

Investigating the Volcano Curve Correlation for Formic Acid Decomposition on Bulk Metal Catalysts

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Introduction

Formic acid (HCOOH) decomposition has been used as a common test of catalytic activity due to the presence of the same surface HCOO* intermediate (chemisorbed formate) on the majority of metal and metal oxide surfaces [1, 2]. The Sachtler-Fahrenfort volcano curve is a famous result of such a study on bulk metal catalysts [3]. The volcano plot is one of the foremost illustrations of Sabatier's principle and has been used to design bimetallic catalysts for optimum activity based on the thermodynamics of adsorption [4].

The fundamental correlation resulting in the volcano plot between bulk heat of formation of formate and catalytic activity has raised some questions in the literature [1, 2, 5]. Primarily, work on bulk metal oxide catalysts analogous to that of Sachtler and Fahrenfort done by Fein and Wachs [2] showed weak or no correlations between formic acid decomposition activity and bulk heat of oxide formation. Thus the question is raised: Should one attempt to correlate bulk thermodynamic properties with a surface property such as specific catalytic activity?

In an attempt to definitively answer this question, catalytic activity data for formic acid decomposition over bulk metal catalysts was gathered using a modern approach: temperature programmed surface reaction (TPSR) spectroscopy and *surface* heats of adsorption by calorimetry. The surface heats of adsorption of formic acid on bulk metals will be correlated with the formate TPSR decomposition temperatures, T_p . If the same volcano plot results when catalytic activity (surface property) is correlated with surface heat of adsorption (surface property), then one can conclude that the bulk thermodynamic property in question is related to the surface property. Thus, the volcano plot will hold or be shown to be a coincidence of linear free energy relationships [1].

Materials and Methods

The HCOOH-TPSR spectroscopy experiments were performed on an Altamira temperature programmed system (AMI-200) equipped with an online quadrupole mass spectrometer (Dycor Dymaxion DME200MS). Gas phase formic acid (2000 ppm in He) was allowed to adsorb over the various metal catalyst: Cu, Co, Fe, W, Ag, Ni, Au, Pt, Pd, and Ru in the temperature range of 35 -100 °C. In some cases the bulk metal oxide was used as a precursor to the bulk metal and was first reduced in 10% H₂ in Ar at appropriately elevated temperatures that were previously determined by temperature programmed reduction experiments. The HCOOH decomposition temperatures, T_p , for each metal were measured during temperature ramping after adsorption.

Results and Discussion

The newly generated T_p data were plotted versus the bulk heats of formation of the formate reported by Sachtler and Fahrenfort. Rather than a volcano trend, the results show a striking similarity to Mark Barteau's work on linear free energy relationships (LFERs) [1]. Barteau concluded that LFERs should be examined within groups on the Periodic Table, but should not be expected to carry over when one makes jumps across groups. This conclusion is significant because it is the Brønsted-Evans-Polanyi (BEP) relation, which is a LFER, which results in the linearity of the left- and right-hand sides of the volcano plot. Surface heats of adsorption data will definitively show if any correlation exists between the bulk heat of formation and activity. However, a correlation between bulk and surface properties would only be a coincidence of a relationship between bulk heat of formation and surface heat of adsorption [2].

Significance

The volcano curve has been widely accepted for many decades as a truth in catalyst design and this acceptance has led many researchers to search for similar volcano correlations in other catalyst systems. This work hopes to shed light on when it is and when it is not appropriate to look for such correlations or to attempt to correlate certain properties. Only if a relationship exist between the bulk and surface property should a strong correlation exist, but initially it would seem best to attempt to correlate surface/surface properties.

References

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