

アカデミックプログラム [A講演] | 07. 無機化学：口頭A講演

2025年3月27日(木) 13:30 ~ 15:20 [C]C304(第2学舎 2号館 [3階] C304)

[[C]C304-2pm] 07. 無機化学

座長：荻原 直希、林 文隆

◆ 日本語

13:30 ~ 13:40

[[C]C304-2pm-01]

貴金属合金サブナノ粒子を触媒に用いた酸素還元反応

○中村 拓篤¹、小林 真由¹、森合 達也¹、ATQA Augie²、今岡 享稔¹、山元 公寿¹ (1. 科学大化生研、2. 東大院理)

◆ 日本語

13:40 ~ 13:50

[[C]C304-2pm-02]

導電性酸化物に担持したPtサブナノ粒子による酸素還元反応

○雑賀 芙美子¹、森合 達也¹、今岡 享稔¹、山元 公寿¹ (1. 科学大化生研)

◆ 日本語

13:50 ~ 14:00

[[C]C304-2pm-03]

Ptサブナノ粒子によって駆動する低温RWGS反応の機構解明

○中条 隼¹、ATQA Augie²、吉田 将隆¹、森合 達也¹、織田 晃³、熊谷 純⁴、今岡 享稔¹、山元 公寿¹ (1. 科学大化生研、2. 東大院理、3. 名大院工、4. 名大IMaSS)

◆ 日本語

14:00 ~ 14:10

[[C]C304-2pm-04]

サレン錯体とPOMを構成要素とする多孔性イオン結晶を用いた水素発生反応

○堤 由太郎¹、下山 雄人¹、荻原 直希¹、内田 さやか¹ (1. 東京大学)

◆ 日本語

14:10 ~ 14:20

[[C]C304-2pm-05]

ポリオキソメタレートとクロム錯体から成る多孔性イオン結晶を用いた水素発生反応

○浅田 響¹、堤 由太郎¹、下山 雄人¹、内田 さやか¹ (1. 東大大学院)

14:20 ~ 14:30

休憩

◆ 日本語

14:30 ~ 14:40

[[C]C304-2pm-06]

構造柔軟性を有する多孔性イオン結晶の分子吸着特性

○笠桐 知愛¹、望月 舜介¹、翁 哲偉¹、内田 さやか¹ (1. 東大 大学院)

◆ 英語

14:40 ~ 14:50

[[C]C304-2pm-07]

In-situ QXAFS study of CO₂ adsorption behavior on Nb and Ta mixed clusters

○Nattamon Panichakul¹, Soichi Kikkawa¹, Takuma Kaneko², Tomoya Uruga², Hideyuki Kawasoko^{1,3}, Naoki Nakatani¹, Seiji Yamazoe¹ (1. Graduate School of Science, Tokyo Metropolitan University, 2. JASRI, 3. JST-PRESTO)

◆ 日本語

14:50 ~ 15:00

[[C]C304-2pm-08]

ピリジン部位を含む環状エーテル基を付与したポリオキソメタレートの合成

○大西 風雅¹、飼鳥 弘人¹、加藤 智佐都¹、眞邊 潤¹、井上 克也^{1,2,3}、西原 禎文^{1,3,4} (1. 広島大学院先進理工、2. 広島大キラルノット超物質拠点、3. 広島大キラル国際拠点、4. JSTさきがけ)

◆ 英語

15:00 ~ 15:10

[[C]C304-2pm-09]

Humidity-induced Electronic Conductivity of POM-based Porous Ionic Crystals

○Seoji Yang¹, Naoki Ogiwara¹, Taisei Kurosaki¹, Shunsuke Mochizuki¹, Tsukasa Iwano¹, Yuji Kikukawa², Sayaka Uchida¹ (1. The Univ. of Tokyo, 2. Kanazawa Univ.)

◆ 英語

15:10 ~ 15:20

[[C]C304-2pm-10]

オレフィンのエポキシ化反応を指向したLinqvist型ポリオキソメタレートを基盤とした多孔性イオン結晶の創製

○高 愛玲¹、岩野 司¹、内田 さやか¹ (1. 東京大学)

貴金属合金サブナノ粒子を触媒に用いた酸素還元反応

(科学大化生研¹・東大院理²) ○中村 拓篤¹・小林 真由¹・森合 達也¹・ATQA Augie²・今岡 享稔¹・山元 公寿¹

Oxygen reduction reaction catalyzed by precious metal alloy sub-nanoparticles (¹Lab. for Chemistry and Life Science, Science Tokyo, ²Graduate School of Science, The University of Tokyo) ○Takuto Nakamura,¹ Mayu Kobayashi,¹ Tatsuya Moriai,¹ Augie Atqa², Takane Imaoka,¹ Kimihisa Yamamoto¹

Metal sub-nano particles (SNPs) with a particle size of approximately 1 nm able to alloy different metal species in any composition. Platinum (Pt) SNPs synthesized using a 4th generation phenylazomethine dendrimer (DPA-G4) originally developed in our laboratory have shown higher catalytic activity than Pt nano particles in the oxygen reduction reaction (ORR)¹⁾. In this work, we aimed to obtain further ORR catalytic activity by alloying Pt SNPs with various metal species. The alloy SNPs were synthesized using DPA-G4 prepared by Convergent method and were subsequently characterized by STEM observation and EDX analysis. Their electronic structure was characterized by XPS and XAFS. Convection voltammograms demonstrated high ORR catalytic activity of the alloy SNPs.

Keywords : Sub-nano Particles; Precious Metal; Oxygen Reduction Reaction; Dendrimer; Electrochemistry

粒径が約 1 nm の金属サブナノ粒子は結晶性を持たず、異なる金属種を任意の組成で合金化できる特異的な性質を有する。当研究室で独自に開発された第 4 世代フェニルアゾメチンデンドリマー (DPA-G4) を用いて合成された白金 (Pt) サブナノ粒子は、酸素還元反応 (ORR) において Pt ナノ粒子を超える触媒活性を示す¹⁾。本研究では、Pt を基軸として様々な金属種と合金化させることで更なる ORR 触媒活性を得ることを目的とした。コンバージェント法により自ら合成した DPA-G4 を用いて合金サブナノ粒子を合成した。同定は STEM 観察や EDX 分析によって行った。また合金サブナノ粒子の電子状態を XPS や XAFS 測定によって評価した。更に対流ボルタモグラムから ORR 触媒活性を評価し、合金サブナノ粒子の高い触媒活性が見出された。

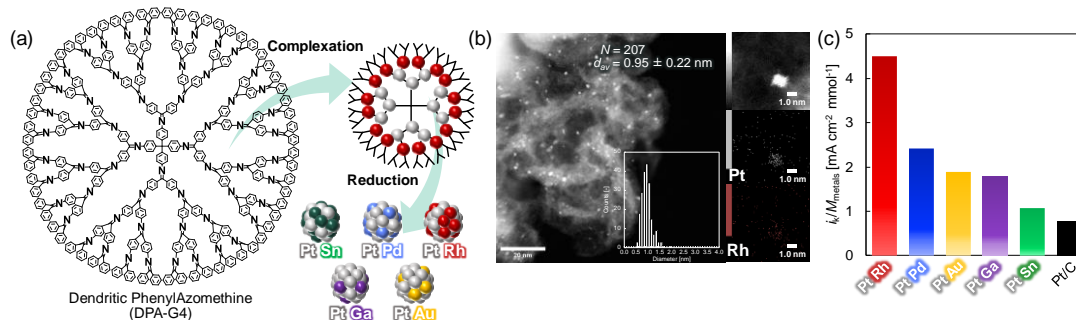


Fig. (a) Illustration of synthesis SNPs using DPA-G4, (b) STEM image (Inset: size distribution) and EDX mappings of Pt-Rh SNPs and (c) ORR catalytic activity of alloy SNPs.

1) K. Yamamoto *et al.*, *Acc. Chem. Res.*, **2017**, 47, 4, 1127-1136.

導電性酸化物に担持した Pt サブナノ粒子による酸素還元反応

(科学大化生研¹⁾) ○雑賀 芙美子¹・森合 達也¹・今岡 享稔¹・山元 公寿¹

Oxygen reduction reaction catalyzed by Pt sub-nanoparticles on conductive oxide supports (¹*Lab. for Chemistry and Life Science, Science Tokyo*) ○Fumiko Saika,¹ Tatsuya Moriai,¹ Takane Imaoka,¹ Kimihisa Yamamoto¹

Sub-nanoparticles (SNPs) with the diameter of approximately 1 nm have specific electronic states. Although carbon-supported SNPs have exhibited high catalytic performance in the oxygen reduction reaction (ORR), oxidative poisoning of the carbon support during the reaction has remained a significant challenge. In this work, Pt SNPs synthesized by the dendrimer template method¹⁾ were supported on conductive oxides to improve their durability as sub-nano ORR catalysts. Pt SNPs were synthesized by the fourth-generation phenylazomethine dendrimer (DPA-G4) as a template and supported on conductive oxides (Fig. 1A). They were applied to ORR using a ring disk electrode (RRDE) as catalysts. As a result, current values depending on the rotation speed of RRDE were obtained indicating that it was succeeded to catalyze ORR (Fig. 1B).

Keywords : Sub-nanoparticles; Platinum; Catalyst; Electrochemistry; ORR

サブナノ粒子は特異的な電子状態を有する 1 nm 程度の粒子である。我々はこれまでに炭素担持サブナノ粒子が高い酸素還元 (ORR) 活性を示すことを見出してきたが、一方で反応に伴う炭素担体の酸化被毒が懸念されていた。そこで本研究では、デンドリマー鑄型法¹⁾により合成した Pt サブナノ粒子を導電性酸化物に担持することで、サブナノ ORR 触媒としての耐久性向上を目指し、触媒活性と耐久性の面から ORR 性能について評価した。第4世代フェニルアゾメチンデンドリマーDPA-G4を鑄型として Pt サブナノ粒子を合成し、スズドープ酸化インジウムを始めとする導電性酸化物に担持した (Fig. 1A)。これを触媒としてリングディスク電極 (RRDE) を用いた ORR を行ったところ、LSV 測定において電極回転数に依存した電流値が得られたことから反応進行に成功した (Fig. 1B)。

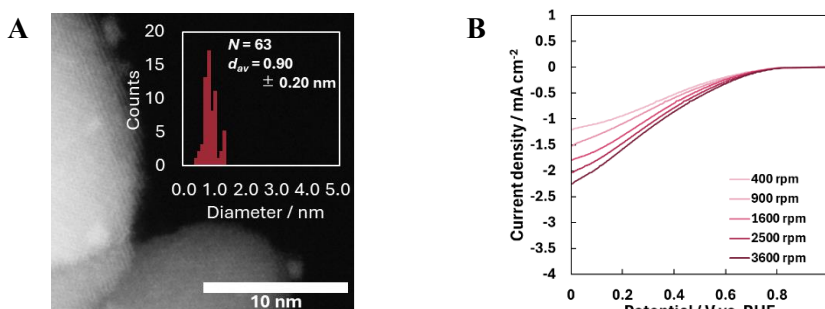


Fig. 1. (A) A STEM image of Pt SNPs/ITO and a histogram of the diameter of Pt SNPs. (B) LSV curves of rotating disk voltammograms of Pt SNPs/ITO in O_2 -saturated 0.1 M $HClO_4$.

1) Synthesis of sub-nanoparticles using dendrimers has been reported. T. Moriai, T. Tsukamoto, M. Tanabe, T. Kambe, K. Yamamoto, *Angew. Chem. Int. Ed.* **2020**, *59*, 23051–23055.

Pt サブナノ粒子によって駆動する低温 RWGS 反応の機構解明

(科学大化生研¹, 東大院理², 名大院工³, 名大 IMaSS⁴) ○中条隼¹・ATQA Augie²・吉田将隆¹・森合達也¹・織田晃³・熊谷純⁴・今岡享稔¹・山元公寿¹

Elucidation of the mechanism of low-temperature RWGS reaction driven by Pt subnanoparticles (¹Lab. for Chemistry and Life Science, Science Tokyo, ²Graduate School of Science, The University of Tokyo, ³Graduate school of Engineering, Nagoya University, ⁴IMaSS, Nagoya University) ○Hayato Nakajo¹, Augie Atqa², Masataka Yoshida¹, Tatsuya Moriai¹, Akira Oda³, Jun Kumagai⁴, Takane Imaoka¹, Kimihisa Yamamoto¹

We recently discovered that Pt sub-nanoparticles supported on TiO₂ in the reverse water gas shift (RWGS) reaction exhibit catalytic activity at low temperatures, which is not observed for nanoparticles. In this study, Pt/TiO₂ catalysts consisting of a wide range of particle sizes in the sub-nano- to nano-region were synthesized, and the size effect on RWGS activity was examined using the synthesized catalysts. The catalytic activity was highest at sub-nanometer sizes, and the reaction initiation temperature was about 40°C. An increase in the reaction initiation temperature and a decrease in activity with increasing particle size were observed. Furthermore, CO-DRIFTS measurements confirmed that Pt particles supported on TiO₂ exhibit different CO desorption capacities depending on the particle size. We observed that sub-nanoparticles have a high CO desorption capacity and desorb CO at the lowest temperature. The oxygen vacancies (Ov) on the TiO₂ surface, which serve as the active sites for CO₂, were characterized by ESR measurements, and a signal around $g=2.003$, attributed to Ov, was observed. This indicates that TiO₂ loaded with Pt sub-nanoparticles contains the highest density of Ov on the surface. These findings suggest that the high activation and low temperature driving force of the RWGS reaction is a mechanism specifically associated with Pt subnanoparticles.

Keywords : subnanoparticle, platinum, titanium oxide, RWGS reaction, oxygen vacancy

我々は逆水性ガスシフト(RWGS)反応において TiO₂ 上に担持された Pt サブナノ粒子が、ナノ粒子には見られない低温での触媒活性の発現を最近発見した¹⁾。本研究では Pt/TiO₂ 触媒の合成を行い合成した触媒を用いて、サブナノからナノ領域の幅広い粒径からなる Pt 粒子/TiO₂ 触媒の RWGS 活性におけるサイズ効果を検証した。触媒活性はサブナノサイズで最も高く、反応開始温度は約 40°C であった。また、粒径の増大に伴い、反応開始温度の上昇・活性低下が確認された。さらに、CO-DRIFTS 測定により、TiO₂ 上に担持させた Pt 粒子は粒径によって CO 脱離能が異なるという結果を確認した。特にサブナノ粒子では高い CO 脱離能を有しており、最も低温で CO が脱離することを発見した。また、ESR 測定によって CO₂ の活性サイトである TiO₂ 表面上の酸素欠損(Ov)の定量を行った。Ov に由来する $g=2.003$ 付近のシグナルを観測し、Pt サブナノ粒子を担持した TiO₂ は表面上に最も多くの Ov を有していることを発見した。以上の結果から、RWGS 反応の高活性化と低温駆動は Pt サブナノ粒子によって特異的に発現する機構であることを初めて解明した。

1) A.Atqa *et al.*, *Chem Comm*, **2023**, 59, 11947

サレン錯体と POM を構成要素とする多孔性イオン結晶を用いた水素発生反応

(東大院総合¹⁾) ○堤 由太郎¹・下山 雄人¹・荻原直希¹・内田 さやか¹

Hydrogen evolution using porous ionic crystals composed of salen complexes and polyacids
(¹Graduate School of Arts and Sciences, Tokyo University) ○Yutaro Tsutsumi,¹ Yuto Shimoyama,¹ Ryota Imashioya,¹ Yudai Suzuki,¹ Naoki Ogiwara,¹ Sayaka Uchida¹

Hydrogen is a promising next-generation energy carrier, while new hydrogen evolution reaction (HER) catalysts are needed to replace expensive platinum group catalysts for hydrogen production. Polyoxometalate (POM)-based compounds have attracted attention as next-generation HER catalysts; however, the composition-structure-activity relationship has not been established because of their complex compositions and structures. In this study, we synthesized a series of crystalline Keggin-type POM ($[\text{XW}_{12}\text{O}_{40}]^{n-}$) complexes as HER electrocatalysts and aimed to clarify the effects of the heterometal (X) and counter cations (Cs^+ or metal-salen, salen = *N,N'*-bis(salicylidene)ethylenediamine) on their functionality. The crystalline complexes showed superior activity to either POM or metal-salen alone, and synergistic effects of complexation were observed. More efficient HER was achieved by constructing crystalline complexes with transition-metal-substituted Keggin-type POMs.

Keywords : Polyoxometalate; Heteropolyacid; Salen complex; Hydrogen Evolution Reaction; Electrocatalyst

水素は次世代エネルギーキャリアとして有望であるが、高価な白金族触媒を使用した水の電気分解による水素生成に代わる新しい水素発生反応 (HER) 触媒の開発が求められている¹。ポリオキソメタレート (POM) は次世代 HER 触媒の一つとして注目されているが、既報の POM 化合物は複雑な組成や構造を有し、HER における POM の役割が明確ではない²。本研究では、組成と構造が規定された一連の結晶性 Keggin 型 POM ($[\text{XW}_{12}\text{O}_{40}]^{n-}$) 複合体を合成し、POM のヘテロ元素 (X) や対カチオン (Cs^+ や金属サレン錯体) が HER 活性に与える影響を明らかにすることを目的とした。結晶性複合体は、単体の POM やサレン錯体を凌駕する活性を示し、複合化による相乗効果が確認された。さらに、遷移金属置換型 POM を用いた結晶性複合体を用いると、より効率的に HER が進行することがわかった。

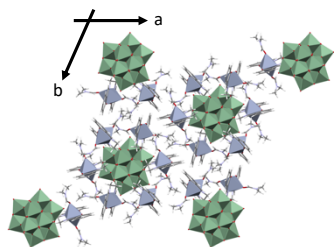


図 1 $[\text{Mn}(\text{salen})]_6[\text{CoW}_{12}\text{O}_{40}]$ の結晶構造

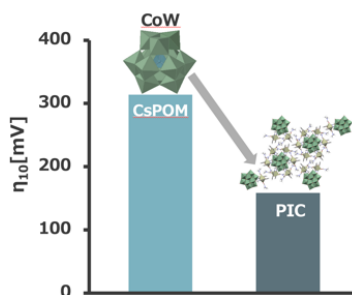


図 2 POM とサレン錯体の複合化による HER 過電圧 (η_{10}) の低下

1) Q. Tang and D. Jiang, *ACS Catal.*, **2016**, 9, 4953-4961.

2) D. Fernandes and M. Araujo, *ChemElectroChem*, **2017**, 11, 273-283.

ポリオキソメタレートとクロム錯体から成る多孔性イオン結晶を用いた水素発生反応

(東大院総合文化¹⁾) ○浅田 響¹・堤 由太郎¹・下山 雄人¹・内田 さやか¹

Hydrogen evolution reaction using porous ionic crystals with polyoxometalates and chromium complexes (¹*Graduate School of Arts and Sciences, The University of Tokyo*)○Hibiki Asada,¹ Yutaro Tsutsumi,¹ Yuto Shimoyama,¹ Sayaka Uchida¹

Toward the realization of a sustainable energy society, polyoxometalates (POMs) with multi-electron redox properties are expected to catalyze hydrogen evolution reactions (HER). Although previous studies on POM-immobilized composites have reported high electrocatalytic activity, the role of POM has remained unclear. In this study, three types of porous ionic crystals (PICs) composed of Keggin-type POMs ($[\text{Co}^{\text{II}}\text{W}^{\text{VI}}_{12}\text{O}_{40}]^{6-}$, $[\text{Zn}^{\text{II}}\text{W}^{\text{VI}}_{12}\text{O}_{40}]^{6-}$, $[\text{Co}^{\text{II}}\text{W}^{\text{VI}}_{11}\text{V}^{\text{IV}}\text{O}_{40}]^{8-}$) and a chromium complex $[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{CN})_6(\text{H}_2\text{O})_3]^+$ are used as electrocatalysts for HER. The η_{10} values, representing the overpotential to achieve a current density of 10 mA cm^{-2} , was evaluated by linear sweep voltammetry (LSV), and the PIC with $[\text{CoW}_{11}\text{VO}_{40}]^{8-}$ showed the smallest η_{10} value and superior performance. At the meeting, the HER mechanism will be discussed on the basis of the crystal structure of PICs and the electronic structure using the XANES region of X-ray absorption spectroscopy.

Keywords : Polyoxometalate; Water-splitting; Porous materials; Ionic crystal; Hydrogen evolution reaction

持続可能なエネルギー社会の実現に向け、多電子酸化還元能を有するポリオキソメタレート(POM)は水素発生反応(HER)触媒として期待されている。これまでに、POMを固定化した複合材料がHER電極触媒として高活性を示すことが報告されているが、POMの役割が不明瞭であった¹。本研究では、Keggin型POM($[\text{Co}^{\text{II}}\text{W}^{\text{VI}}_{12}\text{O}_{40}]^{6-}$, $[\text{Zn}^{\text{II}}\text{W}^{\text{VI}}_{12}\text{O}_{40}]^{6-}$, $[\text{Co}^{\text{II}}\text{W}^{\text{VI}}_{11}\text{V}^{\text{IV}}\text{O}_{40}]^{8-}$)とクロム錯体 $[\text{Cr}_3\text{O}(\text{OOCCH}_2\text{CN})_6(\text{H}_2\text{O})_3]^+$ を構成ユニットとする3種の多孔性イオン結晶(PICs)をHER電極触媒として利用した(Fig.1)。電位掃引に対する電流応答(LSV測定)により過電圧 η_{10} (10 mA/cm^2 を与える電圧)を評価した結果、 $[\text{CoW}_{11}\text{VO}_{40}]^{8-}$ を含むPIC触媒が最も小さな値を示し、触媒として優れることがわかった(Fig.2)。発表当日は、反応メカニズムについて、PICsの結晶構造やX線吸収分光のXANES領域を用いた電子状態を基に議論する予定である。

1) D. M. Fernandes *et al.*, *ChemElectroChem*, **2018**, 5, 273

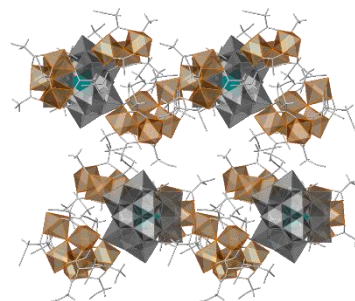


Fig.1. PICsの結晶構造
(灰色: $[\text{WO}_6]$, $[\text{VW}_5\text{O}_6]$ ユニット
茶色: $[\text{CrO}_5\text{N}]$ ユニット)

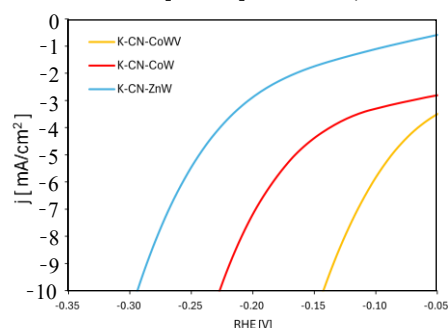


Fig.2. PICsの η_{10}

構造柔軟性を有する多孔性イオン結晶の分子吸着特性

(東大院総合文化¹) ○笠桐 知愛¹・望月 舜介¹・翁 哲偉¹・内田 さやか¹

Molecular Adsorption Properties of Porous Ionic Crystals with Structural Flexibility (¹*Sch. Arts and Sci., The Univ. of Tokyo*) ○Tomochika Kasagiri¹, Shunsuke Mochizuki¹, Zhewei Weng¹, Sayaka Uchida¹

Porous ionic crystals (PICs) comprising polyoxometalate (POM) anions and molecular metal complex cations have been reported for various applications. This study investigates the sorption kinetics of two PICs (**PIC(CH₃)**, **PIC(NH₂)**) with MeOH and CO₂ gas adsorption. **PIC(CH₃)** possesses structural flexibility, while **PIC(NH₂)** forms a stable layered structure (**Fig. 1**). The time course of gas adsorption showed that **PIC(CH₃)** continues to adsorb gas over time, while **PIC(NH₂)** quickly reaches adsorption equilibrium. Kinetic analysis using the linear driving force model revealed that **PIC(CH₃)** exhibits continuous adsorption with lattice expansion, while **PIC(NH₂)** does not (**Fig. 2**), which agrees with the structural characteristics. **Keywords**: Ionic Crystal; Porous Material; Adsorption; Polyoxometalate; Hydrogen Bond

ポリオキソメタレート(POM)と分子性多核カチオンにより構築される多孔性イオン結晶(PICs)は、その細孔構造を活用した様々な応用が報告されている¹⁾。最近、Tris-有機配位子で修飾されたPOMを構成ユニットとするPICsについて、配位子末端に応じて細孔特性やガスや蒸気の吸着特性が系統的に変化することを見出している。本研究では、PICs (**PIC(CH₃)**, **PIC(NH₂)**) (**Fig. 1**)へのガス吸着メカニズムを明らかにすることを目的として、MeOHとCO₂を例に、吸着量の経時変化を重量法により測定し、適切な速度式によって解析した。これまでに、吸着等温線と粉末X線回折の結果から、**PIC(CH₃)**は構造柔軟性を有するのに対し、**PIC(NH₂)**は安定な層状構造を形成することがわかっている。吸着量の経時変化を測定した結果、吸着質によらず**PIC(CH₃)**はその構造柔軟性から吸着量が増加し続け、**PIC(NH₂)**は速やかに吸着平衡状態に達した(**Fig. 2**)。解析の結果、**PIC(NH₂)**は単純な線形駆動力モデルの式で表せるものの、**PIC(CH₃)**は2つの線形駆動力モデルの式の和で表す必要があった。このモデル化から、いずれの吸着質も細孔内拡散により吸着速度が支配されていることが示唆される。

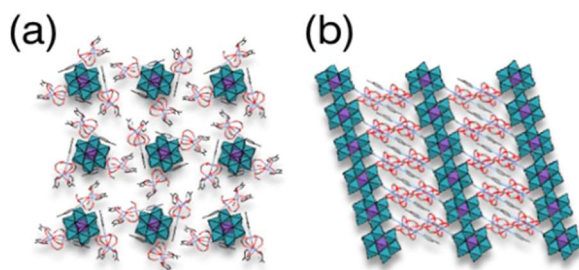


Fig. 1 Structures of PICs of (a) **PIC(CH₃)** and (b) **PIC(NH₂)**

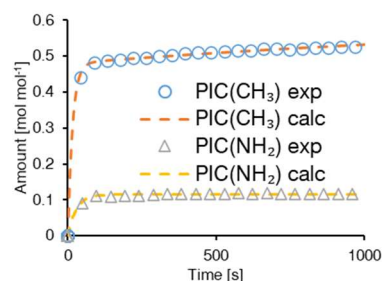


Fig. 2 Time course of CO₂ adsorption amount and the calculation.

1) Y. Shimoyama, S. Uchida, *Chem. Lett.*, 2021, **50**, 21–30.

In-situ QXAFS study of CO₂ adsorption behavior on Nb and Ta mixed clusters

(¹Graduate School of Science, Tokyo Metropolitan University, ²JASRI, ³JST, PRESTO)
 ○Panichakul Nattamon¹, Soichi Kikkawa¹, Takuma Kaneko², Tomoya Uruga², Hideyuki Kawasoko^{1,3}, Naoki Nakatani¹, Seiji Yamazoe¹

Keywords: polyoxometalates, base catalysts, CO₂ fixation reaction, CO₂ adsorption, QXAFS

Polyoxometalates (POMs) composed of Ta and Nb possess base properties that facilitate catalytic activity for Knoevenagel condensation and CO₂ fixation reactions.¹ Recently, TBA_{8-n}H_n(Ta_xNb_{6-x}O₁₉) (defined as TBA-Ta_xNb_{6-x}) with the composition of TBA-Ta₁Nb₅ efficiency promotes CO₂ fixation of styrene oxide to form styrene carbonate with high selectivity.² We proposed that single TaO₆ unit surrounded by NbO₆ units activate CO₂ and undesired styrene activation was suppressed (**Figure 1a**). Hence, this work focuses on CO₂ activation behavior of TBA-Ta₁Nb₅ through the time-resolved quick X-ray absorption fine structure (QXAFS).

TBA-Ta₁Nb₅ was synthesized by the mixture of K₈Ta₆O₁₉·nH₂O and K₈Nb₆O₁₉·nH₂O which were ionized by HCl aq. before washed and dried. The obtained powder was added into TBAOH aq. which underwent microwave irradiation.³ The synthesis was confirmed by ESI-MS, FT-IR, and CHN analysis. The CO₂ adsorption behavior was monitored through *in-situ* experimental setup at SPring-8 BL36XU as illustrated in **Figure 1b**. Accordingly, *ca.* 1 equimolar CO₂ was bound to a unit of TBA-Ta₁Nb₅, likely onto the TaO₆ unit as suggested by the DFT calculations. In **Figure 2a-b**, the decrease in pre-edge peak intensity in Ta L₁-edge XANES of TBA-Ta₁Nb₅ by the initial CO₂ exposure for 20 minutes indicates that local structure changed in the TaO₆ unit, while insignificant change was observed in the Nb K-edge XANES. Furthermore, an increase in Ta L₃-edge white-line region (**Figure 2c**) by CO₂ adsorption indicates the changes in local structure of TaO₆ unit which is consistent with the reported result.⁴ In the presentation, the geometrical parameters calculated by DFT and the obtained QXAFS data will be discussed to understand CO₂ adsorption behavior of the mixed oxide cluster.

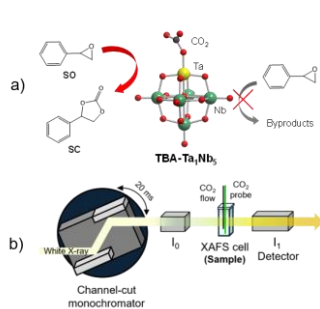


Figure 1. Schematic diagram of a) TBA-Ta₁Nb₅ catalytic activity in CO₂ fixation of styrene oxide² and b) *in-situ* QXAFS set-up.

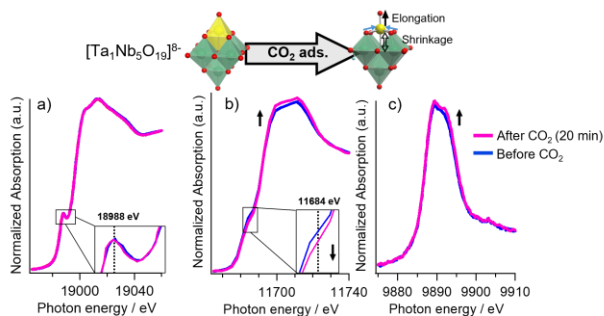


Figure 2. TBA-Ta₁Nb₅ XANES spectra before and after 20 minutes of CO₂ adsorption: a) Nb K-edge, b) Ta L₁-edge and c) Ta L₃-edge.

1) S. Hayashi *et al.*, *J. Phys. Chem. C*, **2018**, 122, 29398–29404, 2) V. Chudatemiya *et al.*, *Catalysts*, **2023**, 13, 432–442, 3) S. Kikkawa *et al.*, *Angew. Chem. Int. Ed.*, **2024**, 63, e202401526, 4) T. Matsuyama *et al.*, *J. Phys. Chem. C.*, **2024**, 128, 2953–2958.

ピリジン部位を含む環状エーテル基を付与したポリオキソメタレート合成

(広島大院先進理工¹・広島大キラルノット超物質拠点²・広島大キラル国際拠点³・JST さきがけ⁴) ○大西 風雅¹・飼鳥 弘人¹・眞邊 潤¹・加藤 智佐都¹・井上 克也^{1,2,3}・西原 禎文^{1,3,4}

Synthesis of the Polyoxometalate with Cyclic Ethers unit Including Pyridine (¹*Grad. Sch. Adv. Sci. Eng., Hiroshima Univ.*, ²*WPI-SKCM², Hiroshima Univ.*, ³*CResCent, Hiroshima Univ.*, ⁴*PRESTO, JST*) ○Fuga Onishi,¹ Hiroto Kaitori,¹ Jun Manabe,¹ Chisato Kato,¹ Katsuya Inoue,^{1,2,3} Sadafumi Nishihara^{1,3,4}

Polyoxometalates (POMs) are molecular metal oxide cluster containing early transition metals. Our research group previously reported **Crown POM**, which incorporates a cyclic ether structure into Preyssler-type POM.¹ This modification imparts crown ether-like ion inclusion properties to the molecule. In this study, we introduced a pyridine unit into **Crown POM** to explore new functional properties, such as organometallic complex formation, due to pyridine's ability to coordinate with metal ions. A pyridine derivative with a phosphonic acid moiety (**PA-Py**) was obtained from 2,6-dichloropyridine in five steps. Subsequently, polyoxometalate with cyclic ethers unit including pyridine (**Pyridine-POM**) was synthesized by adding **PA-Py** and $K_{12}[H_2P_2W_{12}O_{48}]$ in the ratio of 1:2 in solution and heating to 60°C.

Keywords : Pyridine; Polyoxometalate; Organic-inorganic hybrid compound

ポリオキソメタレート (POM) は、前期遷移金属を含む分子性金属酸化物クラスターであり、高い酸化還元能や強固な構造を有している。当研究室では、Preyssler 型 POM に、ホスホン酸部位をもつエーテル構造を付与した **Crown POM** を合成した^[1]。これにより無機分子である POM に有機分子由来のイオン包接能を付与することに成功した。本研究では、新たな有機無機ハイブリッド POM の合成と機能発現を目指し、ピリジンの錯形成能力に着目した。ピリジン誘導体は分子同士が絡み合ったカテナンを形成することが知られており、これを POM 分子に組み込むことでカテナン部位の運動性を利用した機能付加が期待できる。始めに、カテナンを含んだ POM の合成に先立ち、ピリジン部位を有する POM 分子(**Pyridine-POM**)の合成を試みた。

2,6-ジクロロピリジンを出発物として、5 ステップでホスホン酸部位を有するピリジン誘導体 (**PA-Py**) を得た。その後、**PA-Py** と $K_{12}[H_2P_2W_{12}O_{48}]$ を溶液中に 1:2 の割合で加え、60°C に加熱することで **Pyridine-POM** の合成を試みたので報告する (図 1)。

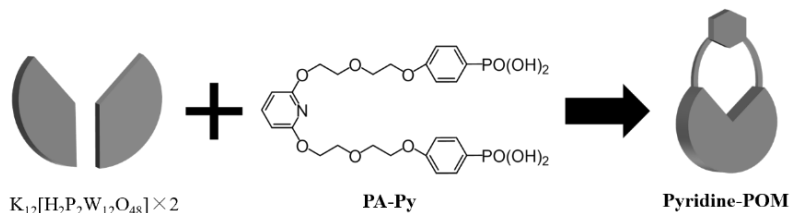


Fig. 1. Schematic diagram of **Pyridine-POM**.

[1] H. Kaitori, S. Nishihara, *et al.*, 日本化学会第 103 回春季年会, K204-3pm-04 (2023).

Humidity-induced Electronic Conductivity of POM-based Porous Ionic Crystals

(¹*School of Arts and Sciences, The university of Tokyo*, ²*College of Science and Engineering, Kanazawa University*) ○ Seoji Yang,¹ Naoki Ogiwara¹, Taisei Kurosaki¹, Shunsuke Mochizuki¹, Tsukasa Iwano¹, Yuji Kikukawa², Sayaka Uchida¹

Keywords: Porous materials, Polyoxometalates, Conductivity

Porous materials, due to their large surface area, are highly valuable for gas/vapor adsorption and separation. In particular, porous materials with electronic conductivity have attracted significant attention because they can modulate their electronic conductivity in response to guest sorption, such as water vapor, offering promise for sensor applications.¹ Among porous materials, porous ionic crystals (PICs) are crystalline porous composites formed by Coulomb interactions between anionic polyoxometalates (POMs) and macrocations such as oxo-centered trinuclear metal carboxylates.² The manipulation of the composition and structure of PICs enables the sorption of molecules/ions, proton conduction, and catalysis. However, the electron conduction of PICs remains relatively unexplored, although modulation of electronic conductivity through guest sorption in PICs is expected, as observed in other electroconductive porous materials.

In this study, Cr-complex cation, $[\text{Cr}_3\text{O}(\text{OOCH})_6(4\text{-methylpyridine})_3]^+$, was assembled with two different POMs, $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$ (**V₁₀**) and $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ (**SiW₁₂**) to construct two PICs, namely **PIC-V₁₀** and **PIC-SiW₁₂**. Single crystal XRD of each PIC revealed different arrangements of the Cr-complex (**Fig. 1**): **PIC-V₁₀** formed a hexagonal lattice, whereas **PIC-SiW₁₂** formed a rectangular lattice. The electronic conductivity of the PICs, measured by chronoamperometry (CA), was low under dry conditions but their conductivity increased with increasing humidity levels. Their trend and the value of electronic conductivity differed, suggesting a variation in conductivity with crystal structure. The relationship between the crystal structures and electronic conductivity, as well as the potential mechanism behind humidity-induced electronic conductivity, will be discussed.

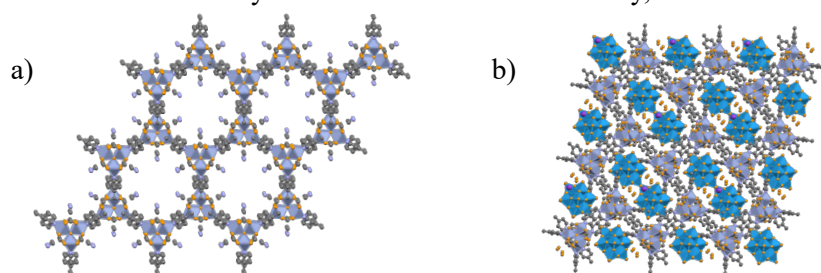


Fig 1. Crystal structure of a) **PIC-V₁₀** (**V₁₀** was disordered and could not be assigned by single crystal XRD) and b) **PIC-SiW₁₂**. Purple and blue polyhedra show the $[\text{CrO}_5\text{N}]$ unit of Cr-complex cation and the $[\text{WO}_6]$ unit of **SiW₁₂**, respectively.

1) W. Deng, G. Xu *et al.*, *Angew. Chem. Int. Ed.* **2023**, 62, e202305977. 2) Y. Shimoyama, S. Uchida *et al.*, *J. Am. Chem. Soc.* **2022**, 144, 2980–2986.

Porous Ionic Crystals Based on Lindqvist-Type Polyoxometalates for Olefin Epoxidation

(¹Graduate School of Arts and Science, The Univ. of Tokyo) ○Ailing Gao,¹ Tsukasa Iwano,¹ Sayaka Uchida¹

Keywords: Lindqvist-type cluster; Polyoxometalate; Olefin epoxidation

The epoxidation of olefins is an important reaction in the chemical industry. Polyoxometalates (POMs) are a class of early-transition-metal oxides and have demonstrated remarkable catalytic performance in selective oxidation of olefins.¹ Recent research has focused extensively on achieving the heterogenization of homogeneous POM catalysts to address their drawbacks. Various preparation strategies have been developed to create heterogeneous POM-based catalysts.² These strategies include self-assembling POMs with organic compounds to form supramolecular structures.³

Currently, research on POM based materials for olefin epoxidation reactions are mainly focuses on the Keggin $[XM_{12}O_{40}]^{n-}$ and Dawson $[X_2M_{18}O_{62}]^{n-}$ types, while studies on the Lindqvist-type $[M_6O_{19}]^{n-}$ POMs are relatively scarce. Therefore, we synthesized five novel Lindqvist-type POM based porous ionic crystals (PICs) named $H_n-4[Cr_3O(OOCC_6H_5)_6(H_2O)_3]_4[M_6O_{19}](OH)_{4-n}$ and investigated their performance in olefin epoxidation reactions. We characterized the five novel PICs using IR, PXRD, TG, CV and SXRD etc., and the results demonstrated successful synthesis. Additionally, GC was employed to study the conversion and selectivity of olefin epoxidation, revealing excellent catalytic performance (Figure 1). Furthermore, the catalyst can be recycled after the reaction and reused at least twice.

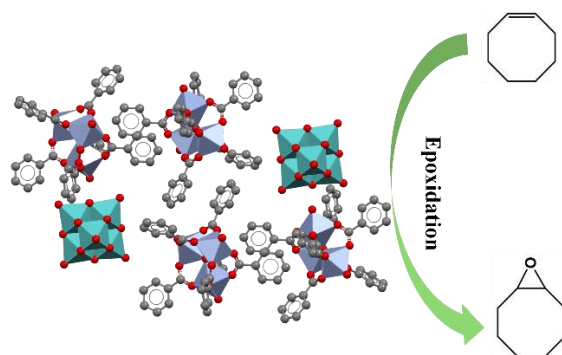


Figure 1. Schematic illustration of cyclooctene's epoxidation using Lindqvist-type POMs based PIC.

1) N. Mizuno, K. Yamaguchi, K. Kamata, *Coordination Chemistry Reviews* **2005**, 249, 1944-1956. 2) E. Tebandeke, C. Coman, K. Guillois, G. Canning, E. Ataman, J. Knudsen, L. R. Wallenberg, H. Ssekaalo, J. Schnadt, O. F. Wendt, *Green Chemistry* **2014**, 16, 3. 3) S. Uchida, E. Takahashi, N. Mizuno, *Inorg Chem* **2013**, 52, 9320-9326.