Functionality of ligand-free alloy nanoparticles for heterogeneous catalysis made by scaleable laser synthesis

<u>Galina Marzun¹</u>, Philipp Wagener¹, Ina Haxhiaj¹, Sebastian Kohsakowski¹, Sven Reichenberger¹, Ralf Becker², Niko Bärsch³, Helmut Bönnemann⁴, Keming Du⁵, Rainer Kiemel⁶, Robert Schlögl⁷, Stephan Barcikowski¹*

¹Technical Chemistry I and Center for Nanointegration Duisburg-Essen (CENIDE), Research Canter for Nano Energy Technology (NETZ), University of Duisburg-Essen, Germany ²Huntsman Pigments and Additives, Duisburg, Germany ³Particular GmbH, Langenhagen, Germany ⁴ Max Planck Institute for Coal Research, Mülheim an der Ruhr, Germany ⁵EdgeWave GmbH, Innovative Laser Solutions, Würselen, Germany ⁶ Heraeus Deutschland GmbH & Co. KG, Hanau, Germany ⁷Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

Introduction

The usage of stabilizers and ligands is a major disadvantage of conventional methods for nanoparticle synthesis such as chemical reduction of precursors. Ligands and stabilizers have to be removed by calcination and additives may cause catalysts poisoning. Characterization of active sites proves to be elusive. Furthermore upscaling is not trivial and synthesis parameters are often difficult to transfer to other materials. Together with an advisory support from experts in academia and industry, our BMBF Junior Research Group InnoKat addressed these drawbacks by establishing a process for the full-continuous synthesis of **highly pure, active and durable** nano-catalysts for several reactions (e.g. alcohol oxidation and electro-catalysis).

Materials and Methods

Colloidal nanoparticles were produced by pulsed laser ablation of a liquid-covered pellet (PLAL, Fig. 1a). A laser beam with nanosecond pulses (Nd:YAG) with a fundamental wavelength (1064 nm) was focused onto the target in a continuous self-made ablation chamber.

Results and Discussion

We fabricated ligand-free nanoparticles with high purities [1] and controlled size distribution [2] for a variety of materials (e.g. Au, Pt, Ni, alloys...). The **transferability** of the synthesis route to a variety of materials and liquids enables high-throughput screening of molar fraction series of oxidation catalysts [3]. Catalytically **active alloy nanoparticles** were synthesized by irradiating an alloy or a compressed target consisting of a mixture of discrete micro powders [4]. The significance of pure particle surfaces has been demonstrated by kinetic modelling of a catalytic reaction, showing better agreement between experiment and theory than chemically produced nanoparticles. Thus, laser-generated nanoparticles may be used as ligand-free reference materials [1]. Good **reproducibility and a linear up-scaling** of nanoparticle generation was achieved by a continuous flow synthesis using a high-power picosecond laser system consisting of a 500W ps-laser source and a laser scanner with

scanning speeds of up to 500m/s. Productivities of up to 4 g/h colloidal nanoparticles were achieved (Fig.1e) [5]. Downstream fabrication of heterogeneous catalysts is driven by electrostatic attraction to the support in a **continuous process**, with a **quantitative yield**. Due to additive-free surfaces, **no further activation steps such as calcination** are necessary (see Fig. 1b-d) [6]. First catalytic tests of laser-generated nanomaterials have confirmed their potential for the manufacturing of **active** [4] and **stable** [7] catalysts even at elevated temperatures. Our recent progress in exploration of the unique properties and potential applications of laser-generated nanoparticles in heterogeneous catalysis is presented.



Figure 1. Functional nano-catalysts made by Laser Ablation in Liquids: synthesis of ligand-free nanoparticles (a), particles on support materials (b), transferability and proof of concept (c,d) and Up-Scaling (e).

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