CRITICAL REVIEW

INTRINSIC REACTIVITY OF Ni, Pd AND Pt SURFACES IN DRY REFORMING AND COMPETITIVE REACTIONS: INSIGHTS FROM FIRST PRINCIPLES CALCULATIONS AND MICROKINETIC MODELING SIMULATIONS

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Journal of Catalysis, Volume 343, 2016, Pages 196-207, ISSN 0021-9517, https://doi.org/10.1016/j.jcat.2016.02.030.

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ABSTRACT

The paper investigates on the activity and intrinsic mechanisms of Dry Reforming of Methane (DRM) on various catalysts (Ni, Pt and Pd) and energies of competing mechanisms and reactions. The main reactions involved are the ones below:

$$CH_4 + H_2O \rightleftharpoons CO + H_2 \quad (1)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad (2)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (3)$$

$$CH_4 \rightleftharpoons C + 2H_2 \quad (4)$$

$$2CO \rightleftharpoons C + CO_2 \quad (5)$$

The analysis is done by Density Functional Theory Calculations and related Microkinetic models.

AREA OF WORK AND SIGNIFICANCE

The work is completely computational, and it compares some of the data with available data in the literature. It is significant both economically and ecologically. DRM is a substitute to Steam reforming (SRM) and can be used whenever water is not available. Moreover, it gives a controllable ratio of CO:H_2 which is rigid in the steam reforming. It also takes up CO_2 as a reactant, converting a waste into fuel. Thus, it is a very relevant paper in today's water and global warming crisis. Also, this can be used (not mentioned in the paper) to extract the tremendous amount of energy present under India's soil as methane hydrates.

CRITIQUE

The paper is a novel attempt to compare various catalysts to compare a particular reaction. Although the paper doesn't suggest any final conclusions as to which catalyst is the best, it does expand every aspect of the reaction and analyses it separately.

At the end of the paper, the reader does have insights about which mechanism is favoured in which catalyst but still unsure of which catalyst is the best one to use. In essence, this paper is a starting of an analysis, but requires more work to draw any useful conclusions.

Also, the authors have used DFT (Density Functional Theory) well, but it comes with its own pros and cons. It is a strong method, which is computationally less expensive than wavefunction based methods, but is strongly dependant on the exchange corelation functional used. This allows errors to creep in as is mentioned in one of the references.

A lot of places were mentioned where the DFT results matched with the experimental ones except in the introduction where the RDS (Rate Determining Step) was discussed. But there, according to me the interpretation of experimental data is incorrect.

A good point about the paper is that it analyses various cases in which the reaction might change, for example, High v/s low pressures, the reverse water gas shift reaction, the catalyst poisoning by coke etc. But at the same time, the paper also mentions some of the unanswered aspects like what if surfaces other than (1 1 1) are analysed, or effect thermal conditions on reverse water gas shift. Moreover, the equilibrium constant for adsorption, a constant that can be easily determined through experiments was considered from DFT simulations and not verified experimentally.

We also observe that stability of an intermediate was directly corelated to its adsorption enthalpy which may not be entirely accurate interpretation. Moreover, all the defects in catalyst and adsorbate-adsorbate interactions are ignored which might lead to inaccuracies seeping into the analysis.

Next, we go to the microkinetic analysis. This analysis predicts rates of various steps based on DFT calculations and first principles of Thermodynamics. One major drawback is that the model assumes the catalyst surface and properties remain constant throughout the reaction, but this is untrue, owing to Coke deposition. Moreover, all these calculations are DFT based, hence the mistakes of that analysis make the microkinetic analysis slightly inaccurate. Also, it was mentioned in Section 3.7 that since the accurate models were computationally expensive, approximate models were used, which might cause deviations in the results. This deviation is also observed when the data is compared with the experimental data. This is given in Section 3.7.

According to the references mentioned, Microkinetic modeling can be helpful in a lot of ways like:

1) Providing insights into the reaction mechanisms
2) Aid in new catalyst design
3) Account for effects of Temperature and Pressure

It comes with its own disadvantages like:

1) Is very sensitive to assumptions
2) Is computationally expensive
3) Can't capture effect of mass and heat transfer

While the first two disadvantages are relevant to this work, the third one is accounted for properly by analysing energy of adsorption separately.

One good part was that even though results were all computational, the authors have tried their best to give physical interpretations to the results. This can be observed in section 3.5 where H* stability is explained.

With the drawbacks pointed out, I must also mention that though there are inaccuracies, but these are smaller as compared to the main results. More often than not, these corrections change only magnitude of the numbers obtained but not the interpretation. Thus, the authors have done a pretty good job of choosing the analytical methods for analysis.

WRITING STYLE

The paper is clearly and concisely written. The only thing missing is a final summary where all different factors are accounted for, and a catalyst is suggested for usage. No heavy words were used, making the paper crisp and easy to read. A skimming followed by thorough reading is enough for a person to get a good grip over what work has been done.

OTHER COMMENTS

The conclusions are drawn perfectly and there are no interpretations that are not backed by data. The paper is a part of a bigger work that needs to be done to make industrial use of this knowledge. This is a good academic paper that epitomes the application and limitations of DFT and microkinetic analysis.

ACKNOLEDGEMENTS

I would like to thank Tanmay Lodha (200020152) for his help in formatting and citations.

CITATIONS

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