed peroxides (O-OOH* and HOOH*) form and weaken O–O bonds before cleavage, thus allowing activation on low-index planes. DFT-derived O₂ dissociation barriers are much lower on bare Pt surfaces, but such surfaces are nearly saturated with CO* during CO oxidation. A dearth of vacant sites causes O₂* to react with CO* to form OOCO* intermediates that undergo O–O cleavage. NO–H₂ reactions occur on Pt clusters saturated with NO* and H*; direct NO* dissociation requires vacant sites that are scarce on such surfaces. N–O bonds cleave instead via H*-assistance to form HNOH* intermediates, with barriers much lower than for direct NO* dissociation. CO hydrogenation on Co and Ru occurs on crowded surfaces saturated with CO*; rates increase with increasing Co and Ru cluster size, indicating that low-index surfaces on large clusters can activate CO*. Direct CO* dissociation, however, occurs with high activation barriers on low-index Co and Ru surfaces, and even on defect sites (step-edge, corner sites) at high CO* coverages. CO* dissociation proceeds instead with H*-assistance to form HCOH* species that cleave C–O bonds with lower barriers than direct CO* dissociation, irrespective of surface coordination. H₂O increases CO activation rates by assisting H-additions to form HCOH*, as in the case of peroxide formation in Au-catalyzed oxidations. N₂ dissociation steps in NH₃ synthesis on Ru and Fe are thought to also require defect sites; yet, barriers on Ru(0001) indicate that H*-assisted N₂ activation — unlike O₂, CO, and NO — is not significantly more facile than direct N₂ dissociation, suggesting that defects and low-index planes may both contribute to NH₃ synthesis rates.

The activation of strong chemical bonds often occurs via bimolecular reactions. These steps weaken such bonds before cleavage on crowded low-index surfaces, thus avoiding the ubiquitous kinetic hurdles of direct dissociations without requiring defect sites.

INTRODUCTION

Low-index planes of noble metal surfaces are often unable to activate diatomic molecules containing double or triple bonds, such as O₂, NO, N₂, and CO (in order of increasing bond dissociation energies (BDE)).¹ via direct interactions with ensembles of bare metal atoms. Bare Au(111) surfaces do not even activate O₂ (weakest bond among these molecules).²,³ such kinetic hurdles have led to proposals indicating O₂ dissociation occurs on low-coordination sites at edges or corners of Au nanoparticles,²—⁴ or at atomic contacts between Au clusters and reducible oxides.⁴—⁶ Bare Pt(111) surfaces, in contrast, dissociate O₂ with low activation barriers, but become saturated with chemisorbed CO (CO*) during CO oxidation; in such cases, a dearth of vacant sites and strong adsorbate–adsorbate interactions render any exposed Pt atoms less reactive (more noble) by a combination of electronic and steric effects, leading to higher barriers and lower O₂...
CO oxidation on Au

Au nanoparticles catalyze the oxidation of CO (to CO2),26 propene (to propylene oxide),27 and alkanols (to aldehydes and carboxylic acids) in gaseous28 or aqueous23,29 phases at low temperatures (<400 K). The reactivity Au demonstrates contradicts large O2 dissociation barriers on extended Au(111) surfaces (190–215 kJ mol\(^{-1}\)).2,3 Higher turnover rates on smaller Au clusters have suggested that low-coordination sites are necessary for O2 dissociation,2–4 while higher turnover rates on reducible supports have implicated Au-coordinated O2.2,3

These studies have suggested that strong bonds cleave on bare surfaces at low-coordination surface atoms. Such atoms, however, may bind adsorbed species strongly and remain inaccessible for direct dissociation steps during catalytic cycles at high coverages often prevalent during catalysis. Such coverages are inaccessible in theoretical studies of flat extended surfaces, but prevail on curved surfaces (where low-index planes are in contact with edge, corner, and defect sites), which allow coverages near saturation, consistent with spectroscopic and kinetic observations.8,19,20

Here, we show how diatomic molecules with strong bonds dissociate predominantly via reactions with vicinal co-adsorbed species on crowded low-index surfaces relevant for catalysis, instead of dissociating on vacant terrace or defect sites, which are scarce and less reactive than on bare surfaces. As will be described, H* (from H2) adds to CO* and NO* to weaken their strong bonds by forming *HCOH* and *HNOH*, (*—* indicates binding at two vicinal sites) before C–O or N–O cleavage.19,21,22 Co-adsorbed H2O can act as a co-catalyst in forming O–H bonds in *OOH/*HOOH* (from O2) and *HCOH* (from CO) to mediate O–O23–25 and C–O20 activations. NO* species disproportionate to form N2O and O*;22 CO* species react with O*,2 to form CO2 and O* when H2 and H2O are absent, consistent with the prevalence of bimolecular events even in the absence of a reductant. These bimolecular routes carry an entropic penalty because their transition states are larger and more ordered than those for unimolecular dissociations, but have lower enthalpy barriers, which compensate for unfavorable entropies at the modest temperatures (300–600 K) of these catalytic reactions.

catalyzed oxidations of CO and alkanols in gaseous (Au/SiO2 doped with NaOH)33 or alkaline aqueous (Au/TiO2 and Au/C) media.23,29

Kinetic and isotopic studies have shed light on the mechanism for H2O-assisted O2 dissociation during CO oxidation on small Au clusters (<5 nm).25 CO oxidation rates increased with increasing H2O pressure, and ultimately decreased as H2O* or H2O-derived species (such as OH*) cover Au surfaces at higher pressures (Figure 1). Such enhancements are not caused by water–gas shift reactions, because CO2 did not form from CO–H2O reactants and H2O was not consumed during CO–O2 reactions. CO2 formation rates increased with increasing CO and O2 pressure (Figure 1) in a manner consistent with Langmuir–Hinshelwood rate equations on surfaces with CO* and O2* present below saturation coverages.

These data are consistent with kinetically-relevant transition states requiring the concurrent involvement of species derived from CO, O2, and H2O. OOH* species can form via quasi-equilibrated proton transfer from H2O to O2* (step 1.4 in Scheme 1), and their O–O bond can then cleave by assistance from CO* (step 1.5). OH* species formed (in steps 1.4 and 1.5) can then react in a kinetically-irrelevant step to re-form H2O (step 1.6), which acts as a co-catalyst in this cycle. Scheme 1 leads to a rate equation:

\[
n = \frac{a([CO][O_2][H_2O])^{2/3}}{[1 + K_{CO}[CO] + K_{O_2}[O_2] + K_{H_2O}[H_2O]^2]} \quad (3)
\]
which accurately describes all CO oxidation rate data (288 K, 0.80–8.25 kPa CO, 0.25–7.15 kPa O2, 0.03–1.15 kPa H2O) on Au clusters, irrespective of support (Al2O3, TiO2, and Fe2O3).23 Such similar rate equations and mechanistic interpretations for all supports stand in sharp contrast with previous proposals that O2 activation occurs at Au–TiO2,24 but not Au–Al2O3 interfaces. The effects of support on turnover rates under anhydrous conditions (0.54 and 0.08 mol s$^{-1}$ (g-at Au$_{surf}$)$^{-1}$ on TiO2 and Al2O3, respectively) may reflect instead trace amounts of H2O adsorbed on such supports, which leaves the reactor with time on stream, leading to the rapid deactivation ubiquitous without added H2O.34 H2O (0.5 kPa) increased CO oxidation rates and eliminated support effects on turnover rates (2.55 vs 2.70 mol s$^{-1}$ (g-at Au$_{surf}$)$^{-1}$) on TiO2 vs Al2O3, respectively). Highly dispersed Au particles have been shown to be necessary for C–H and O–H activations of formic acid (HCOOH). Formic acid decomposition turnover rates (to H2 and CO2 in the absence of H2O) decreased by a factor of ~10 upon treatment of Au/Al2O3 with 20% O2/He (1000 K for 2 h), which sintered small Au moieties (undetectable by TEM) required for HCOOH decomposition.34 Similar treatments, however, did not affect CO oxidation turnover rates on Au/Al2O3, indicating that such small structures are not required for O2 dissociation when H2O is present.

H-addition to O2* before its dissociation was also proposed in Au-catalyzed oxidations of alkanols and polyols.7 Kinetic and isotopic data, together with DFT calculations, indicated that ethanol and glycerol react with OH groups (present in aqueous media or on Au surfaces) in multiple steps to form acetic and glyceric acids, respectively. C–H and O–H bond activations during oxidative alcohol dehydrogenation proceed via *OH-assisted pathways rather than via reactions with the Au surface,33 similar to proposals for O*-assisted activations on Au surfaces doped with O* via O3 decomposition.35 Alkanol reactions with 18O2/H218O incorporated only 18O within the acids formed at low conversions (reactions with 16O2/H218O incorporated only 18O), indicating that OH groups (from H2O) act as the oxidants. O2 reacts with H2O at Au–solvent interfaces to form *OOH and *HOOH* species via sequential proton-transfer reactions; the latter species, detected as H2O2, side products, dissociate to form *OH, thus replacing the OH groups consumed. These cycles at Au–solvent interfaces represent two local electrochemical half-reactions:

\[
\text{RCH}_2\text{OH} + 4\text{OH}^- \rightarrow \text{RCOOH} + 2\text{H}_2\text{O} + 4e^- \quad (4)
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (5)
\]

**Scheme 1. Mechanism for CO Oxidation on Au**

\[
\begin{align*}
\text{CO} + * & \rightarrow \text{CO}^* \quad (1.1) \\
\text{O}_2 + * & \rightarrow \text{O}_2^* \quad (1.2) \\
\text{H}_2\text{O} + * & \rightarrow \text{H}_2\text{O}^* \quad (1.3) \\
\text{O}_2^* + \text{H}_2\text{O}^* & \rightarrow \text{OOH} + \text{HO}^- \quad (1.4) \\
\text{OOH} + \text{CO} & \rightarrow \text{OH} + \text{CO}_2 + * \quad (1.5) \\
\text{OH} + \text{HO}^- & \rightarrow \text{H}_2\text{O} + \text{O}^- \quad (1.6) \\
\text{CO} + \text{O}^- & \rightarrow \text{CO}_2 + 2* \quad (1.7)
\end{align*}
\]

The circled double arrow indicates a quasi-equilibrated reaction.

**CO Oxidation on Pt**

Low-temperature (360–473 K) CO oxidation on Pt occurs on surfaces saturated with CO* as with CO hydrogenation (Fischer–Tropsch synthesis) on Ru and Co catalysts.39,40 CO oxidation rates are proportional to O2 pressure and inversely dependent on CO pressure on Pt8,37 (Figure 2), Pd,39 and Rh38 catalysts:

\[ r = \frac{a[O_2]}{[1 + K_{CO}[CO]]} \quad (6) \]

The first-order dependence on O2 pressure may reflect irreversible molecular O2 adsorption as the sole kinetically-relevant step (step 2A.2 in Scheme 2),37 which requires that...
Scheme 2. Mechanisms for Low-Temperature CO Oxidation on Pt-Group Metals

\[
\text{CO} + \text{O}^* \rightarrow \text{O} + \text{CO}^* \tag{2.1}
\]

**Irreversible O2 adsorption and direct O2 dissociation**

\[
\text{O}_2 + \rightarrow \text{O}_2^* \tag{2A.2}
\]

\[
\text{O}_2^* + \rightarrow 2 \text{O}^* \tag{2A.3}
\]

\[
\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2 + 2^* \tag{2A.4}
\]

**Reversible O2 adsorption and CO*-assisted O2 dissociation**

\[
\text{O}_2 + \rightarrow \text{O}_2^* \tag{2B.2}
\]

\[
\text{O}_2^* + \text{CO} \rightarrow \text{OOCO}^* \tag{2B.3}
\]

\[
\text{OOCO}^* \rightarrow \text{CO}_2 + \text{O}^* + 2^* \tag{2B.4}
\]

\[
\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2 + 2^* \tag{2B.5}
\]

O2* dissociation occurs with smaller barriers than O2* desorption, consistent with theoretical treatments on bare Pt(111) surfaces.7 At 0.44 ML CO* coverage, however, O2* desorption barriers are 33 kJ mol\(^{-1}\) smaller than those for O2* dissociation, indicating that molecular O2 adsorption would be quasi-equilibrated during steady-state catalysis at relevant CO* coverages. Quasi-equilibrated adsorption (step 2A.2) and subsequent O2* dissociation on vicinal vacancies (*) (step 2A.3) would give rates proportional to [CO]\(^{-2}\) on CO*-saturated surfaces, while quasi-equilibrated dissociation (step 2A.3) and subsequent irreversible reactions of O* with CO* (step 2A.4) would give rates proportional to [O2]\(^{-1}\). These two routes have been proposed previously but are inconsistent with rate data.57–59

DFT treatments at CO* coverages near 1 ML require nanoparticle models (cuboctahedral Pt201 consisting of 201 atoms; ∼1.5 nm diameter) because flat extended surfaces cannot sufficiently relax CO* adlayers.8 On Pt201 clusters with 1 ML CO*, O2* adsorption requires vacancy formation events (CO* desorption) that are endothermic (79 kJ mol\(^{-1}\)). O2* species react with vicinal CO* to form OOCO* species (step 2B.3 in Scheme 2) with small barriers (15 kJ mol\(^{-1}\)). The subsequent dissociation of OOCO* into CO2 and O* (step 2B.4) is essentially barrierless (2 kJ mol\(^{-1}\)), indicating that OOCO* formation is irreversible and that bimolecular O2 dissociation routes prevail over direct O2 dissociation events that require additional energetically disfavored CO* desorption events. Unlike O2 dissociation on Au, O2 can dissociate via direct interactions with Pt atoms on low-index bare surfaces, but such surfaces become covered with CO* during steady-state catalysis, rendering them much less reactive than bare Pt surfaces. CO* also binds strongly to Rh and Pd surfaces, which exhibit identical CO oxidation rate equations (eq 6),38,39 suggesting that O2 dissociation occurs via bimolecular mechanisms similar to Scheme 2B on Rh and Pd catalysts.

**NO REDUCTION BY H2 ON Pt**

Nitric oxide (NO) (BDE of 631 kJ mol\(^{-1}\)) has a significantly stronger bond than O2 (BDE of 498 kJ mol\(^{-1}\)).1 As a result, NO dissociation barriers (236 kJ mol\(^{-1}\))22 are much higher than those for O2 (31 kJ mol\(^{-1}\))7 on bare Pt(111) surfaces.

NO–H2 reactions occur at modest temperatures (<500 K), thus making H2 an attractive reductant. Previous studies of H2, H2O, and O2 effects on NO–H2 rates and selectivities for Pt,41 Pd,42 and Rh43 catalysts have reached contradictory conclusions about the mechanism for NO activation. Large NO* dissociation activation barriers (236 kJ mol\(^{-1}\)) have led to proposals that NO* activation must require step-edge defect sites on Pt18 and Ru47 based on theoretical assessments on extended bare surfaces.

NO–H2 turnover rates are proportional to H2 pressure at low pressures (<5 kPa H2) and become independent of H2 pressure at higher pressures (>500 kPa) (Figure 3),22 consistent with NO activation via Scheme 3D on surfaces saturated with NO* and H* species (and few vacant sites), leading to rates,

\[
r = \frac{a[\text{NO}][\text{H}_2]}{[K_{\text{NO}}^\text{NO}][H_2]^{1/2} + K_{\text{NO}}]} \tag{7}
\]

consistent with those measured (1–760 kPa H2 at 0.2 kPa NO (●), 398 K) and at <5 kPa H2 (inset, 383 K) at 0.1 kPa NO (▲), 0.3 kPa NO (●), and 0.5 kPa NO (▼) on 0.6 wt % Pt/Al2O3 (4.4 nm Pt clusters).22

![Figure 3. Effects of H2 on NO–H2 turnover rates from 1 to 760 kPa H2 at 0.2 kPa NO (●), 398 K) and at <5 kPa H2 (inset, 383 K) at 0.1 kPa NO (▲), 0.3 kPa NO (●), and 0.5 kPa NO (▼) on 0.6 wt % Pt/Al2O3 (4.4 nm Pt clusters).22](image-url)
described by eq 7.\textsuperscript{18} $H^*$-assisted NO$^*$ activation via NOH$^*$ intermediates (Scheme 3C) is mediated by a transition state with only one H atom, leading to a $[H_2]^{0.5}$ numerator term of the rate law that is inconsistent with eq 7. $H^*$-assisted NO$^*$ activation via sequential H-additions to form $^*HNOH$ species (Scheme 3D) is consistent with rate data (eq 7), and exhibits the lowest enthalpy and free energy barriers (relative to an NO$^*$-covered surface) among the four routes in Scheme 3 at all NO$^*$ coverages (Figure 4). These data and theoretical treatments indicate that bimolecular NO activation routes prevail over direct routes at all coverages, in contrast with O$_2$ dissociation during CO oxidation on Pt, which occurs via bimolecular routes only at high CO$^*$ coverages because of a dearth of vacant sites. Such differences reflect the much stronger bonds in NO (than O$_2$), which render even bare Pt(111) surfaces less reactive for direct dissociation than for $H^*$-assisted dissociation routes that weaken N–O bonds by H atoms. In the absence of $H_2$ such as during NO reduction with CO, NO$^*$-assisted NO$^*$ activation reactions prevail over direct NO$^*$ dissociations, and reactions of NO$^*$ with CO$^*$ (similar to O$_2^*$–CO reactions in Scheme 2B) may become relevant.

\section*{FISCHER–TROPSCH SYNTHESIS ON Co AND Ru CATALYSTS}

Fischer–Tropsch synthesis (FTS) produces liquid fuels from synthesis gas (CO + H$_2$) derived from natural gas, coal, or biomass.\textsuperscript{40} The pathways by which C–O bonds cleave have remained controversial.\textsuperscript{10,11,14,15,21,40,44} C–O bonds in CO$^*$ can dissociate directly to form $C^*$ and $O^*$ via reactions with vicinal vacant sites ($^*$), which are present as minority species on the CO$^*$-saturated surfaces prevalent in practice. CO$^*$ can also react with $H^*$ to weaken its C–O bond before cleavage in $H^*$-assisted CO activation mechanisms. FTS occurs on Co and Ru surfaces nearly saturated with CO$^*$, as shown from measured rates that depend inversely on CO pressure (Figure 5) and infrared spectra during FTS.\textsuperscript{19,21,40,45–47} FTS rates are proportional to $H_2$ pressure on Co and Ru catalysts at all relevant FTS reaction conditions (453–520 K; Figure 5). The accepted rate equation for this reaction (eq 8)\textsuperscript{19,21,40,45,46} is

\begin{equation}
\text{FTS} = \frac{k \cdot [\text{CO}] \cdot [\text{H}_2]}{[\text{Pt}]} \text{mol}\text{-gcat}^{-1}\text{atm}^{-1}
\end{equation}
Large barriers for direct CO\* dissociation (step 4A.3 in Scheme 4) on Co(0001) (230 kJ mol\(^{-1}\))\(^9\) and Ru(0001) (227 kJ mol\(^{-1}\))\(^10\) are consistent with large BDE values for CO (1070 kJ mol\(^{-1}\)), and have led to proposals that direct CO\* dissociation requires low-coordination surface sites (e.g., steps or edges). These conclusions are consistent with CO\* dissociation rates at 450–500 K on atomically stepped Ru(109) surfaces, which were suppressed by blocking step-sites with C atoms.\(^14\) Indeed, DFT-derived direct CO\* dissociation barriers on bare stepped surfaces of Co\(^{9,11}\) (68–136 kJ mol\(^{-1}\)) and Ru\(^{10,11}\) (47–89 kJ mol\(^{-1}\)) are much smaller than on Co(0001) and Ru(0001) surfaces. FTS, however, occurs on curved surfaces crowded with CO\* on which a dearth of vacant sites and the strong binding of CO\* at low-coordination sites render such sites unavailable for FTS turnovers. Furthermore, turnover rates on Co\(^{10,44}\) and Ru\(^48\) catalysts increase with increasing particle size, and become constant for particles larger than 6–10 nm, indicating that turnovers predominantly occur on low-index terrace sites prevalent on larger clusters. H\*-assisted CO\* activation fully reconciles (1) rates that are proportional to H\(_2\) pressure, (2) particle size effects that show that CO\* activates on low-index terrace sites, and (3) DFT treatments indicating that CO\* cannot activate directly on such low-index Co and Ru surfaces, but can do so on such surfaces via H\*-assistance.

The evidence for defect-catalyzed CO\* dissociation during FTS turnovers\(^9\),\(^11,14,15\) was obtained from theory and experiments on essentially bare surfaces, instead of surfaces that are nearly saturated with CO\* present at practical FTS conditions.\(^19,21,40,43,44\) Recent theoretical studies of CO\* activation on sites with varying coordination on curved surfaces at catalytically relevant CO\* coverages\(^9,20\) have resolved these enduring contradictions by demonstrating that H\*-assisted CO\* activation is preferred over direct CO\* dissociation at all sites, irrespective of their metal-atom coordination.\(^19,20\) These studies used the curved surfaces of small cuboctahedral Ru particles (~200 atoms, ~1.7 nm, shown in Figure 6), which allow exothermic CO\* adsorption (~108 kJ mol\(^{-1}\)) even at 1 ML coverages, in contrast with the endothermic adsorption prevalent on flat extended Ru(0001) surfaces (+18 kJ mol\(^{-1}\)).\(^19,20\) The very different adsorption energies of CO\* on Ru\(^{201}\) particles and Ru(0001) extended surfaces at 1 ML CO\* are not reflected in their respective bare surfaces, on which CO\* binds with similar strength (Ru(0001), ~160 kJ mol\(^{-1}\); Ru\(^{201}\), ~159 kJ mol\(^{-1}\)).\(^19\) High CO\* coverages cause longer Ru–Ru bonds and lateral CO\* adlayer relaxation on Ru\(^{201}\) particles; these are absent in periodic Ru(0001) surfaces due to the periodic nature of these calculations.

The Ru particles in these recent studies expose low-index terrace sites, step-edge (B\(_5\)) sites, and corner sites, thus allowing a rigorous theoretical assessment of coordination effects on C–O bond cleavage via direct and H-assisted routes.\(^19\) Intrinsic barriers for direct CO\* activation on step-edge sites are much larger at 1.07 ML CO\* on Ru\(^{201}\) (150 kJ mol\(^{-1}\)) than at 0.25 ML CO\* on Ru(010\(\overline{5}\)) surfaces (89 kJ mol\(^{-1}\))\(^10\) because of repulsion among co-adsorbed CO\*. Effective activation barriers (which include the CO\* desorption energy to form the required vacancy) for direct CO\* dissociation on step-edge sites (269 kJ mol\(^{-1}\)) are smaller than on low-index Ru(111) terraces (322 kJ mol\(^{-1}\); Figure 6), but remain much larger than measured activation energies (~120 kJ mol\(^{-1}\))\(^19\) and those for H-assisted CO\* activation.

In H\*-assisted CO\* dissociation routes on low-index planes of Ru\(^{201}\) particles, the first H-addition forms HCO\* (step 4B.3) in a quasi-equilibrated step; the second H\* addition is irreversible and forms *HCOH\* (Figure 6), whose C–O bond then cleaves to form CH\* and OH\* (step 4B.4).\(^19\) CO\* activation thus proceeds via H\*-assisted routes involving *HCOH\* formation and dissociation.\(^21\) These H\*-assisted routes lead to...
the rate equation (eq 8) that describes most reported FTS rate data on Co and Ru catalysts at conditions relevant to their practice.\textsuperscript{19,21,40,45,46} The effective activation barrier for H*-assisted CO activation is 165 kJ mol\textsuperscript{-1}, a value 104–191 kJ mol\textsuperscript{-1} smaller than that for direct CO\textsuperscript*} dissociation on terrace (322 kJ mol\textsuperscript{-1}), corner (356 kJ mol\textsuperscript{-1}), or step-edge (269 kJ mol\textsuperscript{-1}) sites (Figure 6).\textsuperscript{19} These DFT-derived barriers show that CO* species react with H* on crowded low-index Ru surfaces to form *HCOH* species before C–O activation, instead of reacting with vacant sites present as minority species during FTS catalysis. Parallel calculations performed on Co(0001) surfaces at 0.5 ML CO* are also consistent with CO* activation via *HCOH* intermediates.\textsuperscript{21} These H*-assisted CO activation routes are analogous to the H*-assisted NO activation routes via *HNOH* intermediates described earlier in this Account.

O atoms in CO are predominantly removed as H$_2$O during FTS on Co and Ru catalysts.\textsuperscript{19,21,40} H$_2$O increases FTS rates on Co\textsuperscript{40,47,49} and Ru\textsuperscript{20} catalysts (Figure 5) but at high pressures decreases rates because of competitive adsorption of H*-derived species and CO-derived reactive intermediates. H$_2$O decreases activation barriers from 152 to 75 kJ mol\textsuperscript{-1} for H-addition to CO* to form COH* (steps 4C.3 and 4C.4),\textsuperscript{20} which allows COH* formation steps, otherwise kinetically inaccessible, to become quasi-equilibrated. These COH* species H-bond with H$_2$O and react with another H* to form *HCOH*, which cleaves its C–O bond (to form CH* and OH*) in the kinetically-relevant step (step 4C.5). The effective enthalpy barrier (which includes energies for all steps forming the kinetically-relevant transition state from a CO\textsuperscript*-covered surface) for the H$_2$O-mediated route is 129 kJ mol\textsuperscript{-1}, which is 64 kJ mol\textsuperscript{-1} lower than for the "anhydrous" H*-assisted route. This enthalpic stabilization is partially offset by entropy losses caused by H$_2$O binding at H$_2$O-mediated transition states that lead to H$_2$O-assisted DFT-derived free energy barriers 5 kJ mol\textsuperscript{-1} larger than for anhydrous routes rather than the 8 kJ mol\textsuperscript{-1} lower values that were experimentally measured, but consistent with their parallel contributions to CO activation pathways.\textsuperscript{20} Such H$_2$O effects on O–H formation rates were described above for O$_2$ activation in Au-catalyzed reactions. H$_2$O-mediated H*-assisted CO dissociation provides another example of how co-adsorbed species weaken (via reduction) and assist the cleavage of strong molecular bonds. These routes become most influential at the high coverages prevalent during catalysis, because surfaces contain few, weakly-binding exposed atoms, and defect sites stabilize unreactive species.

### AMMONIA SYNTHESIS ON Fe AND Ru

N$_2$ dissociation during NH$_3$ synthesis on Ru and Fe was one of the first reactions proposed to take place on defect sites.\textsuperscript{12,13} Biological N$_2$ fixation in nitrogenases, in contrast, occurs at near-ambient temperatures via sequential addition of H*/e\textsuperscript{-} pairs (from MgATP hydrolysis) to N$_2$ to form bound NH$_2$NH$_2$ species before N–N cleavage.\textsuperscript{60}

DFT-derived free energy barriers for direct and H*-assisted (via NNH* formation and dissociation) N–N cleavage on bare Ru(0001) surfaces were similar (247 kJ mol\textsuperscript{-1}) at 673 K.\textsuperscript{51} These values give a ratio of direct to H*-assisted activation rates,

\[
\frac{r_{\text{direct}}}{r_{\text{H-assist}}} = e^{((\Delta G_{\text{fl-diss}}^2 - \Delta G_{\text{fl-diss}}^{\text{H-assist}})/(RT))(H_2/\text{bar})^{-0.5}} \tag{9}
\]

that is smaller than one at high-pressure NH$_3$ synthesis conditions (600–773 K, >5 bar H$_2$), Figure 7. H*-assisted N$_2$ cleavage that occurs through transition states with more H atoms (N$_2$H$_x^*$) shows larger effective free energy barriers (≥286 kJ mol\textsuperscript{-1}) than direct or H*-assisted N$_2$ activation via NNH*, ruling out such routes. Thus, on Ru(0001) surfaces, H*-assisted N$_2$ activation (via NNH*) prevails over direct dissociation; however, its barrier (247 kJ mol\textsuperscript{-1}) is higher than expected from measured turnover rates; thus, step-edge sites may be required for N$_2$ activation at the temperatures of NH$_3$ synthesis practice.\textsuperscript{15} Further investigation is required to determine the kinetic effects of H$_2$ pressure and relevant coverages of abundant surface intermediates, such as NH$_2^*$ (x = [0, 3]) species.

### OUTLOOK

Experimental and theoretical inquiries into the reactivity of bare extended surfaces tend to magnify the significance of defect sites in activations of strong chemical bonds. In doing so, a seemingly consistent picture of reactivity obscures what matters most at high coverages often present at practical conditions of catalysis. Theoretical treatments, when brought to these relevant considerations through the use of curved surfaces, show how low-index planes are able to activate strong bonds through bimolecular events involving co-adsorbed intermediates. The methods to address crowded and curved surfaces, in theory and experiment, are available. DFT calculations can examine surfaces of metal particles (~500 atoms), which contain exposed atoms with different coordination. The relaxation of intermolecular repulsion on such curved surfaces allows monolayer coverages, while dispersive forces, now incorporated into many functional accounts, for van der Waals forces that strongly influence the stability of adsorbed intermediates and
transition states at high coverages. Rate, isotopic, and spectroscopic data at conditions of strict kinetic control have sharpened our proposals about the relevant intermediates and their reaction paths. Today, experiment and theory are closer than ever before to being able to probe the same chemical event at the level of surface-catalyzed elementary steps occurring within the local environments that prevail during the practice of relevant catalysis. After more than a century of inquiry into the mechanistic details of heterogeneous catalysis, we find surprises, brought to light by the emerging clarity of our inquiries.

**SUMMARY**

High coverages, often present in catalytic practice, result in few vacancies at defect sites, which are made more inert through co-adsorbate interactions but are catalytically significant on bare surfaces for direct activations of strongly bound diatomic species (O2, NO, and CO). Low-index surfaces, inactive for direct dissociation, instead catalyze bimolecular reactions between co-adsorbed reagents and these species. H-addition reactions (from H2 or H2O) act to reduce the double or triple bonds present in O2, NO, and CO to *HOOH*, *HNOH*, and *HCHO* intermediates prior to bond cleavage. Similarly, direct reactions of O2→CO, NO→NO*, and NO→*CO result in O=O or N=O cleavages without H-involvement or direct dissociation across vacancies. These bimolecular routes are entropically disfavored compared to direct dissociation because of the involvement of multiple reagents within their transition states, but such penalties are compensated by lower activation enthalpies that govern rates at the modest temperatures (300–600 K) common in the reactions described in this Account.

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Notes

The authors declare no competing financial interest.

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