



Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Hydroxamic Acid Pre-Adsorption Raises the Efficiency of Cosensitized Solar Cells

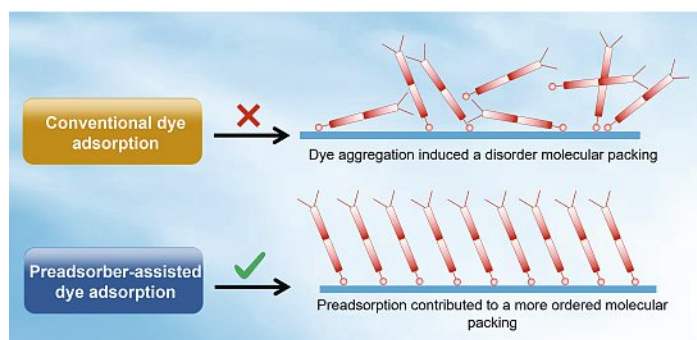
Yameng Ren, Dan Zhang, Jiajia Suo, Yiming Cao, Felix T. Eickemeyer, Nick Vlachopoulos, Shaik M. Zakeeruddin, Anders Hagfeldt, Michael Grätzel*

Nature, 2023, 613, 60, <https://doi.org/10.1038/s41586-022-05460-z>
Ecole Polytechnique fédérale de Lausanne (EPFL)

Dye-sensitized solar cells (DSCs) have emerged as a low-cost and efficient technology to convert light into electricity by using photosensitizers adsorbed on nanocrystalline mesoporous TiO_2 films along with electrolytes or solid charge-transport materials. While highly absorbing sensitizers with a broad spectral response greatly enhance the photovoltaic (PV) performance of DSCs, these materials tend to quench the photoexcited sensitizers by aggregating on the TiO_2 surface. Herein, the authors pre-adsorbed a monolayer of an hydroxamic acid derivative on TiO_2 and improved the dye molecular packing of two newly designed co-adsorbed sensitizers that harvest light quantitatively across the entire visible domain. The resulting semi-conductors exhibited high power conversion efficiency and long-term operational stability. Overall, this study offers promising prospects for DSCs applications as renewable energy supply and paves the way for achieving grid parity by installing these sustainable, cheap, highly efficient and transparent thin film solar cells in many locations.

Authors' comments:

“Our findings pave the way for facile access to high performance dye sensitized solar and offer promising prospects for applications in solar energy harvesting and as battery replacement for powering electronic devices using ambient light as energy source.”



Platinum-Iron(II) Oxide Sites Directly Responsible for Preferential Carbon Monoxide Oxidation at Ambient Temperature: An Operando X-ray Absorption Spectroscopy Study

Iliia I. Sadykov, Vitaly L. Sushkevich, Frank Krumeich, Rob Jeremiah G. Nuguid, Jeroen A. van Bokhoven, Maarten Nachtegaal, Olga V. Safonova*

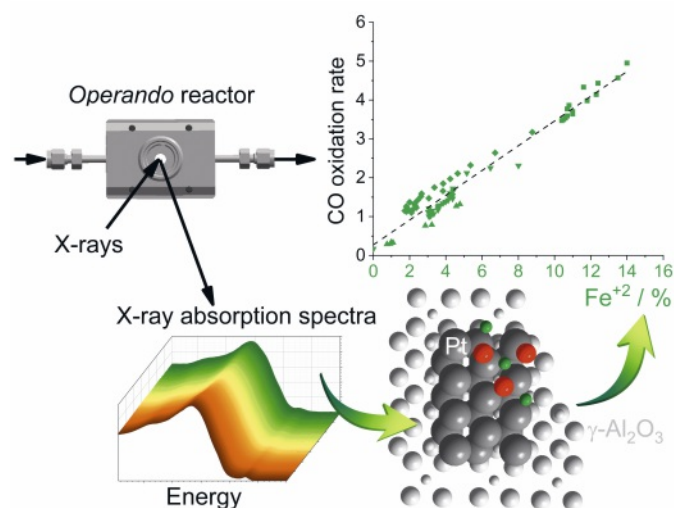
Angew. Chem. Int. Ed. 2023, 62, e2022140, <https://doi.org/10.1002/anie.202214032>

Paul Scherrer Institute, Villigen PSI; ETH Zurich, Zurich

Operando X-ray absorption spectroscopy identified that the concentration of Fe^{2+} species in the working state-of-the-art Pt- FeO_x catalysts quantitatively correlates to their desired carbon monoxide oxidation rate at ambient temperature. It proves that Fe^{2+}O -decorated platinum nanoparticles constitute active sites and Fe^{2+} is the resting state of the active iron. Catalyst deactivation is found to be directly linked with irreversible oxidation and aggregation of Fe^{2+}O species. Atomically-dispersed platinum and Pt-Fe alloy do not play any significant role in the ambient temperature preferential carbon monoxide oxidation as found by in situ infrared and operando X-ray absorption spectroscopies. Pre-treatment conditions determine the concentration of active Fe^{2+}O at the platinum interface and, therefore, define the catalytic activity. High hydrogen pressure during pre-treatment is crucial to generate active Fe^{2+}O sites.

Authors' comments:

“Operando spectroscopy simultaneously follows catalytic conversion, selectivity, and structure of catalysts in real-time. Following the state of platinum and iron using this method, we were able to extract the signal of a small fraction of catalytically active sites and distinguish them from spectators.”



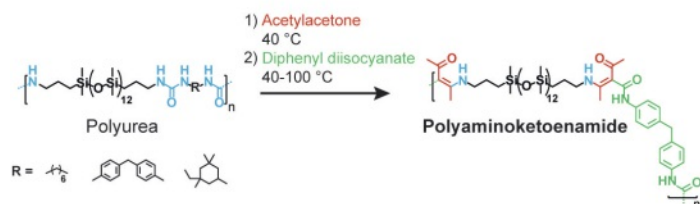
Chemical Upcycling of Conventional Polyureas into Dynamic Covalent Poly(aminoketoenamides)

Youwei Ma, Xuesong Jiang, Jie Yin, Christoph Weder,* José Augusto Berrocal,* Zixing Shi*
Angew. Chem. Int. Ed. **2023**, *62*, e202212870,
<https://doi.org/10.1002/anie.202212870>
 Adolphe Merkle Institute, University of Fribourg; Shanghai Jiao Tong University, Shanghai, 200240 P. R. China

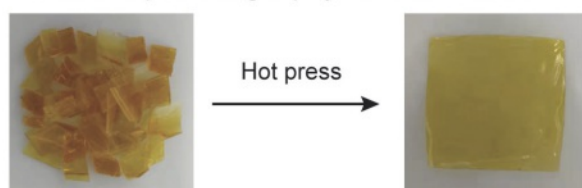
In this publication the authors report a strategy to upcycle linear and cross-linked polyureas, which are widely used in marine, aerospace, and automotive applications. The key step of their chemical transformation is the conversion of polyureas into divinyllogous amide-terminated compounds using acetylacetone, an inexpensive and commercially available compound. The process was initially validated on model urea compounds, which showed that the conversion rate depends on the reaction temperature and nature of the urea group. The di-vinyllogous amide-terminated products could then be reacted with aromatic isocyanates to create new polymer networks comprising aminoketoenamide bonds. The latter are highly dynamic at elevated temperatures, which renders the networks healable and reprocessable by thermal treatment and without any additional catalyst.

Authors' comments:

"It was remarkable to see how particularly stubborn chemical motifs such as urea bonds can be transformed into extremely dynamic and adaptive chemical linkages via two relatively simple chemical transformations".



Thermal reprocessing of polyaminoketoenamides



Production of Benzene by the Hydrodemethylation of Toluene with Carbon-Supported Potassium Hydride

Fei Chang, Alexey Fedorov*
ChemSusChem. **2023**, *16*, e2022202,
<https://doi.org/10.1002/cssc.202202029>
 ETH Zürich

Benzene, an essential chemical for the synthesis of numerous products, is made industrially by the hydrodemethylation (HDM) of toluene and xylenes *via* the Houdry Detol process. While this HDM method is common, it is energy-intensive and costly due to high operating temperatures (*ca.* 500 °C). A new, low-temperature (125–250 °C) method for the HDM of toluene has been reported that relies on the use of carbon-supported potassium hydride (KH/C). The authors found 63% selectivity to benzene when neat toluene was heated to 250 °C in the presence of 80 bar of hydrogen gas and 0.8 mol% KH/C, achieved at 15.3% conversion of toluene. At low hydrogen pressure of 6 bar, selectivity to benzene was 98%, although the reaction became stoichiometric on KH.

Authors' comments:

"Chemically inert substrates such as toluene rarely undergo selective C–C bond-cleaving reactions, especially if conditions are mild. The present results are interesting owing to the intriguing reaction mechanism and potential for applications in organic chemistry."

