

Experiment Report Form



Experiment title: Dynamic transformations of model catalysts during dehydrogenation of Liquid Organic Hydrogen Carriers under realistic conditions

Experiment number:
HC-3847

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Report:

We have investigated the dynamic formation and decomposition of Pd carbides in a Pd/ α -Al₂O₃(0001) model catalyst by in-situ high-energy grazing incidence X-ray diffraction (HE-GIXRD) during dehydrogenation of a model liquid organic hydrogen carrier (LOHC), methylcyclohexane (MCH), in a flow reactor. The phase composition of supported Pd nanoparticles was investigated as a function of particle size and a flow rate of reactant gas. Under operating conditions, we detected the formation of a Pd₆C phase. The dynamic stability of this phase results from the balance between uptake and release of carbon by the supported Pd nanoparticles in combination with the thermodynamically favorable growth of carbon deposits in the form of graphene. For small Pd nanoparticles (4.4 nm), the Pd₆C phase is kinetically stable under low flow rate of reactants. At high reactant flow, the Pd₆C phase decomposes shortly after its formation due to the growth of graphene. More complex structural behaviour was observed in the case of big Pd nanoparticles (8.1 nm). Here, the reciprocal space map obtained from the big Pd nanoparticles after the cleaning procedure shows an overlap of the Pd(111) Bragg reflection with an intense Debye-Scherrer ring (Figure 1a). The radial intensity profile of the Pd(111) Bragg

reflection is plotted in Figure 1b as a function of time under exposure to MCH. Selected intensity profiles fitted with the Voigt peaks associated with contributions from pure Pd, Pd_xC, and Pd₆C phases are shown in Figure 1c. Here, the stoichiometry parameter x in the Pd_xC phase is below 6. The integrated intensities from these contributions along with the position of the Pd_xC contribution are plotted in Figure 1d. Prior to MCH exposure, the big Pd nanoparticles contain two phases, Pd_xC and pure Pd. Under MCH exposure, two types of carbides coexist, Pd₆C and Pd_xC. Here, the formation and decomposition of Pd₆C proceeds via the Pd_xC phase. Most interestingly, the growth of graphene triggers the decomposition of carbides after an incubation period. The process is accompanied by segregation of carbon from the bulk of the nanoparticles to the graphene phase. In general, our studies demonstrate that metastability of palladium carbides is an intrinsic phenomenon in LOHC dehydrogenation on Pd-based catalysts. It is associated with dynamic formation and decomposition of Pd₆C and Pd_xC phases and strongly depends on particle size and reaction conditions.

A manuscript reporting the metastability of supported Pd carbide during dehydrogenation of LOHC has been submitted for publication.¹

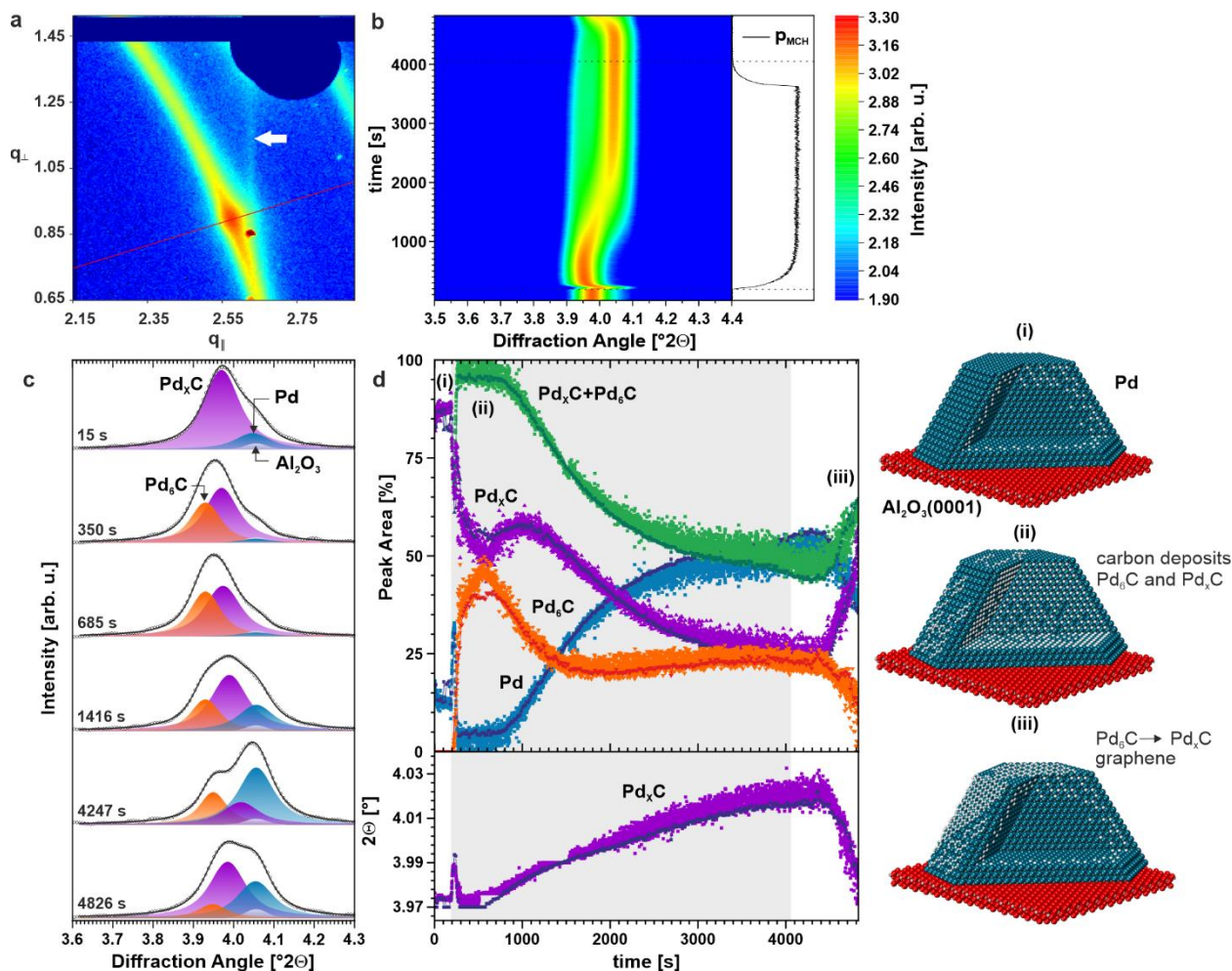


Figure 1. Pd nanoparticles (diameter 8.1 nm) on α -Al₂O₃(0001) under a flow of 5 ml/min: (a) Reciprocal space map around the Pd(111) Bragg reflection. The red line indicates the direction of the radial intensity profile; The white arrow indicates the truncation rod from the α -Al₂O₃(0001) substrate; (b) The intensity of the Pd(111) Bragg reflection and MCH partial pressure as a function of time; (c) Selected intensity profiles of the Pd(111) Bragg reflection; (d) Fractions of pure Pd (blue squares), Pd₆C (orange triangles), Pd_xC (purple triangles) phases, and the sum of the Pd₆C and Pd_xC contributions (green squares) as a function of time. The grey box indicates exposure to MCH.

References

- Schuster, R.; Bertram, M.; Runge, H.; Geile, S.; Chung, S.; Vonk, V.; Noei, H.; Poulain, A.; Lykhach, Y.; Stierle, A.; Libuda, J., Metastability of Palladium Carbide Nanoparticles During Hydrogen Release from Liquid Organic Hydrogen Carriers. **2020**, submitted.