Academic Program [Oral B] | 08. Catalysts and Catalysis：Oral B

Wed. Mar 26, 2025 1:00 PM - 3:30 PM JST | Wed. Mar 26, 2025 4:00 AM - 6:30 AM UTC
[C]C404(C404, Bldg. 2, Area 2 [4F])

[[C]C404-1pm] 08. Catalysts and Catalysis

Chair: Sho Yamaguchi, Takafumi Yatabe

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[C]C404-1pm-01]

Low Hydrogen Pressure Hydrogenolysis of Polyethylene Enabled by Synergistic Effect in Ru-Pt Alloy Catalyst

○Yukari Yamazaki[1], Xiongjie Jin[1], Weihan Sun[1], Katsutoshi Nomoto[2], Kohei Takahashi[1], Hiroki Miura[2], Tetsuya Shishido[2], Akira Nakayama[1], Kyoko Nozaki[1] (1. The University of Tokyo, 2. Tokyo Metropolitan University)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[C]C404-1pm-02]

Generation and Synthetic Utility of Oxyallyl Cation from Cyclic Enol Carbonate : An Experimental and DFT Study

○Sangita Karanjit[1], Emiko Tanaka[1], Aoi Minamide[1], Ryota Sato[1], Kosuke Namba[1] (1. Tokushima University)

Japanese
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[[C]C404-1pm-03]

Boomerang-type polymer-immobilized Cp*Ir catalysts for formic acid dehydrogenation

○Keito Sawahara[1,2], Shinji Tanaka[2], Ryoichi Kanega[2], Hajime Kawanami[2,1] (1. University of Tsukuba, 2. AIST)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[[C]C404-1pm-04]

Aluminum-oxide-supported Nickel Carbide Nanoparticle Catalyst for Selective Hydrogenation of Furfural to Tetrahydrofurfuryl Alcohol

○Taiki Kawakami[1], Sho Yamaguchi[1], Takato Mitsudome[1], Tomoo Mizugaki[1] (1. Osaka University)

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

Break

Japanese
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC
[[C]C404-1pm-05]

Azobenzene synthesis from non-aromatic compounds enabled by Au–Pd nanoparticle catalysts

○Takafumi Yatabe[1,2], Wei-Chen Lin[1], Tomohiro Yabe[1], Kazuya Yamaguchi[1] (1. The University of Tokyo, School of Engineering, 2. JST, PRESTO)

English
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

[[C]C404-1pm-06]

Visualization of catalytic active sites of multi-element alloy for hydrogen evolution reaction by machine learning

○Yuto Maruta[1], Kohei Kusada[1,2], Aspera Menez Susan[3], Gerardo Valadez Huerta[3], Yusuke Namba[3], Kaoru Hisama[3], Michihisa Koyama[3], Hiromasa Kaneko[4], Hiroshi Kitagawa[1] (1. Grad. Sch. Sci., Kyoto Univ., 2. HAKUBI Centre, Kyoto Univ., 3. RISM, Shinshu. Univ., 4. Grad. Sch. Sci. and Tech., Meiji Univ.)

Japanese

3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC

[[C]C404-1pm-07]

C–S/C–Br metathesis enabled by a supported Au–Pd alloy nanoparticle catalyst

○Takehiro Matsuyama[1], Takafumi Yatabe[1], Kazuya Yamaguchi[1] (1. The University of Tokyo)

Low Hydrogen Pressure Hydrogenolysis of Polyethylene Enabled by Synergistic Effect in Ru-Pt Alloy Catalyst

([1]*The University of Tokyo*, [2]*Tokyo Metropolitan University*) ○Yukari Yamazaki,[1] Xiongjie Jin,[1] Weihan Sun,[1] Katsutoshi Nomoto,[2] Kohei Takahashi,[1] Hiroki Miura,[2] Tetsuya Shishido,[2] Akira Nakayama,[1] Kyoko Nozaki[1]

Keywords: Hydrogenolysis; Polyethylene; Ru-Pt alloy; Cerium oxide; C−C bond cleavage

Hydrogenolysis of polyethylene (PE) is an important reaction for chemical recycling of plastic waste. The mechanism of PE hydrogenolysis has been reported; (i) C−H bond cleavage of PE followed by adsorption on catalyst surface, (ii) C−C bond cleavage, (iii) hydrogenation followed by desorption of alkane products from the catalyst (Figure 1a). [1] In most reported cases, supported-Ru catalysts exhibit high performance in C−C bond cleavage of PE backbone however it requires high pressure hydrogen atmosphere such as ≥20 bar. [2] The hydrogenolysis under low pressure of hydrogen is more desirable for energy-efficient plastic recycling.

In this study, we developed Ru-Pt alloy catalyst supported on CeO_2 for low hydrogen pressure hydrogenolysis of low-density PE (LDPE). Under 5 bar of hydrogen, the $RuPt/CeO_2$ catalyst exhibited higher activity than conventional Ru/CeO_2 or Pt/CeO_2 catalysts (Figure 1b). The mechanistic studies and density functional theory calculations indicated that Ru-alkyl intermediate was formed on Ru species by C−C bond cleavage, then active H species on Pt species efficiently transfer to the intermediate to generate alkane products. Therefore, the synergistic effect of C−C bond cleavage by Ru species and efficient hydrogenation of Ru-alkyl intermediates by Pt species contributes to the higher activity of the bimetallic catalyst compared to the corresponding monometallic catalyst.

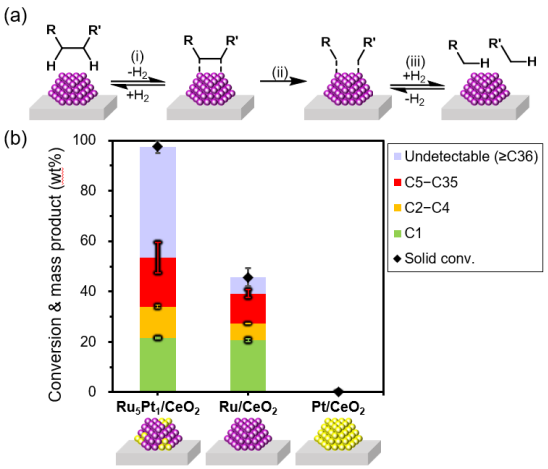


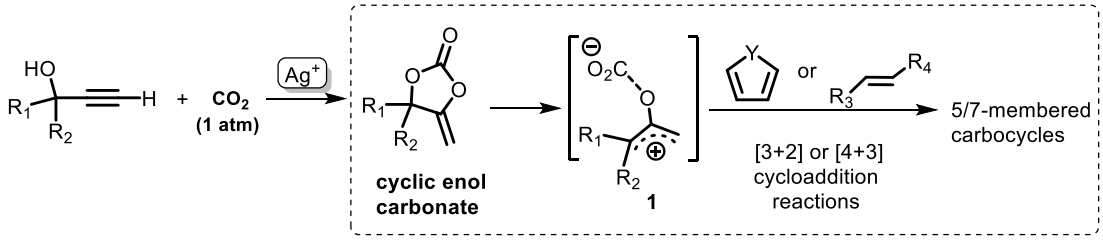
Figure 1. (a) Reported reaction mechanism for hydrogenolysis of PE. (b) Comparison of the catalytic activity in hydrogenolysis of LDPE under 5 bar of hydrogen at 200 °C for 12 h.

1) a) C. Wang, T. Xie, P. A. Kots, B. C. Vance, K. Yu, P. Kumar, J. Fu, S. Liu, G. Tsilomelekis, E. A. Stach, W. Zheng, D. G. Vlachos, *JACS Au* **2021**, *1*, 1422. b) C. Wang, K. Yu, B. Sheludko, T. Xie, P. A. Kots, B. C. Vance, P. Kumar, E. A. Stach, W. Zheng, D. G. Vlachos, *Appl. Catal. B* **2022**, *319*, 121899. 2) a) Y. Nakaji, M. Tamura, S. Miyaoka, S. Kumagai, M. Tanji, Y. Nakagawa, T. Yoshioka, K. Tomishige, *Appl. Catal., B* **2021**, *285*, 119805. b) M. Tamura, S. Miyaoka, Y. Nakaji, M. Tanji, S. Kumagai, Y. Nakagawa, T. Yoshioka, K. Tomishige, *Appl. Catal. B* **2022**, *318*, 121870.

Generation and Synthetic Utility of Oxyallyl Cation from Cyclic Enol Carbonate: An Experimental and DFT Study

([1]*Graduate School of Pharmaceutical Science, Tokushima University*)
○Sangita Karanjit[1], Emiko Tanaka[1], Aoi Minamide[1], Ryota Sato[1], Kosuke Namba[1]
Keywords: Oxyallyl cation, Cyclic enol carbonate, decarboxylation

Cycloaddition reactions between oxyallyl cations and alkenes are very important transformations and is a powerful approach for constructing ring systems. Conventionally, oxyallyl cations are generated from α-halo or sulfonyl-substituted ketones or enol ethers which readily react with conjugated dienes or electron rich olefins. With the pioneering work by Murai et al.[1] which opened up the access to the oxyallyl cation from a new source i.e., cyclic enol carbonates for Pd-catalyzed reactions, several catalytic transformations via oxyallyl cation intermediate to form C-C bond has been reported.[2] The cyclic enol carbonates which are the starting material for this decarboxylative transformation can be easily prepared from the Ag-catalyzed reaction of CO_2 with propargyl alcohol. In this context, we recently developed a mild and efficient, reusable heterogeneous silver catalyst immobilized on silica support[3] via alkoxysilane linkage ($Im^+Cl^-@SiO_2$) for the synthesis of cyclic carbonates from propargyl alcohols and CO_2. Herein, we presented experimental and density functional theory (DFT) study to generate oxyallyl cation **1** via decarboxylation of these cyclic carbonates and the cycloaddition reaction which forms the cyclopentenone core skeleton in many natural products. This decarboxylation strategy which is simple, mild, efficient, and green route involves the elimination of CO_2 as the driving force for the application in construction of bicyclic key intermediates containing cyclopentenone.



1. K. Ohe, H. Matsuda, T. Ishihara, S. Ogoshi, N. Chatani, S. Murai *J. Org. Chem.* **1993**, *58*, 1173.
2. a) W. Chai, Q. Zhou, W. Ai, Y. Zheng, T. Qin, X. Xu, W. Zi *J. Am. Chem. Soc.* **2021**, *143*, 3595. b) Y. Zheng, T. Qin, W. Zi *J. Am. Chem. Soc*. **2021**, *143*, 1038.
3. S. Karanjit, E. Tanaka, L. K. Shrestha, A. Nakayama, K. Ariga, and K. Namba, *Catal. Sci. Technol.* **2022**, *12*, 3778.

ブーメラン型高分子固定化 Cp*Ir 触媒を用いたギ酸脱水素反応

（筑波大院[1]・産総研[2]）○澤原 馨登[1,2]・田中 真司[2]・兼賀 量一[2]・川波 肇[1,2]
Boomerang-type polymer-immobilized Cp*Ir catalysts for formic acid dehydrogenation
([1]*Graduate School of Science and Technology, University of Tsukuba*, [2]*AIST*) ○ Keito Sawahara,[1,2] Shinji Tanaka,[2] Ryoichi Kanega,[2] Hajime Kawanami[1,2]

Formic acid is a promising candidate as a hydrogen carrier. Previously, we developed homogeneous Ir catalysts capable of generating hydrogen from formic acid with high efficiency. However, homogeneous catalysts face challenges such as recovery, highlighting the need for immobilized catalysts. In response, we developed an Ir catalyst immobilized on a polymer support. Despite this, issues such as Ir leaching after the reaction and reduced catalytic activity due to immobilization persisted. To address these challenges, we introduced the "Boomerang-type" catalyst concept and developed a new immobilized Ir catalyst. This catalyst completely suppresses Ir leaching after the reaction while maintaining the high catalytic efficiency of homogeneous catalysts.
Keywords: *Hydrogen, Immobilized catalysts, Formic acid, Dehydrogenation, Polymer*

ギ酸は水素キャリアとして期待されており、これまでに我々は、高効率でギ酸から水素を取り出すための均一系 Ir 触媒を開発してきた（図 1 左下(a)）。[1] これらの均一系触媒には、触媒の回収等の課題があり、触媒の固定化が望まれていた。このような背景のもと、我々は最近、高分子固相担体に錯体を固定化した触媒を開発した。[2] しかし、固定化に伴う触媒活性の低下や、反応初期に Ir が溶出する点に課題があった。

この課題の解決のため、本研究では、触媒活性を維持しつつ、反応後の触媒の溶出を抑える「ブーメラン型固定化触媒」を新たに開発した（図 1 左下(b)）。[3] 本触媒は 1) 反応開始と共に、溶液中に活性種が溶出し、反応終了に伴い、99%以上の活性種が担体に再度固定化される。2) 均一系触媒と同等の触媒活性を有する特徴を持つことが確認された。（図 1 右）詳細な触媒の合成方法および反応については、当日報告する。

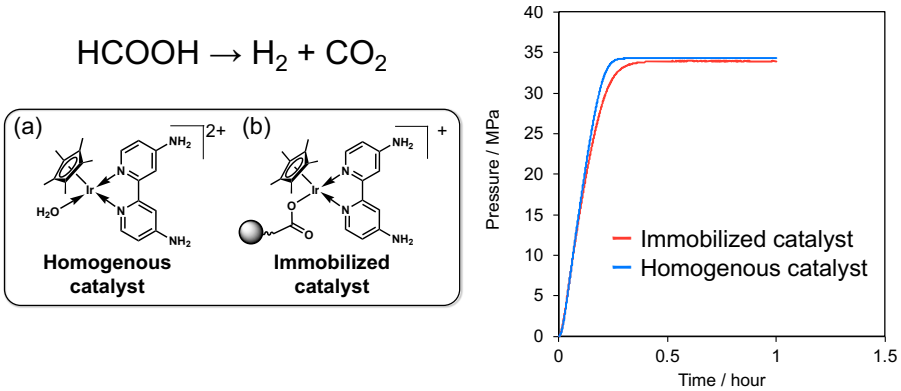


図 1　ブーメラン型固定化触と固定化前後での触媒活性の比較

[1] H. Kawanami *et al. Inorg. Chem.* **2020**, *59*, 4191, [2] K. Sawahara *et al. ChemSusChem* **2024**, *17*, e202301282, [3] K. Sawahara *et al.* **2025**, *Catal. Sci. Tech.*, *15*, 52

酸化アルミニウム担持炭化ニッケルナノ粒子触媒によるフルフラールからテトラヒドロフルフリルアルコールへの高選択的水素化反応

（阪大院基礎工[1]）○川上 大輝[1]・山口 渉[1]・満留 敬人[1]・水垣 共雄[1]

Aluminum-oxide-supported Nickel Carbide Nanoparticle Catalyst for Selective Hydrogenation of Furfural to Tetrahydrofurfuryl Alcohol ([1]*Graduate School of Engineering Science, Osaka University*) ○Taiki Kawakami,[1] Sho Yamaguchi,[1] Takato Mitsudome,[1] Tomoo Mizugaki[1]

The hydrogenation of furfural (FUR) is a key reaction for the synthesis of tetrahydrofurfuryl alcohol (THFA) used as a solvent and an intermediate in pharmaceutical production. Herein, we report that aluminum-oxide-supported nickel carbide nanoparticles (Ni_3C NPs/Al_2O_3) acts as highly active heterogeneous catalysts for the hydrogenation of FUR to THFA. The catalytic performance of Ni_3C NPs/Al_2O_3 was significantly higher than that of Ni NPs/Al_2O_3. Remarkably, Ni_3C NPs/Al_2O_3 provided THFA in excellent yield even at ambient H_2 pressure.

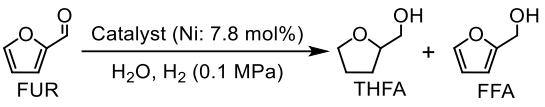
Keywords : Nickel Carbide; Hydrogenation; Furfural; Tetrahydrofurfuryl Alcohol; Biomass Transformation

フルフラール(FUR)は、木質系バイオマス由来の基幹化合物として注目されている。FUR の水素化反応により得られるテトラヒドロフルフリルアルコール(THFA)は、医薬中間体や溶媒等に利用される有用化合物である。本反応において、これまでに安価で資源豊富な非貴金属を基盤とする触媒の開発が盛んに行われてきたが、これらの触媒は一般に高温・高水素圧の厳しい反応条件を必要とする。本研究では、酸化アルミニウム担持炭化ニッケルナノ粒子(Ni_3C NPs/Al_2O_3)触媒が極めて温和な条件下で FUR から THFA への高選択的水素化反応を促進することを見出した。

Ni_3C NPs/Al_2O_3 触媒を用いて、H_2 0.1 MPa、90 ºC、反応時間 12 h の条件下、FUR 水素化反応を行った(Table)。本反応は効率よく進行し、転化率 68%、THFA およびフルフリルアルコール(FFA)収率はそれぞれ 23%、33%であった(Entry 1)。反応条件の最適化により、THFA 収率は 93%に向上した(Entry 2)。Al_2O_3 以外の金属酸化物に担持した Ni_3C NPs 触媒では、転化率と THFA 収率は低下した(Entries 3 and 4)。また、炭化していない Ni NPs/Al_2O_3 は、ほとんど THFA を与えなかった(Entry 5)。さらに、Ni_3C NPs/Al_2O_3 は FUR 以外のフラン化合物にも適用可能であり、対応するテトラヒドロフラン化合物が高収率で得られた。

本発表では、種々の対照実験および構造解析の結果に基づき、Ni_3C NPs/Al_2O_3 の優れた触媒機能の発現要因を議論する。

Table. Hydrogenation of FUR over various Ni catalysts.[a]



Entry	Catalyst	Conv. (%)	Yield (%) THFA	Yield (%) FFA
1	Ni_3C NPs/Al_2O_3	68	23	33
2[b]	Ni_3C NPs/Al_2O_3	>99	93	0
3	Ni_3C NPs/ZrO_2	52	12	25
4	Ni_3C NPs/TiO_2	22	2	13
5	Ni NPs/Al_2O_3	13	1	9

[a] Reaction conditions: FUR (0.5 mmol), H_2O (5 mL), 90 ºC, 12 h. [b] Catalyst (Ni: 15.6 mol%) and 48 h.

日本化学会 第105春季年会 (2025)

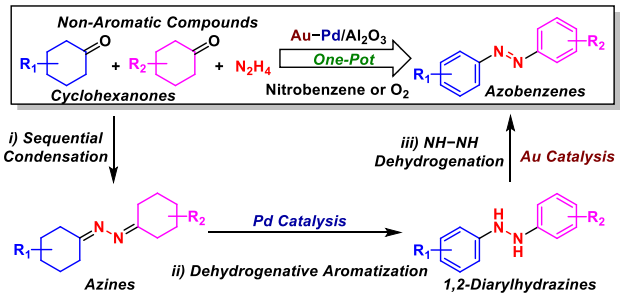
Au–Pd ナノ粒子触媒による非芳香族化合物を基質としたアゾベンゼン合成

（東大院工[1]・JST さきがけ[2]）○谷田部 孝文[1,2]・林 威辰[1]・矢部 智宏[1]・山口 和也[1]

Azobenzene Synthesis from Non-Aromatic Compounds Enabled by Au–Pd Nanoparticle Catalysts ([1]*School of Engineering, The University of Tokyo*, [2]*JST, PRESTO*) ○Takafumi Yatabe,[1,2] Wei-Chen Lin,[1] Tomohiro Yabe,[1] Kazuya Yamaguchi[1]

Azobenzenes have been widely utilized in various fields such as dyes and synthesized from aromatic compounds in diverse methods represented as azo coupling since 19th century[1,2]; however, the regioselectivity of substituents was intrinsically restricted by *o*/*m*/*p*-orientation derived from the use of aromatic compounds as the substrates, frequently leading to multistep synthesis with high environmental burdens and the limitation of the available azobenzene structures. Thus, azobenzene synthesis from only non-aromatic compounds is desired as the method to overcome the problems intrinsically, although such synthetic methods have never been reported. Here, we achieved the novel one-pot synthesis of azobenzenes including unsymmetrical ones from only non-aromatic compounds, i.e. cyclohexanones and hydrazine, with no limitation of the *o*/*m*/*p*-orientation via i) condensation, ii) dehydrogenative aromatization, and iii) NH–NH dehydrogenation by using Au–Pd alloy nanoparticle catalysts with high Au/Pd ratios in the presence of nitrobenzene[3] or O_2 as the hydrogen acceptor.
Keywords : Azobenzene, Au–Pd Nanoparticle Catalysts, Dehydrogenative Aromatization, Ensemble Effect, Product Selectivity

アゾベンゼンは染料をはじめとする幅広い分野で利用され、19 世紀から芳香族化合物を基質としたアゾカップリングに代表される様々な手法で合成されてきたが [1,2]、*o*/*m*/*p*-配向性に置換基の位置選択性が制限され一般に多段階合成を要することや合成可能な構造が制限されることが課題であった。したがって、本質的にこれらの課題を解決する手法として、非芳香族化合物のみからアゾベンゼンを合成する手法が望まれるが、アゾベンゼン合成の長い歴史にも関わらずそのような手法は未開発であった。本研究では、水素アクセプターとしてニトロベンゼン [3]または酸素分子存在下、高い Au/Pd 比を有する Al_2O_3 担持 Au–Pd ナノ粒子触媒を用いた、ヒドラジン及びシクロヘキサノン類からの縮合/脱水素芳香環形成/NH–NH 脱水素により、非芳香族化合物のみを基質とした非対称構造を含むアゾベンゼン One-Pot 合成を初めて達成した。



1) F. A. Jerca, V. V. Jerca, R. Hoogenboom, *Nat. Rev. Chem*. **2022**, *6*, 51.
2) M.-Y. Zhao, Y.-F. Tang, G.-Z. Han, *Molecules* **2023**, *28*, 6741.
3) W.-C. Lin, T. Yatabe, T. Yabe, K. Yamaguchi, *ChemRxiv* **2024**, doi: 10.26434/chemrxiv-2024-slmcb.

Visualization of catalytic active sites of multi-element alloy using machine learning

(1. Grad. Sch. Sci., Kyoto Univ., 2. HAKUBI Centre, Kyoto Univ., 3. RISM, Shinshu Univ., 4. Grad. Sch. Sci. and Tech., Meiji Univ.) ○Yuto Maruta[1], Kohei Kusada[1,2], Aspera Menez Susan[3], Gerardo Valadez Huerta[3], Yusuke Namba[3], Kaoru Hisama[3], Michihisa Koyama[3], Hiromasa Kaneko[4], Hiroshi Kitagawa[1]

Keywords: Nanoparticles, Multi-element alloys, Electrocatalysts, Machine learning, Hydrogen evolution reaction

Multi-element solid-solution alloy nanoparticles (MEA NPs) have attracted much attention as a new class of catalysts because they have high activity and stabilities for many kinds of reactions. For example, equimolar platinum-group metal (PGM) quinary alloy NPs show extremely high catalytic activity for electrochemical hydrogen evolution reaction (HER)[1,2]. However, it is still very challenging to design them and elucidate their complex mechanisms. Here, we focused on machine learning (ML) to find the optimal composition and to get an insight into the local active sites of MEA catalysts.

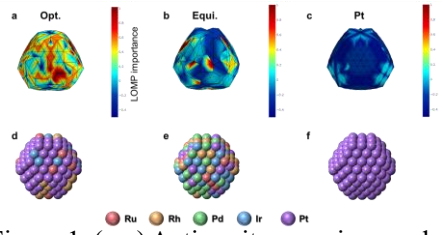


Figure 1. (a-c) Active site mappings and (d-f) NPs models of the optimized sample, equimolar sample, and Pt NP. These active site mappings show that the red-colored sites have a high possibility of being the local active sites of MEA.

We firstly synthesized PGM quinary alloy NPs with 75 different compositions directly on carbon support and evaluated their HER activities. Gaussian process regression (GPR) model was constructed for the dataset using only experimental data: turnover frequency (TOF) and composition obtained from X-ray fluorescence analysis as objective and explanation valuables, respectively. Then, the virtual experiment with 10,000 compositions using the final GPR model was performed to predict the optimal composition with the highest HER activity. Finally, a catalyst with the predicted optimal composition was synthesized and showed 6.3 times higher HER activity than Pt NPs.

To elucidate the catalytic mechanism, H, OH, and H_2O adsorption energies on all the catalytic sites of 201-atom NP models with the 76 compositional were calculated by PreFerred Potential[3]. A GPR model between experimental HER activities and these adsorption energies was constructed, and this model was interpreted by the local slope of model prediction (LOMP). LOMP importances of the ML model between experimental activities and adsorption energies suggested the contribution of the adsorption energy ranges to HER activity. Since alkaline HER involves the three adsorbates, the sum of the LOMP importance of H, OH, and H_2O adsorption energies was mapped onto the NP models (Fig. 1). The maps indicated that the optimal catalyst has larger active regions composed of multi-elements, suggesting that multiple elements concertedly promote the reaction on MEA NP. In contrast, the equimolar NP whose activity is about half of the optimal one has sparse active sites depending on the local configurations.

1) D. Wu et al., *Chem. Sci.*, 2020,11, 12731-12736. 2) Y. Maruta et al., *Chem Commun.*, 2022, 58, 6421-6424. 3) S. Takamoto et al., *Nat. Commun.*, 2022, 13, 2991

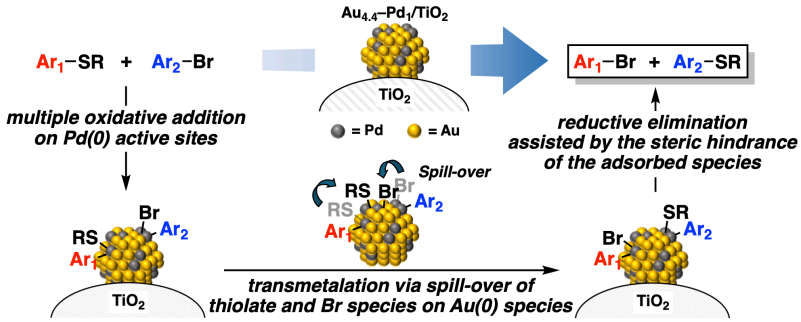
C–S/C–Br metathesis enabled by a supported Au–Pd alloy nanoparticle catalyst

([1]*School of Engineering, The University of Tokyo*) ○Takehiro Matsuyama, Takafumi Yatabe, Kazuya Yamaguchi

Keywords: Au–Pd alloy nanoparticles; C–S/C–Br metathesis; Transmetalation; Reductive elimination

Metathesis via C–S oxidative addition/reductive elimination to/from transition-metal catalysts has been attracting much attention as a functionalization of sulfur-containing molecules while the molecular frameworks are intact.[1] C–S/C–Br metathesis, a reaction that enables interconversion between both useful bromoarenes and thioethers, is especially attractive because it enables various transformative functionalization into valuable compounds in addition to the importance of bromoarenes themselves in diverse fields of chemistry; however, C–S/C–Br metathesis has not been reported so far likely due to the difficulties in the construction of catalytic systems compatible for reversible C–Br reductive elimination/oxidative addition and fast transmetalation between two kinds of oxidative adducts.[2]

In this study, we achieved unprecedented C–S/C–Br metathesis by a supported Au–Pd alloy nanoparticle catalyst with the Au/Pd molar ratio of 4.4 ($Au_{4.4}$–Pd_1/TiO_2).[3] This catalytic system was applicable to different thioethers and bromoarenes to afford both metathesis products in high yields. Additionally, this catalytic system enabled late-stage bromination of bioactive molecules and depolymerization of polyphenylene sulfide (PPS) into a monomer equivalent via C–S/C–Br metathesis. Based on a series of control experiments combined with density functional theory (DFT) calculations, the unprecedented C–S/C–Br metathesis was achieved by the following features: (i) multiple reversible oxidative addition of C–S/C–Br bonds on the multiple isolated Pd sites in the same Au–Pd alloy nanoparticles, (ii) transmetalation via spill-over of anion species through Au(0) sites, and (iii) C–Br reductive elimination assisted by the steric hindrance of thioether-derived species moderately adsorbed on the catalyst.



1) *Science* **2017**, *356*, 1059; *J. Am. Chem. Soc.* **2021**, *143*, 3723; *Chem. Sci.* **2024**, *15*, 11884. 2) *Chem. Rev*. **2016**, *116*, 8003; *Nat. Catal.* **2019**, *2*, 843; *Nat. Chem*. **2018**, *10*, 1016. 3) *ChemRxiv* **2024**, doi: 10.26434/chemrxiv-2024-mncv6.