Response to the Reviewer Comments

Dear reviewer,

Thank you for the comments and suggestions. All the comments have been taken into account and revised accordingly in the revised version of the manuscript with highlighted.

Reviewer 1

Comments and Suggestions for Authors

The authors describe catalysts as well as an experimental setup to measure decomposition of formic acid into H2 and CO2. The reaction was performed at different temperatures (30-70°C) on acid solutions with different concentrations. Conversion was monitored by volumetric measurement of gas formation. The paper has several systematic weaknesses:

Catalysts were prepared from PdCl2 as precursor and NaOH (I guess that is what is meant by "Sodium hydrochloride" in line 93?) Was used for pH adjustment. How did the authors ensure that the resulting catalysts are Cl and Na free? Both elements can have an effect on catalytic performance.

Answer:

Thank you for pointing out our mistake. Yes, we added NaOH to adjust the pH before adding sodium borohydride for chemical reduction process. Thus, we have changed the word "sodium hydrochloride" in line 93 to "sodium hydroxide".

Additionally, we confirmed the synthesized catalysts are Cl and Na-free based on the XRD and FESEM-EDX results. The diffractogram does not show any crystalline peaks of Cl and Na, same with elemental composition measurement by EDX.

What is the rational to use carbon nitride as support (especially since the surface area is so low - the authors report values even < 10m²/g)? What is the advantage over e.g. a high surface area carbon? Is a control sample available, demonstrating this benefit? Why is it necessary to use a supported catalyst at all? Is there a benefit over metal particles formed in-situ.

Answer:

Despite the low surface area of carbon nitride, it has several advantages as catalyst support. Its abundant tri-s-triazine groups can serve as anchoring points for metal precursors to produce small and well-dispersed NPs.[1] Apart from that, the rich electrons of nitrogen atoms in g-C3N4 support would transfer to Pd NPs and increase the electron cloud density of Pd to promote dissociation of hydrogen atom.[2]

[1] M. Navlani-Garcia. D. Salinas-Torres, K. Mori, Y. Kuwahara, H. Yamashita, Int. J. Hydrogen Energy 44 (2019) 28483-28493

[2] Y. Wang. J. Yao, H. Li, D. Su, M. Antonietti, J. Am. Chem. Society 133 (2011) 2362-2365

How do the results of the current work compare to other state of the art systems (e.g. Fellay, Céline; Dyson, Paul J.; Laurenczy, Gábor (2008). "A Viable Hydrogen-Storage System Based on Selective Formic Acid Decomposition with a Ruthenium Catalyst". Angewandte Chemie International Edition. 47 (21): 3966–8. doi:10.1002/anie.200800320. or Onishi N, Kanega R, Kawanami H, Himeda Y. Recent Progress in Homogeneous Catalytic Dehydrogenation of Formic Acid. Molecules. 2022 Jan 11;27(2):455. doi: 10.3390/molecules27020455. PMID: 35056770; PMCID: PMC8781907 for a review of homogeneous systems).

Answer:

Thank you for your suggestion. For both papers as mentioned above, it was explained the performance of the homogeneous system with additional agent such as sodium formate to accelerate the decomposition. For our article, we focusing on the heterogeneous system which more dependence on surface and morphology properties of the catalysts. So that we are not compared the findings from this work with the papers reported the performance of the homogeneous system.

Why are catalysts added with the same total amount and therefore varying Pd content in each experiment? The outcome is trivial: more Pd in the reactor should result in higher gas formation. Wouldn't a comparison based on the same amount of Pd but with different concentration on the support give more interesting results as it would probe for Pd dispersion effects?

Answer:

For Pd based catalysts, it was prepared based on different amount (1, 3 and 5 wt %) of Pd on graphitic carbon nitride as support. Total amount of Pd precursor was calculated based on total weight to produce different Pd loadings catalyst. Different weight of $PdCl_2$ precursor will depicted different concentration have been used. Some revision on the method of catalysts synthesis has been included in the article to avoid any confusing. (Page 4 (line 1))

Did the authors analyse the composition of the gas formed in the reaction? Is the H_2/CO_2 ratio constant at all conditions or is there evidence for some CO_2 dissolution in the reaction mixture or in the water used in the gas trapping apparatus? How can the authors be sure, H_2/CO_2 is formed at all? Is it possible that CO/H_2O is formed instead? If the goal of the hydrogen formation is to use the resulting gas in a fuel cell, even traces of CO are problematic, so the selectivity of the catalyst is critical. Therefore, analysis of the reaction gas (e.g. by FTIR) is mandatory and state of the art.

Answer:

Thank you for rising this issue. For this study, we used GC-TCD to analyze the composition of the collected gas produced from the reaction. The results has been provided in Table 5 in the last section (page 17).

The finding that reaction rate depends on temperature is trivial and subject of any textbook on chemical kinetics. I would recommend to re-evaluate the available data with respect to reaction

rates. Since experiments were performed at different temperatures, it would even be possible to estimate the activation energy for each catalyst using an Arrhenius plot.

Answer:

Thank you for the very useful comment. I agreed with your opinion. However, for this study, the detail data to calculate the activation energy is not completed and sufficient. It would be possible for extension of the experiment in the future for the improvements.

All results are reported as absolute amount of gas formed. For some plots, there is even no duration reported, in which this amount of gas is formed. Since also the exact experimental conditions (temperature of the gas during measurement) are not reported, it is impossible to relate the reported data to any result from the literature. Usually, the performance of catalysts is reported as a turn over frequency and turn over number.

Answer:

Duration has been added for all plots including in Figure 15. Table 4 with calculated TOF and TON value has been added. It was also added in methodology section for the calculation (Page 16)

Figure 14 shows that the 3%Pd-catalyst has a pronounced advantage over the 5%Pd sample. This unexpected finding is not discussed at all. Is it significant?

Answer:

Thank you for the comment. The possible explanation has been added with the supporting reference (page 14).

However, for higher temperature up to 70 ºC, it showed a different trend while the total gas was decreased for 5 wt% Pd/C3N4 catalyst. It may be due to the early dehydration reaction of formic acid to produce PdCO or Pd formate caused the inhabitation of the catalyst [29].

What is the relevance of the characterisation data reported? Can any of these data contribute to explain the unexpected ranking shown in Figure14? What is the significance of increasing deviation between target Pd-content and Pd content observed by EDX?

Answer:

Thank you for this comment. The characterization data showed the properties of the fresh catalyst including surface properties, crystallinity and morphology. All the results showed the significant properties which potentially act as the catalysts for this research. The phenomena showed in Figure 14 has been answered accordingly in previous comments.