アカデミックプログラム［Ｂ講演］｜03. 物理化学—構造：口頭Ｂ講演

2025年3月28日(金) 14:00 ~ 15:20 [C]C204(第2学舎 2号館 [2階] C204)

[[C]C204-3pm] 03. 物理化学—構造

座長：伊藤 冬樹、古部 昭広

日本語

14:00 ~ 14:20

[[C]C204-3pm-01]

ESRスピンプローブ法を用いた光重合型歯科材料中の細孔に関する研究

○小林 広和[1]、岩堀 史靖[2]、本多 英彦[1]、山本 雅人[1]、細井 宜伸[3]、小田中 友紀[4]、高木 孝士[5]、田中 玲奈[6]、柴田 陽[6] (1. 昭和大教、2. 日大文理、3. 株式会社リガク、4. 昭和大薬、5. 昭和大電子顕微鏡室、6. 昭和大歯)

英語

14:20 ~ 14:40

[[C]C204-3pm-02]

低温酸化還元特性を示すミクロンサイズのセリア系金属酸化物の合成と構造解析

○LI WENJUN[1,2]、松井 公佑[1]、Chaoqi CHEN[1,2]、邨次 智[1]、唯 美津木[1,2] (1. 名古屋大学、2. 名大物国セ)

英語

14:40 ~ 15:00

[[C]C204-3pm-03]

振動和周波発生分光法を用いた溶媒抽出界面の研究：ジグリコールアミド抽出剤とランタノイドイオンの界面錯体の形成とその構造

○奥寺 洸介[1,2]、浦島 周平[1]、佐々木 祐二[1]、渡邉 雅之[1]、村松 悟[2]、井口 佳哉[2]、日下 良二[1] (1. 日本原子力研究開発機構・基礎工センター、2. 広島大院先進)

英語

15:00 ~ 15:20

[[C]C204-3pm-04]

走査プローブ顕微鏡データの画像処理を用いた二酸化チタン表面における酸素欠損の相互作用解析
-局所構造認識の最適化-

坪倉 奏太[2,3]、河野 翔也[4]、今井 弓子[1]、上田 正[1]、中本 圭一[1]、野間 春生[3]、日置 尋久[2]、○湊 丈俊[1] (1. 分子研、2. 京大、3. 立命館大、4. 九州工業大学)

ESR スピンプローブ法を用いた光重合型歯科材料中の細孔に関する研究

(昭和大教 1・日大文理 2・株式会社リガク 3・昭和大薬 4・昭和大電子顕微鏡室 5・昭和大歯 6) ○小林広和 1・岩堀史靖 2・本多英彦 1・山本雅人 1・細井宜伸 3・小田中友紀 4・高木孝士 5・田中玲奈 6・柴田陽 6

Micropores in a light curing resin studied using ESR spin probe technique

([1]*Fac. of Arts and Sci. at FY, Showa Univ.*, [2]*Col. of Humanities and Sci., Nihon Univ.* , [3]*Rigaku Corp.*, [4]*Sch. of Pharm., Showa Univ.*, [5]*Center for Electron Microsc., Showa Univ.*, [6]*Sch. of Dent., Showa Univ.*)
○ Hirokazu Kobayashi,[1] Fumiyasu Iwahori,[2] Hidehiko Honda,[1] Masato Yamamoto[1], Yoshinobu Hosoi[3], Yuki Odanaka,[4] Takashi Takaki,[5] Reina Tanaka,[6] Yo Shibata[6]

Recently, light curing composite resin (CR) has been used as a material for dental restorations of teeth structure. Micropores in CR affect hardness of CR and the interaction between CR and fillings for increase of its hardness. In this study, TEGDMA, one of the most famous monomers used in light curing CRs, including a tiny amount of a few kinds of probe radical, such as TEMPO, was cured with visible blue light. Temperature-dependent electron spin resonance (ESR) measurements and spectral reproductions were conducted for TEGDMA polymers including TEMPO, indicating that probe TEMPO radicals underwent uniaxial rotational diffusion in their axial symmetric nanospaces.

Keywords : ESR spin probe technique, light curing composite resin, porous material, molecular motion, stable free radical

近年、歯質の成形修復材料として光重合型高分子1)を原料とするコンポジットレジン（CR）が用いられている。CR 中には微細な細孔が存在し、材料の性質に影響を与えていると考えられる。このような細孔の大きさや形状を調べるには、フリーラジカルをプローブとした電子スピン共鳴(ESR)の測定が有効である。2)本研究では CR の材料としてよく用いられる TEGDMA にフリーラジカルをドープした状態で光重合を行い、温度依存 ESR スペクトルを測定した。その結果、低温では運動停止状態のスペクトルが、室温では TEMPO ラジカルの軸性回転拡散運動を表す ESR スペクトル（図；測定結果と EasySpin プログラムにより再現したもの）が得られた。この結果より、TEGDMA ポリマー中に軸対称のナノ空間が存在することが明らかになった。

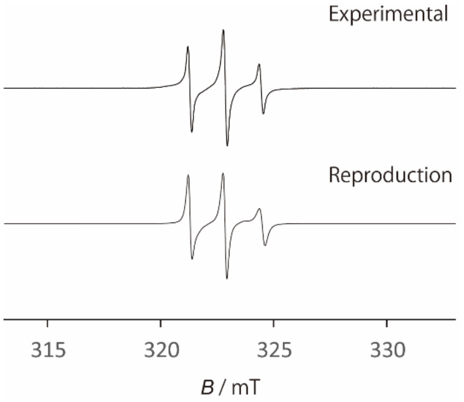

図 室温における TEGDMA ポリマー中の TEMPO ラジカルの ESR スペクトル。

---

1) ESR studies on radical polymerization has been reported. M.Kamachi, *Adv. Polym. Sci*. **1987**, *82*, 207.
2) Investigation of Various Organic Radicals Dispersed in Polymethylmethacrylate Matrices Using the Electron Spin Resonance Spectroscopy Technique has been reported. H. Kobayashi, *et al*., *ACS Omega* **2021**, *6*, 20855.

Micron-Sized Ceria-Based Metal Oxides for Low-Temperature Redox Properties: Synthesis and Characterization

([1]*Research Center for Materials Science, Nagoya University*, [2]*Graduate School of Science, Nagoya University*)
○Wenjun Li,[1,2] Hirosuke Matsui, [2] Chaoqi Chen,[1,2] Satoshi Muratsugu,[2] Mizuki Tada[1,2]

Keywords: Mixed Metal Oxide, Ceria, Redox property, Transition Metal, X-ray Imaging

Ceria (CeO_2) is widely recognized as a vital material in heterogeneous catalysis due to its unique redox properties. Pure ceria typically activates at temperatures above 673 K and the redox property at low temperature is quite limited. Increasing oxygen vacancies, often achieved by doping with transition metals, lowers its redox activation temperature by modifying its electronic and chemical properties. Our group has previously reported the synthesis and catalytic performance of $Cr_{0.19}Rh_{0.06}CeO_z$. This catalyst exhibits reversible redox activity at temperatures as low as 373 K, facilitating unique catalytic reactions.[1-3]

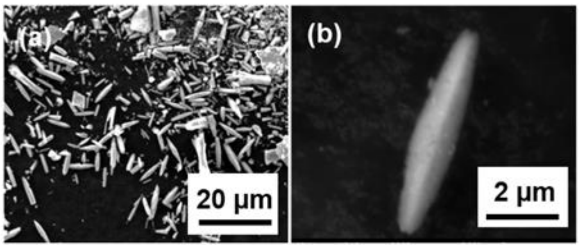

Figure 1. SEM image of microrod $Rh_{0.05}Cr_{0.11}CeO_x$; (a) overview, (b) single particle of the microrod.

In this study, we report the synthesis and characterization of microrod-shaped ceria catalysts incorporating transmition metal for the visualization of the redox behavior on ceria domian by X-ray spectroimaging. This microrod-shaped ceria-based catalyst exhibited remarkable, reversible redox properties at temperatures below 373 K. Its micrometer-scale size is suitable for X-ray spectroimaging,[4] facilitating a detailed elucidation of the spatial catalytic mechanisms on ceria. SEM images revealed the formation of microrods in the size range of length 5-20 μm with diameters of 1~5 μm (Fig. 1(a, b)). Temperature-programmed reduction (TPR) with H_2 suggested that $Rh_{0.05}Cr_{0.11}CeO_x$ exhibited the lowest redox temperature compared to $Rh_{0.02}CeO_x$, $Cr_{0.11}CeO_x$, and CeO_2 similarly prepared (Fig. 2). The detail characterization and X-ray imaging of the $Rh_{0.05}Cr_{0.11}CeO_x$ microrods will be presented.

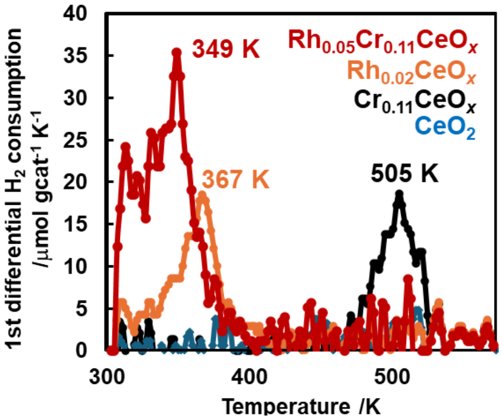

Figure 2. First differential plots of H_2 consumption in TPR on $Rh_{0.05}Cr_{0.11}CeO_x$ (red), $Rh_{0.02}CeO_x$ (orange), $Cr_{0.11}CeO_x$ (black) and CeO_2 (blue).

1) S. Ikemoto, M. Tada, *et al. ACS. Catal.*, **2022**, *12,* 431. 2) S. Ikemoto, M. Tada, *et al.*, *J.Am.Chem.Soc.* **2023**, *145*, 1497. 3) S. Ikemoto, M. Tada, *et al.*, *Phys. Chem. Chem. Phys.* **2019**, *21*, 20868. 4) H. Matsui, M. Tada, *et al.*, *ACS Appl. Mater. Interfaces*, **2022**, *14*, 6762.

Study of solvent extraction interfaces using vibrational sum frequency generation spectroscopy: Formation and structure of interfacial complexes between diglycolamide extractants and lanthanide ions

(*[1]Nuclear Science and Engineering Center, Japan Atomic Energy Agency (JAEA),*
[2]Graduate School of Advanced Science and Engineering, Hiroshima University)
○Kosuke Okudera[1,2], Shu-hei Urashima[1], Yuji Sasaki[1], Masayuki Watanabe[1], Satoru Muramatsu[2], Yoshiya Inokuchi[2], Ryoji Kusaka[1]

Keywords: Sum Frequency Generation Spectroscopy; Interface; Lanthanide; Diglycolamide; Solvent Extraction

High-level radioactive waste generated from the reprocessing of spent nuclear fuel contains highly radiotoxic elements, such as americium (Am). Solvent extraction using diglycolamide (DGA) extractants (Fig. 1), which act as chelating agents to transfer lanthanide and actinide ions from the aqueous phase to the organic phase, is a promising method for separating radioactive elements and reducing radioactive waste. In this study, vibrational sum frequency generation (VSFG) spectroscopy was employed to investigate the chemical states of DGA extractants at the solvent extraction interface, aiming to gain insights into the transport mechanism of lanthanide ions between the two liquid phases.

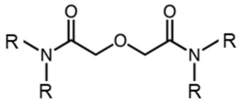

Fig 1. Structure of diglycolamide (DGA)

Figure 2 shows the VSFG spectra in the C=O stretching vibrational region, obtained at the air/tetrabutyl DGA (TBDGA)/aqueous model solvent extraction interface. Under conditions where [Gd^{3+}] concentrations range from 0 to 0.001 M, the C=O stretching band of TBDGA is observed at approximately 1660 cm^{-1}. A low wavenumber shift of approximately 20 cm^{-1} is observed for [Gd^{3+}] concentrations exceeding 0.001 M. This low wavenumber shift in the C=O stretching vibration suggests that TBDGA forms a complex with Gd^{3+} at the interface through its C=O groups. The decrease in SFG intensity with increasing [Gd^{3+}] concentrations is likely due to the C=O groups of TBDGA in interfacial complexes adopting a higher-symmetry environment compared to uncomplexed TBDGA. The molecular structure of the interfacial complexes will be discussed in the presentation, based on data obtained with DGAs featuring different alkyl chain lengths.

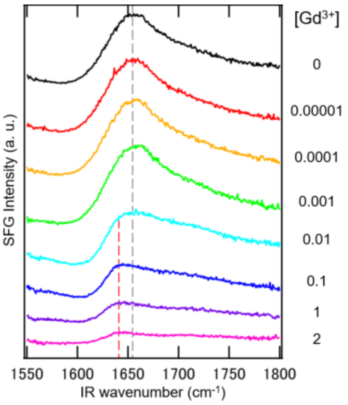

Fig 2. VSFG spectra of the air/TBDGA/aqueous interfaces. The concentrations of Gd^{3+} in the aqueous phase are expressed in mol/L.

Image Processing of Scanning Probe Microscopy Data for Analyzing the Interactions of Oxygen Vacancies on the Surfaces of Titanium Dioxide
-Optimization of Local Structure Recognition-

Sota Tsubokura[1,2], Shoya Kawano[3], Yumiko Imai[4], Tadashi Ueda[4], Kei-ichi Nakamoto[4], Haruo Noma[2], Hirohisa Hioki[1], ○Taketoshi Minato[4]
(1. Kyoto Univ., 2. Ritsumeikan Univ., 3. Kyushu Inst. Tech., 4. IMS,)

Scanning Probe Microscopy (SPM) is an excellent measurements for analyzing structural, electrical, electronic, and magnetic properties at the nanoscale and atomic scale, providing high-resolution data. Conventional SPM image analysis widely employs methods such as Fourier transforms and autocorrelation analysis. However, these methods struggle to analyze local interactions in data with non-periodic or complex structures.

In this presentation, we introduce a newly developed method [1] that uses a portion of an SPM image as a template to locally analyze differences with data images. This approach enables the identification of specific local structures and elucidates local interactions. First, we demonstrate the effectiveness of this new analysis method by analyzing SPM images of nanostructures fabricated via lithography. Additionally, we report the first successful elucidation of local interactions in energy materials worldwide through the analysis of SPM images [2, 3] of the rutile-type TiO_2 (110) surface.

Keywords : Scanning Probe Microscopy, Local Interaction, TiO_2, Energy Materials, Nanostructures

References

[1] Sota Tsubokura, Shoya Kawano, Yumiko Imai, Tadashi Ueda, Kei-ichi Nakamoto, Haruo Noma, Hirohisa Hioki and Taketoshi Minato, *Appl. Phys. Exp.*, **17**, 035003 (2024).
[2] Taketoshi Minato, *Chem. Rec.*, **14**, 923–934 (2014).
[3] Taketoshi Minato *et al.*, *ACS Nano*, **7**, 6837–6842 (2015).

Acknowledgments

This research was conducted with the collaboration of Sachiyo Kimura, Noriko Takada, and Takuhiko Kondo (IMS). We express our gratitude to them. Part of this research was supported by the Ministry of Education, Culture, Sports, Science and Technology's "Program for Advanced Research Infrastructure for Materials and Nanotechnology" (Project Nos. JPMXP1222MS0032, JPMXP1223MS0011) and conducted at the Institute for Molecular Science, National Institutes of Natural Sciences.