

AScreening of desulfurization catalysts

Keywords: heterogeneous catalysis, desulfurization, fuels, computations

The present screening study demonstrates how the combination of experimental activity data, crystallographic information from structural databases, and first-principles computation of binding energies is used to identify potential new catalysts.

1 Applied example

Increasingly stringent environmental regulations required a lowering of sulfur in fuels. Desulfurization is accomplished by a catalytic process transforming sulfur-containing molecules into H_2S , which is removed from the liquid phase. Larger sulfur-organic molecules are more difficult to attack and new catalytic materials are needed. Measurements such as those reported by Pecoraro and Chianelli [2] show that transition metal sulfides containing the expensive metals Rh, Ir, Ru, and Os have a particularly high activity as hydrodesulfurization catalysts while other sulfides such as MnS and TaS₂ with more common metal atoms exhibit quite low activity. Given the large quantities of material to be processed, there is a strong incentive to find active catalysts containing less expensive metals such as Ir and Ru.

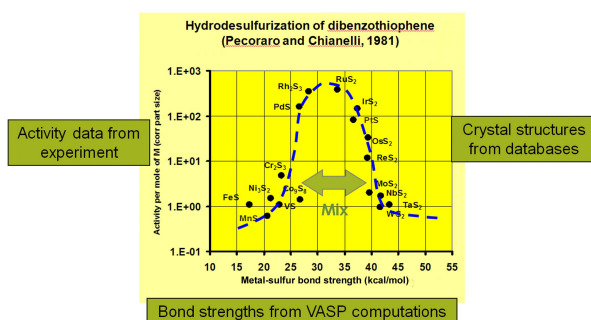


Figure 1: Volcano curve correlating activity with computed metal-sulfur bond strength.

[2] T. A. Pecoraro, and R. R. Chianelli, "Hydrodesulfurization catalysis by transition metal sulfides", *J. Catal.* **67**, 430 (1981) (DOI).

2 Computational results

The bond strength in bulk transition metals sulfides show an interesting correlation with the catalytic activity [3] as illustrated in Figure 1. This fact led to the development of a patented method [4] that uses a combination of experimental activity data, crystallographic structural information, and first-principles calculations to screen a range of elements for their potential activity.

3 Significance

During the last century, the search for novel catalysts was mostly based on extensive experiments guided by chemical intuition and experience. For example, when Alwin Mittasch developed the iron-based catalyst for the Haber-Bosch ammonia synthesis at today's BASF company in Germany, he reportedly performed well over 10,000 experiments. More recently, combinatorial experimental methods have increased the efficiency of this process without changing the basic empirical character of the approach. In the last two decades, computational approaches have been increasingly applied in the design of catalysts, but the high complexity of this endeavor is daunting.

The present approach demonstrated in this note exploits the concept of Sabatier, namely that an optimal catalyst binds the reactants and products neither too strongly nor too weakly. Rather than trying to simulate the details of molecules interacting with the catalyst surface (which is difficult to characterize), the present approach focuses on the essential interaction, namely the bonding of a metal to neighboring sulfur atoms. Furthermore, it exploits beautifully the richness of information that exists in crystallographic databases by targeted calculations of the key bonding energies in these systems.

[3] H. Toulhoat, P. Raybaud, S. Kaztelan, G. Kresse, and J. Hafner, "Transition metals to sulfur binding energies relationship to catalytic activities in HDS: back to Sabatier with first principle calculations", *Catal. Today* **50**, 629 (1999) (DOI).

[4] H. Toulhoat, US Patent US6799089B2 assigned to the French Petroleum Institute.

The result is a partitioning of the candidates into two categories, namely those where the metal-sulfur bond is too weak and the other where it is too strong. Mixing the two types of candidates leads to the desired effective bond strength. In fact, MoS₂doped with Co is actually used industrially as hydrodesulfurization catalyst and it is very gratifying that the current approach correctly predicts this mixture to be among the optimal candidates. Inspection of the volcano curve shown in Figure 1 provides a large number of other potential candidates, thus helping to guide and prioritize experimental and detailed mechanistic investigations. [5]

4 *MedeA* modules used for this application

The present calculations were performed with the *MedeA*® [1] platform using the following integrated

modules of the *MedeA Environment*

- *MedeA Environment* including crystal structure builders and geometric analysis
- *MedeA JobServer* and *TaskServer*
- *MedeA InfoMaticA* with structural databases (COD, ICSD, Pearson, or Pauling)
- *MedeA VASP* and its graphical user interface
- PrediBond™

[5] H. Schweiger, P. Raybaud, and H. Toulhoat, "Shape and edge sites modifications of MoS₂catalytic nanoparticles induced by working conditions: a theoretical study", *J. Catal.* **212**, 33 (2002) (DOI).

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