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Surface Science Study of Electrochemically Active Liquid Organic Hydrogen Carriers

The rise of green energy from renewable sources such as wind and solar power is driving the need for efficient ways to store and convert energy to accommodate fluctuations in power generation and demand. One innovative solution is the use of liquid organic hydrogen carriers (LOHCs) [1-5]. The basic idea behind LOHCs is that they can store hydrogen through a reversible chemical process [1-5]. This method allows hydrogen to be stored and transported in liquid form at room temperature and normal pressure using the existing fuel infrastructure [4].

However, converting the chemical energy stored in LOHCs back into electrical energy presents a number of challenges. The two-step process of producing hydrogen in a dehydrogenation reactor and converting it to electricity in a proton-exchange membrane fuel cell (PEM-FC) is complex, expensive, space-consuming, and requires additional safety measures due to the handling of gaseous hydrogen [6]. In addition, the temperature required for the dehydrogenation reaction is much higher than the operating temperatures of fuel cells (≤ 80 °C for low-temperature PEM-FC, ≤ 180 °C for high-temperature PEM-FC) [7] which impedes heat integration and reduces efficiency [6, 8, 9].

A newer concept, electrochemically active LOHCs (EC-LOHCs), tackles these challenges (Figure 1) [6, 10, 11]. EC-LOHCs can be used directly in fuel cells where they are oxidized to release electrons and protons [6, 10, 11]. The isopropanol/acetone redox pair is one of the most promising EC-LOHC systems [6, 10-14]. A clever solution proposed by Sievi et al. combines conventional LOHCs with EC-LOHCs through a transfer hydrogenation process [10]. This approach reduces the temperature difference between the dehydrogenation reactor and the fuel cell, significantly increasing the efficiency from ≤ 38% to over 50% [10].

Bimetallic Pt–Ru catalysts are the state-of-the-art for isopropanol fuel cells due to their high activity and resistance to acetone poisoning [6, 10, 12]. Khanipour et al. found that these catalysts have a low overpotential peak for isopropanol oxidation with an onset potential at 0.05 V_{RHE} [12], which is about 0.25 V lower than for Pt catalysts [6, 10, 12]. However, the exact reason for the high activity of Pt–Ru catalysts is not fully understood [6, 12]. It is speculated that the activity is related to specific structures on the electrode surface [12], although these active sites have not yet been clearly identified.

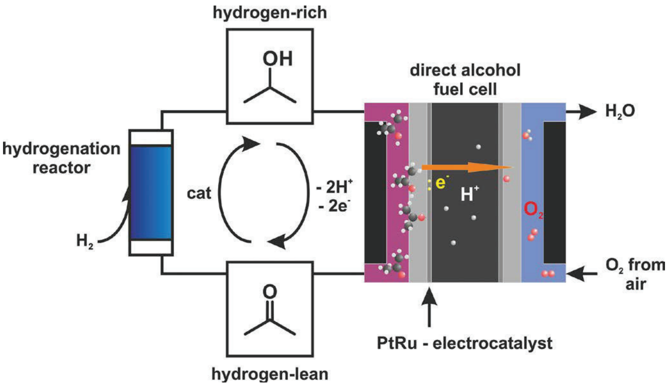

Fig. 1: Electrochemically active liquid organic hydrogen carriers (EC-LOHCs).

Here we reveal the nature of the active state of the Pt–Ru surface alloy catalysts responsible for the electro-oxidation of isopropanol at low potentials and demonstrate that it is possible to prepare surfaces completely dominated by these highly active sites. These model surfaces (Figure 2a) were prepared by a surface science approach using preparation methods studied in detail by H. Hoster and R. J. Behm [15, 16]. The surface composition of the model catalysts was characterized by synchrotron radiation photoelectron spectroscopy (SRPES) coupled with an ex situ emersion electrochemical cell.

First, the stability of the 0.5 ML Pt–Ru surface alloy catalyst was investigated under varying potentials in 0.2 M isopropanol and 0.1 M $HClO_4$ (pH=1). We found that increasing the potential beyond the oxidation potentials of Pt and Ru (1.2 V_{RHE}) causes oxidation of the surface, resulting in the formation of PtO and RuO_x on the surface. Returning to 0.0 V_{RHE} reduces the oxides back to the Pt^0 and Ru^0. We observed a shift and broadening of the Pt^0 peak, indicating the formation of ultra-small Pt aggregates. This implies that the electrochemical oxidation and reduction of the Pt–Ru alloy triggers a dealloying process (Figure 2b).

In the next step, we investigated the effect of the dealloying procedure on the catalytic activity by cyclic voltammetry and in situ electrochemical infrared reflection absorption spectroscopy (EC-IRRAS). Prior to the dealloying procedure, the onset of isopropanol oxidation occurred around 0.5 V_{RHE} with a peak

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at ~0.75 V_{RHE}. After dealloying, a new oxidation peak appears at a much lower overpotential (onset potential at 0.05 V_{RHE}), forming acetone. Our work demonstrates that by tuning the initial composition of the Pt–Ru surface alloy, we maximized the density of highly active Pt sites after dealloying.

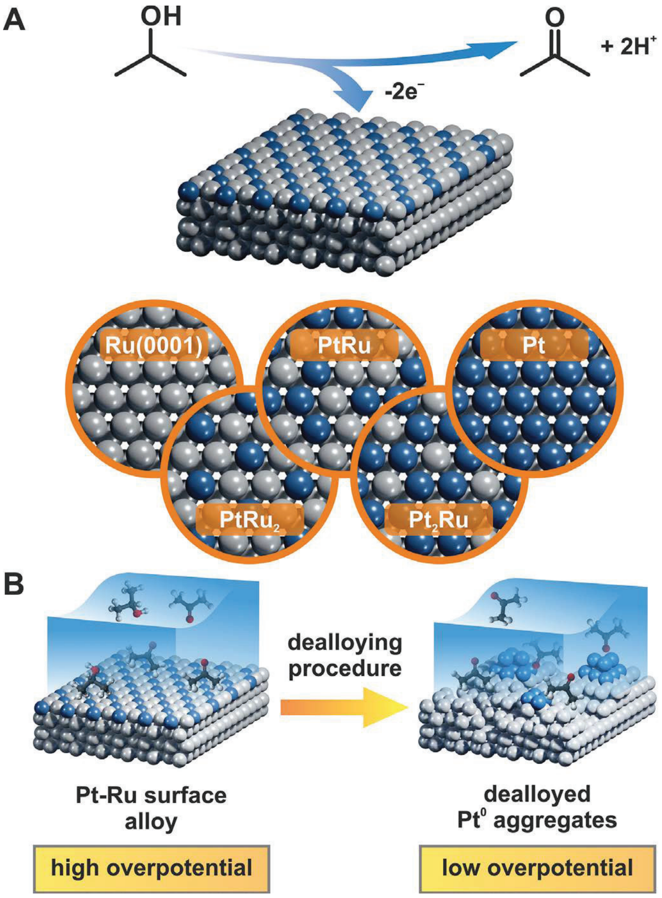

Fig. 2: Model approach for the investigation of electrochemical isopropanol oxidation using well-defined Pt-Ru surface alloys (A). Schematic representation of the dealloying procedure of the Pt-Ru surface alloys, in which ultra-small Pt^0 aggregates are formed on a rough Ru surface (B). The catalytic activities of the Pt-Ru surface alloys and the dealloyed Pt^0 aggregates are associated with high and low overpotentials, respectively.

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Zurück zum Inhaltsverzeichnis

Alexander Simanenko

Alexander Simanenko completed his master's degree in chemistry from the Novosibirsk State University in Novosibirsk, Russia in 2021. During his master's thesis, he worked on the investigation of low-temperature catalytic activity in CO and methane oxidation reactions on noble metal-based catalysts using ex situ X-ray photoelectron spectroscopy (XPS) and ex situ X-ray diffraction (XRD). Alexander Simanenko is currently in his last year of doctoral studies in the research group of Prof. Dr. Jörg Libuda at the Friedrich-Alexander-Universität (FAU) Erlangen-Nürnberg, Germany. His research focuses on the investigation of chemical reactions at surfaces and interfaces of well-defined model (electro)catalysts of different complexity using synchrotron radiation photoelectron spectroscopy (SRPES) in combination with electrochemical methods.

Dr. Olaf Brummel

Dr. Olaf Brummel received his PhD at the Friedrich-Alexander-Universität (FAU) Erlangen-Nürnberg in 2018. Presently, he is a group leader for "Model Electrocatalysis" at the Chair of Interface Research and Catalysis at the FAU Erlangen-Nürnberg and senior lecturer (Akademischer Oberrat). The expertise of Dr. Olaf Brummel is centered around model electrocatalysis in energy conversion with a special focus on reaction mechanisms and kinetics at electrified solid/liquid interfaces. His group employs model systems with different levels of complexity including simple single crystalline surfaces, real electrocatalysts, and complex, well-defined nanostructured model electrocatalysts prepared by surface science methods. His group uses a variety of electrochemical in situ methods for mechanistic studies with a special emphasis on electrochemical infrared spectroscopy.

Dr. Yaroslava Lykhach

Dr. Yaroslava Lykhach received her PhD in Physics of Surfaces and Interfaces at the Charles University in Prague, Czech Republic. Presently, she is a group leader and coordinator for the "Synchrotron Radiation Research" at Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Germany. The expertise of Dr. Yaroslava Lykhach involves an investigation of chemical reactions at the surfaces and interfaces of well-defined model catalysts by means of spectroscopic techniques including synchrotron radiation photoelectron spectroscopy (SRPES) and resonant photoemission spectroscopy (RPES) with a special emphasis on redox interactions and charge transfer. At the Chair of Interface Research and Catalysis, Dr. Yaroslava Lykhach manages all research activities that involve synchrotron radiation. She coordinates a team of researchers performing scheduled experiments at the synchrotrons Elettra (Italy), DESY (Germany), BESSY II (Germany), ESRF (France), MAX IV (Sweden).

Prof. Dr. Jörg Libuda

Jörg Libuda holds a full professorship (W3) for Interface Research and Catalysis at the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU). He received his doctorate degree in 1996 from the Ruhr-Universität Bochum, was group leader at the Fritz-Haber-Institut der Max-Planck-Gesellschaft (Berlin), postdoctoral researcher at Princeton University (NJ, USA), and received his habilitation from the Humboldt-Universität zu Berlin. In 2005 he accepted a professorship for physical chemistry and in 2019 a full professorship at FAU. Jörg Libuda is member of the Academia Europaea, Fellow of the European Academy of Sciences, elected member of the DFG Review Board, and vice spokesperson of the Collaborative Research Center 1542 "Catalysis at Liquid Interfaces" and the Research Unit 5499 "Molecular Solar Energy Management". The Libuda group studies functional surfaces, interfaces, and nanomaterials, with a special focus on catalysis, electrocatalysis, energy technology and conversion, and nanotechnology.

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