

## Synchrotron radiations shed light on formation mechanism of aromatic polyimide precursor

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Synchrotron radiations shed light on the mechanism for dehydrogenative coupling of dimethyl phthalate catalyzed by palladium and copper complexes. Credit: Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology

Aromatic polyimide is a thermal- and chemical-resistant polymer with high mechanical strength, which is widely used for electrical insulation materials and aerospace materials. One of the major polyimides is made from tetramethyl biphenyltetracarboxylate, which is prepared by



dehydrogenative coupling of dimethyl phthalate catalyzed by conventional  $[Pd(OAc)_2]/[Cu(OAc)_2]/1,10$ -phenanthroline (phen) system. However, the product yield is normally less than 10 percent. Nevertheless, this process is used for industrial production. The mechanism was largely unknown because the process needed harsh conditions (over 200 degrees Celsius), cross-linked catalyses using Pd and Cu complexes, and very diluted catalyst conditions.

Synchrotron radiation experiments now shed light on the mechanism. A joint team of TUAT, Osaka university and Kyoto University, first focused on the potential intermediates such as  $[Pd(OAc){C_6H_3(CO_2Me)_2}(phen)]$  based on the theorized catalytic cycle, and they prepared them via independent reactions. Some stoichiometric reactions using the intermediates suggested the formation of tetramethyl biphenyltetracarboxylate, the product, by subsequence of disproportionation, giving  $Pd{C_6H_3(CO_2Me)_2}_2(phen)$  and the reductive elimination.

They confirmed that these potential intermediates worked as the catalysts, and the turn over numbers (TONs) reached to 91. They also used Pd K-edge (24.357 keV) XANES and EXAFS measurements using SPring-8 BL01B1 at the Japan Synchrotron Radiation Research Institution. They found that an in situ catalyst solution in dimethyl phthalate starting from  $[Pd(OAc)_2]/[Cu(OAc)_2]/phen converted into [Pd(OAc){C_6H_3(CO_2Me)_2}(phen)] by the XAFS study. This new methodology and results have been published in the ACS Catalysis.$ 

"This process has been used for an industrial production of an aromatic polyimide precursor, despite of the low catalytic efficiency. This is an awesome process originally found by industrial researchers for production of the precursor because of high atom efficiency and direct access from readily available dimethyl phthalate. Our results are surely service to the further development on the catalysts, that leads to the more



economical production of the polyimide. Although some pioneering groups have studied the related catalyses, we are glad to contribute some," said Masafumi Hirano, a TUAT professor of chemistry and a principal of the study.

The current scope is, however, limited to the Pd catalyst side. Although the detailed study on the Cu <u>catalyst</u> is more difficult, this is the way to the perfect understanding of this catalysis.

"The in situ solution XAFS analysis of homogeneous catalyses is still difficult but our team works well in all stages in organometallic chemistry, catalytic chemistry and the XAFS study. I appreciate diversity of the team members with different back ground in chemistry," said Masafumi.

**More information:** Masafumi Hirano et al, Mechanistic Insights on Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate, *ACS Catalysis* (2018). DOI: 10.1021/acscatal.8b01095

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