HCOOH Volcano Curve

Revisiting Formic Acid Decomposition on Metallic Powder Catalysts:

Exploding the HCOOH Decomposition Volcano Curve

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Abstract:

This study revisits the classic volcano curve for HCOOH decomposition by metal catalysts by taking a modern catalysis approach. The metal catalysts (Au, Ag, Cu, Pt, Pd, Ni, Rh, Co and Fe) were prepared by H₂ reduction of the corresponding metal oxides. The number of surface active sites (Ns) was determined by formic acid chemisorption. *In situ* IR indicated that both monodentate and bidentate/bridged surface HCOO* were present on the metals. Heats of adsorption (ΔH_{ads}) for surface HCOO* values on metals were taken from recently reported DFT calculations. Kinetics for surface HCOO* decomposition (k_{rds}) were determined with TPD spectroscopy. Steady-state specific activity (TOF = activity/Ns) for HCOOH decomposition over the metals was calculated from steady-state activity ($\mu\text{mol/g-s}$) and Ns ($\mu\text{mol/g}$). Steady-state TOFs for HCOOH decomposition weakly correlated with surface HCOO* decomposition kinetics (k_{rds}) and ΔH_{ads} of surface HCOO* intermediates. The plot of TOF vs. ΔH_{ads} for HCOOH decomposition on metal catalysts does not reproduce the classic volcano curve, but shows that TOF depends on both ΔH_{ads} and decomposition kinetics (k_{rds}) of surface HCOO* intermediates. This is the first time that the classic catalysis study of HCOOH decomposition on metallic powder catalysts has been repeated since its original publication.

Keywords: formic acid, decomposition, catalysts, metal, unsupported, volcano curve

1. Introduction

Sabatier famously hypothesized that the best catalyst for a given reaction will possess a moderate binding strength of the reaction intermediate complex with the catalyst surface.[1] Sachtler and Fahrenfort experimentally investigated this hypothesis for the decomposition of formic acid (HCOOH) by a series of transition metal powder catalysts and obtained the classic “volcano curve,” shown in Fig. 1 [1], that has been taken as strong support for Sabatier’s hypothesis. The Sachtler-Fahrenfort volcano curve plots the formic acid decomposition temperature (T_r) at a fixed conversion ($\log r = -0.8$), as the representative kinetic parameter (high activity (rate) corresponds to a low values of T_r and vice versa) vs. the thermodynamic heat of formation of *bulk* metal formate (HCOO-M), as the correlating parameter representative of the *surface* intermediate compound. The metals on the left slope, such as Ag and Au, were interpreted to be adsorption-limited while metals on the right slope, such as Ni and Cu, were concluded to be decomposition-limited. The metals towards the top of the curve, such as Pt and Ir, were assigned to moderately binding surface formate intermediates having the optimum steady-state catalytic reactivity for HCOOH decomposition.

Fig. 1 The Sachtler- Fahrenfort volcano curve[1]

The Sachtler-Fahrenfort volcano curve has been accepted as proof of Sabatier’s hypothesis, but a close examination of the Sachtler-Fahrenfort study raises several concerns not generally appreciated: 1) Sachtler-Fahrenfort only studied unsupported, *bulk* Ni and Au powder catalysts and the data for the remaining metals were collected from seven different investigations of HCOOH decomposition on unsupported, *bulk* Ag, Pt, Pd, Ir, Rh, Ru, Cu, Co, Fe and W powder catalysts by other researchers,[1] which introduces significant experimental variability from lab-to-lab of the set of data; 2) the reaction rate

of formic acid decomposition (T_r) is normalized by the surface area of the *bulk* metal catalysts, but the low surface areas of the *bulk* metal catalysts may contribute to significant experimental error in reaction rates; 3) the appropriate reactivity parameter, which was not used, is the turnover frequency (TOF: HCOOH molecules converted per exposed active metal site per second) that allows comparison of specific reaction rates among the metal catalysts[2]; and 4) the heat of formation of the *bulk* metal formates was estimated from statistical mechanics, which represents the stability of the *bulk* metal formates and not *surface* metal formates that represent the reaction intermediate complexes with the catalyst. The stability of the *bulk* metal formates is not an appropriate metric for generating relationships with a surface property such as catalytic activity.

The Madix group extensively examined decomposition of surface HCOO* intermediates with temperature programmed decomposition (TPD) spectroscopy and model, well-defined single crystal metals (Ag, Au, Pt, Pd, Ru, Ni, Cu, Co and Fe) [3]. The TPD method, however, only measures the decomposition of the surface formate intermediates and does not provide information about the kinetics of the preceding HCOOH adsorption step. The TPD results reveal that just the decomposition rate of surface HCOO* exhibits the volcano-type curve behavior when the decomposition temperature, T_d , is plotted on the Sachtler-Fahrenfort plot. This brings into question the conclusion that the low steady-state activity for HCOOH decomposition rates for Ag and Au catalysts in the Sachtler-Fahrenfort plot is solely due to the adsorption step being rate limiting [1].

The continued interest in the classic Sachtler-Fahrenfort volcano curve plot has also attracted recent extensive density functional theory (DFT) calculations for HCOOH decomposition on slabs of metal surfaces with different facets [4,5]. The DFT studies examined the decomposition of HCOOH via two reaction pathways: formation of CO₂ and H₂ via surface HCOO* intermediates and formation of CO and H₂O via surface COOH* intermediates. Herron *et al.* systematically examined different facets of Au, Ag, Cu, Ni, Pd, Pt, Rh, Ir, Co, Ru, Os and Re for their interaction with HCOOH and its reaction intermediates. The DFT calculations suggested that the first dehydrogenation step, producing COOH* or HCOO*, is most facile on under-coordinated sites of reactive metals (those on the left of the transition metals in the Periodic Table (Re, Ru and Os)), while the second dehydrogenation step, elimination of CO₂, is mostly driven on highly coordinated sites of the relatively inert metals (those on the right of the transition metals in the periodic table (Cu, Ag, and Au)). This suggests that the optimal catalyst balances these requirements and should lie in the middle of the transition metals (Pt and Pd). The structure of the metal surface was also found to affect the two dehydrogenation steps, but each step responded differently to changes in the metal facet. These DFT calculations suggest that HCOOH decomposition on Ir facets is unfavorable, in contrast to the experimentally observed high activity of Ir for this decomposition reaction

(see Figure 1). The Yoo *et al.* DFT calculations also incorporated the decomposition of COOH^* to CO_2 and H^* reaction pathway for Ag, Cu, Pd, Pt and Rh surfaces and extended the results to other metals (Au, Ru, Ir and Ni) by application of scaling methods applied to the adsorption energies of reaction species. Incorporation of the scaling relations into a microkinetic model allowed determination of TOFs for formic acid decomposition over the metal surfaces. Formic acid decomposition was found to primarily take place via dehydrogenation ($\text{CO}_2 + \text{H}_2$) rather than dehydration ($\text{CO} + \text{H}_2\text{O}$). The precious metals (Ir, Pd, Pt, Ru and Rh) were calculated to show high rates for hydrogen production while the coinage metals ($\text{Cu} > \text{Ag} \sim \text{Au}$) indicated lower reaction rates reflecting a volcano-type relationship when the TOFs were plotted vs. adsorption energies of reaction intermediate complexes. Both theoretical calculations revealed the sensitivity of the HCOOH decomposition to the nature of the exposed metal facets and metal particle size. The inherent assumption of the theoretical calculations is that the metal surfaces remain clean and do not become contaminated during the HCOOH decomposition reaction, but experimental studies have shown that as much as ~ 0.5 - 0.6 monolayer coverage of C and O may accumulate on the metal catalyst surface during steady-state HCOOH decomposition [6].

Several research groups have also investigated supported metal catalysts containing metallic nanoparticles for formic acid decomposition and determined the TOF values by titration of the exposed metal atoms, but the number of metals examined in each study was limited. Solymosi *et al.* measured the TOFs for Pt group metals supported on carbon and found the specific reactivity varied as $\text{Ir} \sim \text{Pt} \sim \text{Pd} > \text{Ru} > \text{Rh}$ [7]. Bulushev *et al.* only studied HCOOH decomposition on only Pd/C, Au/ TiO_2 and Au/C and found the specific rates to be $\text{Pd/C} > \text{Au/TiO}_2 > \text{Au/C}$ [8]. Ojeda *et al.* showed that highly dispersed gold nanoparticles supported on Al_2O_3 can exhibit considerable formic acid decomposition activity even exceeding that of supported Pt nanoparticles [9]. The reported supported metal catalyst studies, however, are complicated by particle size (dispersion), quantum size and support effects while the DFT and Sachtler-Fahrenfort studies involve unsupported, bulk metal catalysts. Thus, it is difficult to attempt to relate the catalytic results for supported metal nanoparticles with those of Sachtler-Fahrenfort or the DFT calculations that focused on large metallic particles and slabs, respectively.

The objective of this investigation is to experimentally examine HCOOH decomposition on the same unsupported, bulk metal catalysts studied by Sachtler-Fahrenfort and apply a modern catalysis approach that focuses on catalyst surface aspects (metal surface composition, number of catalytic active sites, nature of surface intermediate, HCOOH adsorption equilibrium, surface intermediate decomposition temperature and specific steady-state reaction rates). Importantly, all the measurements will be systematically performed in one laboratory that will reduce the variability of the catalysts from eight different laboratories found in the original Sachtler-Fahrenfort study and allow direct comparison of the

catalysts. Surprisingly, there has not been any attempt in more than five decades to reproduce the classic Sachtler-Fahrenfort volcano curve for unsupported, bulk metal catalysts shown in Figure 1.

2. Experimental

2.1 *Synthesis of Metal Catalysts via H₂ - Temperature Programmed Reduction (TPR)*

The selected metals closely matched those in the Sachtler-Fahrenfort study. The only catalyst available in metallic form was Au (Alfa Aesar, 99.9994%), but a mild reduction with 10% H₂/Ar at 200 °C for 2 hours was applied to remove any passive oxide layer. The other metal catalysts (Cu, Co, Fe, Ag, Ni, Rh, Pt and Pd) were reduced from their bulk metal oxides, which were commercially available with research grade purity: CuO (Johnson Matthey, Puratronic, 99.995%), Co₃O₄ (Alfa Aesar, 95%), Fe₂O₃ (Alfa Aesar, 99.99%), Ag₂O (Sigma-Aldrich, 99.99+%), NiO (Alfa Aesar, Puratronic, 99.998%), PtO₂ (Alfa Aesar, Premion, 99.95%) and PdO (Alfa Aesar, 99.9%). The Rh₂O₃ powder was obtained from rhodium (III) nitrate hydrate, Rh(NO₃)₃•xH₂O (Sigma-Aldrich), by thermal treatment in air at 500 °C for 5 hours and subsequently reduced to Rh metal.

The metal oxides were reduced to their metals by H₂-temperature programmed reduction (TPR), which provided information that ensured complete reduction of the metal oxides to metals was achieved. The H₂-TPR was performed on an Altamira temperature programmed system (AMI-200) monitored by an online thermal conductivity detector (TCD). Metal oxides were dehydrated prior to reduction, and then were treated in 10% H₂/Ar to a maximum temperature of 800 °C with a heating rate of 10 °C/min. The temperature when the TCD signal returns to zero signifies the point when hydrogen is no longer being consumed and the oxide has completely been reduced to the metal. This temperature was used for pretreatment of bulk oxide catalysts prior to formic acid decomposition.

2.2 *High Sensitivity Low Energy Ion Scattering (HS-LEIS) Spectroscopy*

The surface composition of the metallic powders was determined with a High Sensitivity- Low Energy Ion Scattering (HR-LEIS) spectrometer system (ION-TOF Qtac¹⁰⁰). HS-LEIS is a surface-analysis technique with an extremely high sensitivity (ca. 3 Å) to the outermost atomic layer of a surface. The HS-LEIS experiments were carried out with beam of mono-energetic rare gas ions (typically He⁺, Ne⁺ or Ar⁺ with energies of 1-5 keV) that were directed perpendicularly onto the sample. In this study, 5 keV He⁺ and 3keV Ne⁺ beam were used to check the surface purity of metal catalysts. Atoms are sputtered away from the target surface as a consequence of ion bombardment; therefore, it provided a depth profile of the elements in the sample.

2.3 Thermal gravimetric Analyzer (TGA)

The number of active surface sites for HCOOH chemisorption on metallic powders were determined using a Cahn TGA microbalance (Model TG-131) coupled with a PC for temperature control, weight monitoring and data collection. A flow diagram of the apparatus setting on similar experiment was reported in previous publication.[10] The system allowed a controlled flow of high purity 10% H₂/He during pre-treatment, ultra-high purity Ar for flush, and gas phase 2000 ppm HCOOH in He (GT&S, Inc) for chemisorption. The number of active surface sites was measured by quantifying the amount of chemisorbed formic acid at 100 °C, at which temperature co-adsorbed physisorbed HCOOH has been shown to be minimized.

2.4 HCOOH Temperature Programmed Decomposition (TPD) Spectroscopy

The HCOOH-TPD spectroscopy measurements were performed on an Altamira temperature programmed system (AMI-200) equipped with an online quadrupole mass spectrometer (Dycor Dymaxion DME200MS). Metal oxide samples ranging from approximately 0.2 – 0.7 g were loaded into a “U” shaped quartz bubble tube and initially reduced in 10% H₂/Ar for 120 min at the reduction temperature corresponding to that found during the TPR experiments described above to form the corresponding bulk metal. After cooling to 100 °C, the catalyst was flushed with flowing He for 20 min to remove any possible physically adsorbed gases. Then 2000 ppm HCOOH in He (30 ml/min) was introduced for 60 min at the adsorption temperature which is in the supplementary information. The ideal adsorption temperature was 100 °C, because below this temperature physical adsorption of HCOOH is more likely to occur. Due to low surface area of bulk metal catalysts and a high reactivity of some of metal catalyst, lower adsorption temperatures were sometimes necessary-for successful product detection with the mass spectrometer (MS). After formic acid adsorption, the samples were again purged at the adsorption temperature with flowing He for an additional 50 min to remove any residual physically adsorbed formic acid. The HCOOH-TPD experiments were performed with a heating rate of 10 °C/min in flowing UHP He (30 ml/min) and the desorbing molecules were monitored with the online MS. The m/e values employed to detect the different desorption products were HCOOH (m/e = 46 and 29), H₂ (m/e = 2), CO (m/e = 28), CO₂ (m/e = 44) and H₂O (m/e = 18).

2.5 HCOOH-Temperature-Dependent-Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

The temperature-dependent DRIFTS measurements were collected with a Thermo Scientific Nicolet 8700 Research FT-IR spectrometer with a liquid nitrogen cooled MCT detector. The IR spectrometer

equipped with a Harrick Praying Mantis accessory (model DRA-2) and a Harrick reaction chamber HT-100. In a typical HCOOH temperature-dependent DRIFTS experiment, metal powders were synthesized in the Harrick cell from their corresponding metal oxides in 10% H₂/Ar for 120 mins at their corresponding peak reduction temperatures as determined by H₂-TPR experiments. The pretreated sample was (i) cooled down in 10% H₂/Ar to 110 °C; (ii) the gas stream was switched to ultra-high purity Ar flow at 110 °C for 20 mins to remove any residual H₂ and possible H₂O formed during reduction, and (iii) further cooled down to the corresponding adsorption temperature of formic acid. Formic acid chemisorption was performed by flowing gas phase formic acid (2000 ppm HCOOH in He) (30 ml/min) for 60 mins at the pre-described adsorption temperature in supplemental information. The sample was then purged at the same temperature with flowing UHP He for 20 mins to remove any residual physisorbed HCOOH. The complete removal of physisorbed HCOOH was confirmed by the absence of characteristic IR bands of physisorbed HCOOH (2960, 2620, 1720, 1230 and 980 cm⁻¹)[11]. The DRIFTS spectra were recorded from the adsorption temperature to 400 °C with a heating rate of 10 °C/min. The DRIFTS spectra were recorded every 1-2 minutes (15-20 °C) with spectra resolution of 2 cm⁻¹. The temperature dependent-DRIFTS spectra identified the configuration of *surface* formate species present and monitored the thermal decomposition of the surface formates at elevated temperature.

2.6 HCOOH-Steady state catalytic activities in fixed-bed reactor

The steady state catalytic activity of the unsupported, bulk metal catalysts for formic acid decomposition were obtained in a fixed-bed catalytic reactor (Pyrex glass tubing, 1/4" OD and 1 ft long) at atmospheric pressure. The temperature was controlled by a Digi PID temperature controller (Series 2600). The gas product was analyzed by an on-line gas chromatograph (HP 5840) equipped with TCD and FID detectors and a packed column (Carboxene-1000) for formic acid. The system allowed a controlled flow (Brooks model 5850E series flow controller) of treatment gases: 10% H₂ in Ar for pretreatment of metal surface, helium for purge, and gas phase formic acid for adsorption experiments. Typically about 0.20 g of metal was used for formic acid decomposition. The steady state measurements were performed at 250 °C with a flow of 100 mL/min of gas phase 2000 ppm formic acid in He (GT & S Inc.). The HCOOH conversion was maintained below 2% to ensure differential reaction conditions. The specific TOF (1/s) values were determined by dividing the catalytic activity (HCOOH molecules converted/(g-s)) with the number of active surface sites (HCOOH molecules adsorbed/g) for each metal catalyst.

3. Results

3.1 Surface Composition

The surface compositions of the metallic powders were analyzed with HS-LEIS spectroscopy (see Figures S1-S9 in the Supporting Information) and almost all the surfaces, with only the exception of Ni, were found to possess trace amounts of alkali (Na and K) impurities. The Co, Ni, Fe and Pd samples were also found to contain unidentified heavy elements and Au also showed traces of iodine. Depth profile analysis of the metals indicated that the impurities gradually disappear within 7-10 cycles of inert ion (He^+ and Ne^+) sputter reflecting their surface segregation (see Figures S5-S9 in the Supporting Information). The oxygen present on the metallic powders is from the passive oxide layer formed upon exposure of the samples to the ambient atmosphere. The surface analysis of the metallic powders reveals that bulk metal catalysts are not completely impurity free despite using research grade reagents.

3.2 Thermal gravimetric analysis (TGA)

The number of active surface sites (N_s) on the metal powder catalysts was measured by equilibrium adsorption of HCOOH at 100°C and the values are presented in Table 1. The He purge prior to TPD ensured that no residual physisorbed HCOOH was left on the surface at this temperature, which was confirmed by the lack of any characteristic IR bands of physisorbed HCOOH (2960, 2620, 1720, 1230 and 980 cm^{-1} (see section 2.5). The N_s values are normalized on a weight basis rather than on a surface area basis due to concerns over the possible introduction of error by surface area measurements of the low surface area metallic powders. The N_s values of metallic powders increase in the order of $\text{Cu} < \text{Pt} < \text{Ag} < \text{Pd} < \text{Rh} < \text{Co} < \text{Au} < \text{Ni} < \text{Fe}$ and the trend may reflect the surface areas of the metals. The surface areas of the metallic powders are not needed since the specific catalytic activity will also be normalized on a weight basis and TOF ($1/\text{s}$) = activity ($\mu\text{mol/g-s}$)/ $N_s(\mu\text{mol/g})$.

Table 1 Number of active surface sites (N_s) for metallic powders determined by HCOOH equilibrium adsorption ($\mu\text{mol/g}$)

Catalyst	Cu	Pt	Ag	Pd	Rh	Co	Au	Ni	Fe
$N_s(\mu\text{mol/g})$	1.6	1.9	7.6	9.9	1.5×10^1	3.1×10^1	5.2×10^1	1.6×10^2	1.8×10^2

3.3 Temperature dependent- diffuse reflectance infrared Fourier transform spectroscopy (TD-DRIFTS)

The DRIFTS vibrational frequencies of the surface intermediates on the reduced metallic powders upon HCOOH adsorption are summarized in Table 2 and compared with the vibrations reported for well-defined single crystals. All the catalysts exhibit IR bands at $\sim 2830\text{-}2940 \text{ cm}^{-1}$ and $\sim 1360\text{-}1390 \text{ cm}^{-1}$ characteristic of the $\nu(\text{CH})$ and $\nu_s(\text{OCO})$ vibrations for surface HCOO^* species. There is no indication in the IR spectra that surface carboxylate (OH-C=O) intermediates are present (see Figures S10-S11 for the

representative IR spectra), since these would give rise to $\nu(\text{HOC}=\text{O})$ bands at high $\sim 1700\text{-}1820\text{ cm}^{-1}$ for some of the metals that are not present in any of the spectra [4]. The difference in wavenumber ($\Delta\nu$) between the $\nu_s(\text{OCO})$ and $\nu_{as}(\text{OCO})$ vibrations of surface HCOO^* intermediates facilitates distinguishing between monodentate or bidentate/bridged surface formates. The bidentate/bridged surface formate generally exhibits smaller $\Delta\nu$ values than monodentate surface formate. If $\Delta\nu > 220\text{ cm}^{-1}$, it is generally considered to be monodentate surface formate; if $\Delta\nu \leq 220\text{ cm}^{-1}$, it is generally considered to be bidentate/bridged surface formate.[12] For instance, the $\Delta\nu$ of $\nu_s(\text{OCO})$ and $\nu_{as}(\text{OCO})$ of the surface formate on Cu is 200 cm^{-1} and the $\Delta\nu$ of $\nu_s(\text{OCO})$ and $\nu_{as}(\text{OCO})$ on Ni is 241 cm^{-1} suggesting that the surface formate on Cu is bidentate/bridged and that the surface formate on Ni is monodentate, respectively.

Table 2 Comparison of vibrational frequencies (in wavenumber, cm^{-1}) for *surface* formate intermediates on metallic powders and those on metal single crystals (obtained from indicated references)

Catalyst	$\nu_s(\text{OCO})$		$\nu_{as}(\text{OCO})_{\text{bi}}$		$\nu_{as}(\text{OCO})_{\text{mono}}$		$\nu(\text{CH})$	
	Metallic Powder	Single Crystal	Metallic Powder	Single Crystal	Metallic Powder	Single Crystal	Metallic Powder	Single Crystal
Cu	1376	1352[13]	1576	1560[13]			2881	2855[13]
Au	1373	1380[14]	1585	1500[14]			2862	2930[14]
Pt	1383	1340[15]	1588	-	-		2859	2950[15]
Rh	1361	1330[16]	1581	-		-	2939	2910[16]
Co	1367	1363[17]		-	1610	1614[17]	2827 2777	2778 2692[17]
Ni	1371	1365[18]			1629	-	2919	2840[18]
Fe	1369	1360[19]		-	1610	-	2919	2895[19]
Ag	1388	1340[20]	-	1570[20]	1616	1660[20]	2865	2870 2900[20]
Pd	1358	1340[21]	-	-	1616	1660[21]	2860	2865[21]

3.4 *HCOOH-Temperature Programmed Decomposition (TPD) Spectroscopy*

The HCOOH -TPD spectra from the metallic powders yielded the decomposition gas products of CO_2 , H_2 , CO and H_2O (the latter was not monitored). The HCOOH -TPD spectra for Co are shown in Fig.

2 and all the decomposition products appear simultaneously at a peak temperature (T_p) of $\sim 167^\circ\text{C}$. The H_2O spectrum is not shown since the line from the catalyst bed to the MS was not heated and water vapor was held up in the line. The CO decomposition product in Figure 2 was corrected for cracking of CO_2 in the MS and is a real reaction product. The CO_2/CO product ratios for the different metals are given in Table 3 and show that all metal powder catalysts form both CO_2 and CO suggesting that surface HCOO^* decomposition proceeds via the dehydrogenation and dehydration pathways. The CO_2/CO ratio varied as $\text{Cu} > \text{Au} > \text{Co} > \text{Ni} \sim \text{Fe} > \text{Pt} > \text{Pd} > \text{Rh} > \text{Ag}$. No relationship could be ascertained between the nature of the surface formates and the CO_2/CO selectivity since metallic catalysts exhibiting comparable CO_2/CO selectivity exhibited both monodentate and bidentate/bridged surface formates (compare Tables 2 and 3). The T_p values of all the metal catalysts are displayed in Table 4. The HCOOH -TPD measurement shows that the decomposition of the surface HCOO^* intermediates on the metal powders follows the trend $\text{Pt} > \text{Cu} > \text{Pd} > \text{Co} > \text{Au} > \text{Ni} > \text{Ag} > \text{Fe} > \text{Rh}$. The activation energy (E_a) and 1st-order rate constant (k_{rds}) values for HCOOH decomposition on the metal powders are also summarized in Table 4. The 1st-order rate constant for surface HCOO^* decomposition on the metal powders varies by a factor of $\sim 10^5$ among the catalysts reflecting their wide range of surface reactivity at the reference temperature of 250°C , which corresponds to the steady-state reaction studies below.

Fig. 2 TPD spectra of HCOOH decomposition on Co metallic powder (adsorption of HCOOH occurs at 100°C)

Table 3 Nature of formate based on IR vibrations and the CO₂/CO ratio from formic acid TPD on metallic powders

Metallic powder	Nature of Surface Formate	CO ₂ /CO
Ag	Mono	0.05
Pd	Mono	2.0
Fe	Mono	3.5
Ni	Mono	3.6
Co	Mono	3.9
Rh	Bridged	1.6
Pt	Bridged	2.5
Au	Bridged	6.0
Cu	Bridged	7.5

Table 4 TPD kinetic data for decomposition of adsorbed formic acid from metallic powders

Catalyst	T _p (°C)	CO ₂ /CO molar ratio	E _a ^a (kcal/mol)	k _{rd_s} ^b (s ⁻¹)
Rh	265	1.6	36.8	1.03 x 10 ⁻³
Fe	249	3.5	35.7	2.99 x 10 ⁻³
Ag	243	0.05	35.7	4.57 x 10 ⁻³
Ni	190	3.6	31.6	1.89 x 10 ⁻¹
Au	176	6.0	30.6	5.05 x 10 ⁻¹
Co	167	3.9	30.0	9.49 x 10 ⁻¹
Pd	128	2.0	27.3	1.45 x 10 ¹
Cu	123	7.5	26.9	2.06 x 10 ¹
Pt	90	2.5	24.6	2.07 x 10 ²

^a Calculated using Redhead equation assuming 1st-order kinetics[22]; ^b Calculated using kinetic expression:

$$k_{rds} = \nu * \exp(x \frac{E_a}{RT}), \nu = 10^{13} \text{ s}^{-1} \text{ and } T \text{ is the reference reaction temperature of } 250^\circ\text{C}$$

3.5 TOF values

Turnover frequency (TOF) is the proper metric to use for quantification and comparison of catalytic reactivity of a series of heterogeneous catalysts and is defined as molecules converted per active surface site per second. The TOF values for HCOOH decomposition by the series of metal powders are given in Table 5. The steady-state TOF values for the series of metal powder catalysts vary markedly, $\sim 10^5$ - 10^6 , reflecting the significant differences in reactivity among the metal powder catalysts for HCOOH decomposition (Co < Fe < Ag < Au < Ni < Rh < Pd < Cu < Pt).

Table 5 Number of active surface sites (Ns), and steady-state activity and TOF for formic acid decomposition by metallic powders at 250°C.

Catalyst	N _s ^a (μmol/g)	HCOOH Activity 250 °C ^b (μmol/g•s)	TOF 250 °C ^c (s ⁻¹)
Co	3.1 x10 ¹	9.3 x10 ⁻²	3.0 x 10 ⁻³
Fe	1.8 x10 ²	4.0 x10 ⁰	2.2 x 10 ⁻²
Ag	7.6 x10 ⁰	3.0 x10 ⁰	3.9 x 10 ⁻¹
Au	5.2 x10 ¹	4.0 x10 ¹	7.7 x10 ⁻¹
Ni	1.6 x10 ²	1.5 x 10 ³	9.3 x10 ⁰
Rh	1.5 x10 ¹	4.8 x10 ¹	3.3 x10 ⁰
Pd	9.9 x10 ⁰	1.6 x 10 ²	1.6 x10 ¹
Cu	1.6 x 10 ⁰	5.2 x10 ¹	3.2 x10 ¹
Pt	1.9 x10 ⁰	1.8 x 10 ³	9.8 x10 ²

^a Obtained from TGA experiments; ^b obtained from steady-state activity experiments with fixed-bed reactor;

^c calculated from $\text{TOF} = \frac{\text{HCOOH Activity}}{N_s}$

3.6 Comparison between specific reactivity (TOF) for steady-state HCOOH decomposition and kinetics of surface formate intermediate decomposition by metallic powders

The steady-state TOF values for HCOOH decomposition are compared to the decomposition kinetics (k_{rds}) of the surface HCOO^* intermediates in Figure 3. There is a weak correlation between the steady-state TOF and surface HCOO^* decomposition kinetics suggesting that the more reactive surface formates lead to higher steady-state specific activity. However, there is some scatter in the data points and quite different TOF values were obtained for similar surface formate decomposition kinetics (compare Ni, Au, and Co or Rh, Ag, and Fe). The data points in Figure 3 are also color coded to identify those metal catalysts forming monodentate and bidentate/bridged surface formates, but no relationship could be ascertained between the nature of the surface formate intermediates and their TOF and k_{rds} values.

Fig. 3. Plot of steady-state specific catalytic activity (TOF) for HCOOH decomposition vs. kinetics for *surface* formate decomposition (k_{rds}). Metals in blue form monodentate surface formates and metals in red form bidentate/bridged surface formates. $R^2 = 0.40$.

4. Discussion

4.1 Surface composition of metallic powders and their effect on kinetics

Surface analysis of the metallic powders reveals that unsupported, bulk metallic catalysts contain traces of surface impurities (Na, K, I and heavy metals as shown in Figures S1-S9 in the Supporting Information) even though the concentrations of surface impurities of the research grade metals in the present study are probably lower than would have been present in the original Sachtler-Fahrenfort study.

Furthermore, the catalyst surface can also pick up significant amounts of O and C during steady state HCOOH decomposition.[23-25] Fundamental HCOOH-TPD studies with well-defined single crystals have shown that surface K and O do affect the decomposition rates of adsorbed formic acid. Since it is an electron donor, surface O stabilizes surface formate (T_p increases with increasing loading of surface O) and since it is an electron acceptor, surface K^+ destabilizes surface formate (T_p decreases with increasing loading of surface K^+).[26] The reactivity of HCOOH on Ni(110) was diminished when the surface was covered with carbide and graphite overlayers.[27,28] The T_p values for HCOOH-TPD of well-defined single metal crystals and the corresponding metallic powders are compared in Figure S12 and show that, with the exception of Cu, the T_p values are higher on the metal powders than the single crystals. Note that the T_p values for the single crystals are lower than the corresponding metal powder values despite the fact that the much higher heating rates employed in the single crystal studies shift the T_p values to higher values. The lower T_p for HCOOH decomposition on Cu metallic powder than Cu(110) [29] single crystal was also previously reported.[30] Thus, it appears that the clean single crystals are generally more reactive than the metallic powders. The DFT studies also indicate that HCOOH decomposition is a structure sensitive reaction that depends on the exposed metal surface facets.[4, 5] The presence of surface impurities, multiple exposed facets and surface defects for the metallic powder complicates direct reactivity correlations with clean well-defined single crystals and theoretical calculations with model surfaces. This suggests that the most meaningful relationships will be derived by comparing the reactivity of the transition metals for HCOOH decomposition within each type of catalyst system (single crystals, model facets and metallic powders).

4.2 Searching for volcano curves

The appropriate plot for examining a possible volcano curve relationship for HCOOH decomposition on metallic powders is the TOF vs. ΔH_{ads} . The TOF parameters represent the specific catalytic reactivity and the ΔH_{ads} constants contain the term for the strength of the interaction of HCOOH with the metal surfaces (increasing with stronger heat of adsorption). In the absence of experimental data from *in situ* calorimetry, the ΔH_{ads} values are taken from the DFT-calculated binding energies of HCOO* intermediates on the (111) metal surfaces [5]. Although, these surface ΔH_{ads} values represent single crystals, this data is preferred over the bulk ΔH_f values used in the original HCOOH decomposition volcano curve since it reflects the *surface interaction* rather than the *bulk* formation. The resulting plot of TOF vs. ΔH_{ads} in Figure 4 has a weak trend somewhat consistent with volcano-type variation, but also contains data points for Ag and Co that deviate significantly from a volcano curve relationship. The left side of the curve consists of Au << Pd < Pt that follows increasing ΔH_{ads} values suggesting that the TOF increases with heat of adsorption. The lower TOF for Au is also influenced by a slower k_{rds} rate constant

for surface HCOO^* decomposition ($\text{Au} < \text{Pd} < \text{Pt}$ in Figure 3). The correlation on the right side of the curve consists of $\text{Pt} > \text{Cu} > \text{Ni} > \text{Rh}$ that follow increasing ΔH_{ads} values suggesting that the TOF decreases with heat of adsorption. This trend, however, also parallels the k_{rds} rate constants for surface HCOO^* decomposition ($\text{Rh} < \text{Ni} < \text{Cu} < \text{Pt}$ in Figure 3). Thus, both the ΔH_{ads} and k_{rds} constant influence the overall steady-state TOFs and it is difficult to assign the increase in TOF for the left side of the curve solely to increasing ΔH_{ads} that enhances HCOOH adsorption and the decreasing TOF for the right side of the curve to further increase in ΔH_{ads} that holds onto HCOO^* more strongly. This conclusion is in agreement with the conclusion made 35 years ago by Madix for single crystal metals that only the decomposition of the surface HCOO^* intermediates results in a volcano curve plot and, thus, the HCOOH heat of adsorption cannot be the only dominating parameter for HCOOH decomposition by bulk metal catalysts.[3]

Fig. 4: Plot of steady-state specific catalytic activity (TOF) for HCOOH decomposition vs. ΔH_{ads} for *surface* formate from DFT calculations of HCOO binding energies on metal (111) surfaces [5]. The curve on the left side results from a linear fit of Au, Pd, and Pt ($R^2 = 0.37$). The curve on the right side results from a linear fit of Pt, Cu, Ni, and Rh ($R^2 = 0.51$).

It needs to be emphasized that the above plot in Figure 4 is also far from being consistent with a volcano curve. For example, Pt, Pd and Ag possess similar ΔH_{ads} values, but their TOFs vary by a factor of $\sim 10^4$. The two data points that do not fall on the curve are Ag and Co. The very low overall TOF for

the Ag catalyst primarily results for the slow surface HCOO^* decomposition rate constant since the $\text{HCOOH } \Delta H_{\text{ads}}$ on Ag (111) has an intermediate value. Surprisingly, Co shows a low TOF value for HCOOH decomposition despite an intermediate k_{rds} . The low TOF cannot be attributed to a high ΔH_{ads} alone, since Co has a ΔH_{ads} that is the same as Rh. Finally, it is noteworthy to mention that when compared to the classic Sachtler-Fahrenfort volcano curve, Rh has moved from the left hand side to the right hand side. Regardless of whether or not the proper metrics are used, the outliers in the plot in Figure 4 demonstrate that specific catalytic activity (TOF) may not always be a simple function of a single descriptor. The situation is rather more complicated, requiring both descriptors of surface adsorption and surface reactivity, as demonstrated by recent DFT results [4,5].

4.3 Comments about Sachtler-Fahrenfort volcano curve

In spite of the many limitations of the Sachtler-Fahrenfort volcano curve for the classic HCOOH decomposition on metallic powder catalysts [1], it would be of interest to compare the previous metrics to the ones determined from modern catalysis science methods. Barteau is among the first to challenge the volcano-type correlation by studying formic acid decomposition. Instead of a volcano-type correlation, he observed only the right side of the volcano – a linear free-energy correlation (LFEC) exists within the same column of transition metals on the Periodic Table [29], but correlating parameter in that plot were the same heats of adsorption of bulk formates from the Sachtler-Fahrenfort volcano curve. Also, Given that the HCOOH decomposition catalytic data for the Sachtler-Fahrenfort study came from eight different catalysis laboratories, the variability among the reactivity data must have been quite high. The present investigation overcame this lab-to-lab reactivity variability issue by performing all the studies in one laboratory. Therefore, the new TOF and ΔH_{ads} catalyst metrics are herein compared with the T_{r} and bulk ΔH_{f} parameters used in the original volcano curve study.[1] The plot of T_{r} vs. ΔH_{ads} is shown in Figure 5 and reveals a significant weakening of the volcano correlation when compared to the classic Sachtler-Fahrenfort curve (compare to Figure 1). Once again, Rh is has switched from the left hand side to the right hand side, since the DFT calculation of ΔH_{ads} indicates that Rh is limited by HCOO^* decomposition. This finding is in agreement with the low value of k_{rds} (see Figure 3), experimentally determined in the current study.

Figure 5: Plot of formate decomposition temperature (T_r) vs. ΔH_{ads} for *surface* formate from DFT calculations of HCOO binding energies on metal (111) surfaces [5]. The curve on the left side results from a linear fit of Au, Pd, and Pt ($R^2 = 0.57$). The curve on the right side results from a linear fit of Pt, Cu, Ni, Rh, and Co ($R^2 = 0.86$).

When the proper metric for specific catalytic activity (TOF) is plotted as a function of the bulk heat of formation of metal formates (ΔH_f) from the classic HCOOH decomposition volcano curve, the lack of a strong volcano correlation is readily apparent (Figure 6). For example, for essentially the same ΔH_f value there is a significant variation in the steady-state HCOOH decomposition specific activity (TOF nearly 3 orders of magnitude between Rh, Pd, and Pt). This is not surprising given that ΔH_f is a bulk parameter and ΔH_{ads} is the proper surface metric to use.

Fig. 6: Plot of steady-state specific catalytic activity (TOF) for HCOOH decomposition *vs.* ΔH_f for *bulk* metal formate formation. The curve on the left side results from a linear fit of Au, Ag, Pd, Pt, and Rh ($R^2 = 0.10$). The curve on the right side results from a linear fit of Pt, Pd, Rh, Cu, Ni, Fe, and Co ($R^2 = 0.44$). Data points for Pd and Rh were used in both fits since their proper “side” was ambiguous.

The plot of T_r *vs.* TOF is shown in Figure 7a exhibits a weak linear correlation ($R^2 = 0.60$). Similarly, the plot of HCOOH bulk ΔH_f *vs.* surface ΔH_{ads} shown in Figure 7b also yields a weak linear correlation ($R^2 = 0.65$). This suggests that the T_r activity parameter and the ΔH_f adsorption parameter used in the Sachtler-Fahrenfort study were somewhat representative of the specific reactivity and surface intermediate stability for the HCOOH decomposition by the bulk metal power catalysts. In the current state of catalysis science, there is no denying that the proper metrics for LFECs are derived from surface properties (i.e. TOF, k_{rds} , and ΔH_{ads}). Nonetheless, if the surface properties are serendipitously manifest in the bulk properties, then correlations remain possible. It remains necessary, however, to prove the relationship between surface and bulk exists, as done here (see Figure 7). The existence of the of the classic Sachtler-Fahrenfort volcano curve should not be taken as *a priori* evidence of bulk-surface relationships in other catalytic systems.

Figure 7: (a) Plot of format decomposition temperature (T_r) vs. steady-state specific catalytic activity (TOF) for HCOOH decomposition ($R^2 = 0.60$) and (b) plot of ΔH_f for *bulk* metal formate formation vs. ΔH_{ads} for *surface* formate from DFT calculations of HCOO binding energies on metal (111) surfaces ($R^2 = 0.65$) [5].

Beeck[31] used the heat of adsorption of ethylene (ΔH_{ads}) and the rate constants ($\log k$) as appropriate parameters to correlate to the thermal stability of *surface* intermediates and catalytic reactivity of metal catalysts, respectively. This study found that only the right slope of volcano curve was observed in the trend of reactivity of metal catalysts in the hydrogenation reaction of ethylene.

The use of improper metrics in the finding of the classic Sachtler-Fahrenfort volcano curve for HCOOH decomposition on metallic powder catalysts should not be taken as proof against the Sabatier hypothesis. The present investigation only demonstrates that the methodology used to establish the Sachtler-Fahrenfort volcano curve for HCOOH decomposition was flawed. For idealized metal surface facets employed in DFT calculations, volcano-type relationships between TOF and ΔH_{ads} are indeed found.[4,5] The situation, however, is much more complicated for metallic powder catalysts that can contain surface inorganic impurities, surface C and O residues from side reactions, and variable amount of surface defects and facet distribution. For example, the presence of surface C and O residues may cloud the true TOF values for HCOOH decomposition on some of the more reactive surface that have high affinity for C and O (Ni, Rh, Pt, Co and Fe). Thus, volcano-type curves for experimental catalytic reactions with metals should be viewed with caution because of all the complicating factors.

5. Conclusions

The classic Sachtler-Fahrenfort volcano curve for HCOOH decomposition by metal powder catalysts was revisited with application of a modern catalysis approach. Metallic powder catalysts contain inorganic surface impurities and may also accumulate significant surface concentrations of C and O from HCOOH decomposition side reactions. Furthermore, a mixture of exposed metal facets and surface defects are usually present for metallic powders. This suggests that it is not straightforward to compare well-defined single crystals with model metal facet surfaces used for DFT calculations and it is best to compare each type of data set independently. The classic volcano curve plot used the temperature for a fixed HCOOH conversion/ m^2 (T_r) as the reactivity descriptor. The low surface areas of the unsupported metal catalysts and the data collected from 8 different laboratories introduced significant experimental error in the collected T_r activity values. The classic volcano curve correlates the catalytic activity with the bulk ΔH_f of HCOO-M as the descriptor for the interaction of HCOOH with the metal surfaces, but ΔH_f is a bulk property and not directly related to surface phenomenon. Reexamining the HCOOH decomposition by metals with a modern catalysis approach employing TOF, ΔH_{ads} , and k_{rds} demonstrates that the classic volcano curve is not achieved since TOF is a function of both the ΔH_{ads} and k_{rds} descriptors. In the classic volcano curve plot, Sachtler-Fahrenfort assign the metals on the left side of the curve to those weakly interacting with HCOOH (Au and Ag) and the metals on the right side of the curve to those strongly interacting with HCOOH (Cu, Ni, Co, Fe, W). The new findings show that catalysts appearing on the left side of the plot may exhibit low TOFs because of low ΔH_{ads} and/or k_{rds} values, while catalysts appearing on the right side of the plot may also exhibit low TOFs because of low k_{rds} and/or ΔH_{ads} values. The current findings reveal that interpretation of the classic Sachtler-Fahrenfort volcano curve for HCOOH decomposition was rather naïve since the actual situation is much more complex with the catalyst surface containing inorganic impurities, C and O, multiple facets and defects that affect the TOF, ΔH_{ads} and k_{rds} HCOOH decomposition descriptors.

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