Monitoring the active site of CeO_2 supported Pd by H_2-D_2 exchange and EXAFS

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Significance and Relevance

In this work we present an investigation of the structure-activity relationship of CeO_2 supported Pd-containing catalysts using H_2-D_2 exchange in combination with EXAFS and the main goal is to monitor the presence of either single atoms or nanoparticles of Pd. The approach was first reported by our group and is further refined, applied for metal oxide-supported catalysts, which previously were difficult to investigate for the presence of single atoms.

Preferred and 2nd choice for the topic: *1st Fundamental advances in understanding catalysis*
2nd Automotive and stationary emission control
Preferred presentation: oral preferred or short oral

Introduction and Motivations

Single atom catalysis represents a promising approach in optimizing noble metal usage, while also offering different performances in terms of activity and/or selectivity compared to bulk or nanoparticles. However, information and knowledge about the structure of alleged single atom catalysts are lacking and difficult to obtain. This is due to the often low amounts of noble metal used, the need for costly analytical methods, such as XAS, and operating these analytical methods at the detection limit. As a result, new approaches are required, which simplify and adapt the process of investigating the structure-activity relationship of single atom catalysts. The main approach is based on the H_2-D_2 exchange in combination with XAS based on the study by *Vennewald et al.*, which reported the inactivity of Pd-single atoms (Pd-SA) compared to Pd-nanoparticles on graphitic carbon nitrides in the H_2-D_2 exchange up to 200°C.[1]

Materials and Methods

In this work, we investigate Pd/CeO_2 and Pd-Cu/CeO_2 using H_2-D_2 exchange in combination with XAS to collect information about the structure and performance of these materials. Moreover, NO reduction with hydrogen was performed to evaluate potential application in hydrogenation reactions.

Results and Discussion

The main methodologies employed consist of the H_2-D_2 exchange and synchrotron based XAS experiments at the Diamond Light source. In the first step, all materials were tested in the H_2-D_2 exchange up to 200°C with either non-reductive or reductive pretreatment conditions. Based on these experiments certain points of interest were determined and chosen for synchrotron experiments, which revealed the structure and changes of the materials. Exemplary of the obtained results for Pd/CeO_2 are shown in Figure 1. During a non-reductive pretreatment, the material does not show activity in the H_2-D_2-exchange starting at 50°C and following a reductive pretreatment, the material catalysed HD formation starting at 50°C (Fig. 1 left). As reported in the literature, this hints towards the lack of Pd-NP (NP: Nanoparticles) for the untreated samples and the formation of Pd-NP during pretreatment or reaction. Fig. 1 right depicts the EXAFS results for Pd/CeO_2, which shows the bond interaction of Pd with its neighbouring atoms. The lack of Pd-Pd bonds in combination with the presence of Pd-O and Pd-Ce bonds is a clear indicator for the presence of Pd-SA in CeO_2 in pristine samples and in line with the H_2-D_2 results.[2-4] Following the pretreatment, Pd-Pd bonds emerge, which further confirm the theories based on the H_2-D_2 results. Interestingly in the case of Pd-Cu/CeO_2, Pd also is present as Pd-SA on CeO_2 with no interaction with Cu in pristine conditions and also starts to develop Pd-NP following a treatment. Yet, for this material, an influence of the Pd-Cu bond starts to

emerge following the reductive pretreatment, which might explain differences in the H_2-D_2 results (see Fig 1. Left).

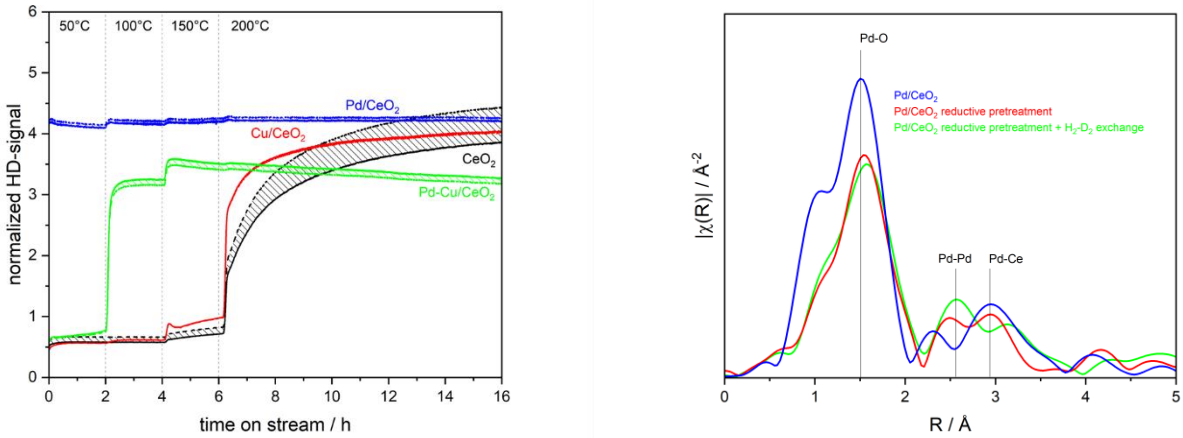

Figure 1. Normalized-HD signals of Pd-Cu/CeO_2, Pd/CeO_2, Cu/CeO_2 and CeO_2 in the H_2-D_2 exchange after a reductive pretreatment (left). And normalized magnitudes of the k-weighted Fourier transform (FT) of the extended X-ray absorption fine structure spectra in radial distance (not phase corrected) for Pd/CeO_2 (right). Normalization and correction of the HD signals are based on either H_2- (full lines) or D_2- (dashed lines) base-conversion rates. Reaction conditions: 2% D_2, 2% H_2, 96% Ar, GHSV = 20000 – 55000 h^{-1}; Pretreatment non-reductive condition: 100% Ar, 50 °C, 2 h; Pretreatment reductive condition: 2% H_2, 98% Ar, 550 °C, 2 h.

Additional experiments were conducted for Pd/CeO_2 in the NO reduction using H_2, which further highlights the importance of understanding the active species for given reactions, as the material containing Pd-NP shows higher activity and N_2 selectivity overall and at lower temperatures.
In conclusion, it can be said that the H_2-D_2 exchange proves to be a simple, yet highly sensitive method for obtaining hints about the Pd active species formed during different treatment conditions. Although, H_2-D_2 does not stand alone as a verification method for the formation of single atom or nanoparticle but supports more complex methods and limits the experimental effort required.

References

1. M. Vennewald, N. M. Sackers, A. Iemhoff, I. Kappel, C. Weidenthaler, A. Meise, M. Heggen, R. E. Dunin-Borkowski, L. Keenan, R. Palkovits, Journal of Catalysis **2023**, *421*, 134.
2. T. Fujikawa, K. Tsuji, H. Mizuguchi, H. Godo, K. Idei, K. Usui, Catalysis Letters, **1999**, *63*, 27.
3. X. Wang, J. Chen, J. Zeng, Q. Wang, Z. Li, R. Qin, C. Wu, Z. Xie, L. Zheng, Nanoscale **2017**, *9*, 6643.
4. F. Xing, J. Jeon, T. Toyao, K.-I. Shimizu, S. Furukawa, Chemical science **2019**, *10*, 8292.
5. Felix Ott, Chalachew Mebrahtu, Julia Nikodemus, Gunjana Yadav, Luke Keenan, Abhishek Khetan, Regina Palkovits, **2024** manuscript in preparation

Acknowledgements

This project was funded by the Cluster of Excellence Fuel Science Center (EXC 2186, ID: 390919832) by the Excellence Initiative by the German federal and state governments to promote science and research at German universities. We would like to thank Diamond Light source for synchrotron measurements.