

## [グリーン合成]

### A-1

#### メタン資化細菌 *Methylosinus trichosporium* OB3b を 用いたメタンからのメタノール合成

宮地輝光・蒲池利章・大倉一郎（東工大大学院生命理工）

Methanol Production from Methane with *Methylosinus trichosporium* OB3b  
MIYACHI Terumitsu, KAMACHI Toshiaki, OKURA Ichiro, Tokyo Institute of  
Technology

Conversion of methane to useful materials such as methanol is one of the most requested reactions. In this study, methanol is produced from methane using methanotroph, *M. trichosporium* OB3b, treated with cyclopropanol and the improvement of methanol yield was accomplished by using a semi-continuous process. In this process, the methanol production increased than that in batch reaction.

### A-2

#### 有機基修飾メソポーラスシリカ固定化酵素の開発

柏木 雅也, 尾中 篤（東大院総合文化）

Immobilization of Enzyme on Functionalized Mesoporous Silica  
KASHIWAGI Masaya, ONAKA Atsushi, University of Tokyo

Enzyme-catalyzed reactions have been applied to organic synthesis. Especially, lipase tolerates various substrates, and lipase-catalyzed reactions are recognized as a useful tool for selective synthesis. Immobilization of enzyme on solid supports enhances the activity and stability of the enzyme. We found that lipase immobilized on functionalized mesoporous silica accelerated the esterification of long-chain carboxylic acid with alcohol.

### A-3

#### 抗体酵素あるいは有機不斉触媒と イオン性液体から構築した反応場の有用性

北爪 智哉・姜 在菊（東工大院・生命理工）

The utility of reaction system constructed with aldolase antibody and/or

## chiral catalyst and ionic liquid

Tokyo Institute of Technology

The utility and reuse of reaction system obtained from ionic liquid and aldolase antibody 38C2 and/or L-(or D-)proline, are described. This reaction system promoted the aldol reaction, and it is possible to reuse the recovered system.

### A-4

#### 新しい反応場としてのイオン性液体の可能性

北爪 智哉・三原 有真・川崎 勇 (東工大院・生命理工)

Possibility of reusable ionic liquid as a new reaction system

Tokyo Institute of Technology

The possibility to open the door to a new road for the reaction system for the stereocontrolled Darzens reaction and Baeyer-Villiger reactions, is described.

### A-5

#### イオン性液体中、加熱下でのいくつかの反応

北爪智哉・三宅徳顕・田村健治・姜在菊 (東工大院・生命理工)

Several types of reactions under heating in ionic liquid

Tokyo Institute of Technology

Miichael additions via the Baylis-Hillman type reaction to (4*S*)-3-[(*E*)-4,4,4-trifluorobut-2-enoyl]-4-substituted-2-oxazolidinone as a acceptor in reusable ionic liquid are described.

### A-6

#### イオン性液体中での有機電解合成-電解フッ素化を中心として-

淵上寿雄・長谷川勝・石井英樹 (東工大総理工)

## Electroorganic synthesis in Ionic Liquids-Application to Electrochemical Fluorination-

Tokyo Institute of Technology

Regioselective anodic fluorination of phthalide, lactones, cyclic carbonates, and cyclic ethers was successfully carried out under solvent-free conditions using ionic liquids such as 1-ethyl-3-methylimidazolynium triflate (1) and  $\text{Et}_4\text{NF} \cdot n\text{HF}$  ( $n=4,5$ ). This is the first example of successful electrochemical synthesis in the ionic liquid (1).

### A-7

#### 新フロン代替化合物を指向した含フッ素エーテル類の電解合成

Electrochemical Synthesis of Fluorine-containing Ethers aimed at the New  
Alternatives of CFCs, HCFCs and HFCs

久保田俊夫\*・小村雅男・高橋和清・深谷知巳(茨城大学工学部物質工学科)

玉井良一・飯島政宏(RITE 新規冷媒等プロジェクト室)

The anodic oxidation of 2-methoxy-2,3,3,3-tetrafluoropropionic acid (MTFPA) in methanol afforded the corresponding coupling product or decarboxylated radicals, 2,3-dimethoxyhexafluorobutane and the non-Kolbe type product, 1,1-dimethoxytetrafluoroethane as a by-product was also obtained through decarboxylation-alkoxylation. The crossed Kolbe electrolysis of MTFPA with difluoroacetic acid in acetonitrile proceeded to form the corresponding methyl 1,1,1,2,3,3-hexafluoro-2-propyl ether.

### A-8

#### 環境調和型固相重合の反応設計：重合原理と結晶構造のデザイン

松本章一・小谷 徹・田中敏弘・永浜 定(阪市大院工・科技団 PRESTO)

Design and Control of Solid-State Polymerization for Green Sustainable Chemistry:  
Polymerization Principles and Design of Crystal Structure

MATSUMOTO Shoichi, Osaka Municipal University

Topochemical polymerization based on crystal engineering is useful for the control of the primary chain and higher-order structures of crystalline polymers. It is a suitable method for green sustainable polymer synthesis because of a organic solvent-free process of solid-state polymerization. The polymerization reactivity is controlled by the crystal structure design and the stacking of diene moieties in the crystals using supramolecular synthon for polymer crystal engineering.

## A-9

### 全無溶媒プロセスによる機能性高分子結晶の合成

小谷 徹・大下晋弥・松本章一（阪市大院工・科技団 PRESTO）

Synthesis of Functional Polymer Crystals via a Totally Solvent-free Process

KOTSNI Tooru, Osaka Municipal University

Recently, organic reactions proceeding in the solid state without any organic solvent attract significant attention in synthetic chemistry. We have reported that the crystalline-state polymerization of alkylammonium muconates gives a stereoregular polymer by UV irradiation and the resulting polymer crystals act as a unique intercalation compound. We have developed totally solvent-free polymer synthesis including monomer synthesis and the transformation of the resulting polymer.

## A-10

### 固体酸を利用する環境調和型高立体選択的グリコシル化反応

戸嶋一敦、永井秀幸、上原慶三、川崎宗次郎、松村秀一（慶應義塾大学理工学部）

Environmentally Benign and Stereocontrolled Glycosidations

Using a Heterogeneous Solid Acid

TOSHIMA Kazuatsu, KEIO Univ.

Carbohydrates are naturally abundant and recyclable feedstock. On the other hand, a number of glycosides are found in many bioactive or functional molecules. One of the most important transformation reactions of carbohydrates is a chemical glycosidation, which is very useful to prepare both natural and unnatural glycosides. Therefore, the greening of chemical glycosidation is very attractive from point of view of green chemistry, and may include the use of heterogeneous and reusable solid acid as an activator. In this study, environmentally benign glycosidations using a heterogeneous solid acid such as montmorillonite K-10, sulfated zirconia or Nafion<sup>®</sup>-H for the stereocontrolled syntheses of  $\alpha$ - and  $\beta$ -2-deoxy glycosides or  $\alpha$ - and  $\beta$ -mannopyranosides have been developed.

## **A-11**

### **アパタイトに分散したポリ酸触媒と尿素-過酸化水素 によるクリーンなエポキシ化反応**

市原潤子・山口俊郎 阪大産研 射手矢勝真・新川剛史・佐々木洋（近畿大理工）

Solvent-free epoxidation using urea-H<sub>2</sub>O<sub>2</sub> and polytungstate catalyst  
dispersed on apatite

ICHIHARA Junko, Osaka Univ.

We have constructed a new epoxidation process using solid disperse phase at aiming sustainable chemistry. Solvent-free epoxidations of alkenes and allylic alcohols were performed in solid phase system using solid urea-H<sub>2</sub>O<sub>2</sub> and cetylpyridinium dodecatungstate catalyst dispersed on fluoroapatite. The harmless solid catalyst phase was recyclable.

## **A-12**

### **水溶性酸化剤を用いたシリカゲル分散 水系におけるオレフィンの酸化反応**

黒星 学・大月一仁・田中秀雄（岡山大工）

Oxidation of Olefins by Silica-Gel Disperse Water System  
with Water-Soluble Oxidants

KUROBOSHI Manabu, Okayama Univ.

Oxidation of olefins were investigated in silica-gel disperse water system. Olefins and transition metal catalysts were adsorbed on the silica gel, and dispersed in water containing water-soluble oxidants. Epoxidation, oxidative cleavage, and dihydroxylation occurred selectively by tuning transition metal catalysts and oxidants. The advantage of this procedure is its simple work-up process; the products were obtained after filtration and rinse of the silica gel followed by concentration of the organic washings.

## **A-13**

### **脱炭酸酵素の逆反応を利用したピルビン酸の合成**

宮崎真佐也、中村浩之、前田英明（産総研九州センター）

Pyruvic acid synthesis using reverse reaction of decarboxylase

MIYAZAKI Masaya, AIST, Kyuushu

A new enzymatic synthesis of pyruvic acid has been developed. Pyruvate decarboxylase (EC 4.1.1.1) is known as a catalyst of the decarboxylation reaction of pyruvic acid, to produce acetaldehyde. In the present study, we demonstrated the usefulness of the reverse reaction of pyruvate decarboxylase in the production of pyruvic acid from acetaldehyde and carbon dioxide. This reaction might become a recommendable, environmentally safe carboxylation procedure for acetaldehyde.

#### A-14

### 塩素ガスを使わない含 N-S 結合複素環化合物の新規合成法

清水政男, 武田文宣, 蒲康夫, 渋谷勲 (産総研)

#### A New Synthetic Method for the Synthesis of S-N Bond Containing Heterocycles without Chlorine Gas

SHIMAZU Masao, AIST

1,2-Benzisothiazolin-3-ones had been synthesized by the reaction of amines and sulfonyl chlorides which were prepared from thiosalicylic acids and chlorine gas. We succeeded in the synthesis of 1,2-benzisothiazolin-3-ones from 2-sulfenamoylbenzoates with safe and convenient method. Furthermore, *N*-substituted 2-sulfenamoylbenzoates were synthesized by transamination of the sulfenamides. Chlorine-free synthetic methods of the N-S bond formation were performed.

#### A-15

### イオン性流体中での、パラジウム触媒による有機ハロゲン化物のカルボニル化反応

水島英一郎、林 輝幸、田中正人 (産業技術総合研究所・グリーンプロセス研究ラボ)

#### Palladium-Catalyzed Carbonylation of Organic Halides in Ionic Liquids

MIZUSHIMA Eiichiro, AIST

The use of non-volatile ionic liquids as solvents is one of the way to improve chemical processes from the viewpoint of product separation and catalyst recycling. We have investigated palladium-catalyzed carbonylation reactions of organic halides. Carbonylations were greatly accelerated by the use of ionic liquids. The catalyst/ionic liquid mixture could be recycled after separation of the product.

## A-16

### ハロゲンフリープロセスによる二酸化炭素からのウレタン合成

阿布拉 馬合木提・崔準哲・坂倉俊康\* (産業技術総合研究所物質プロセス)

Direct Synthesis of Urethane from Carbon Dioxide via Halogen Free Process  
AIST

The transformation of carbon dioxide to urethanes using amine and alcohol is catalyzed by tin complexes. The addition of acetals as a dehydrating agent is quite effective for promoting the reaction. This is the first successful example of the halogen-free process for producing urethanes from carbon dioxide.

## A-17

### 高密度二酸化炭素中での分子触媒反応： パーフルオロオレフィンのヒドロシリル化

崔 準哲・何 良年・坂倉 俊康\* (産業技術総合研究所・物質プロセス研究部門)

Molecular Catalysis in dense Carbon Dioxide: Hydrosilation of Perfluoroolefin

Hydrosilation of perfluoroolefin with dimethoxymethylsilane in dense carbon dioxide was effectively catalyzed by ruthenium and rhodium complexes. The incorporation of polyfluorinated alkyl or aryl group to the conventional hydrosilation catalysts provided enhanced solubility in supercritical carbon dioxide resulting in higher activity and selectivity compared with those in organic solvents.

## A-18

### 酸化カルボニル化による炭酸ジフェニル生成の機構的研究

安田弘之・崔 準哲・阿布拉馬合木提・真木紀子・坂倉俊康\*  
(産業技術総合研究所・物質プロセス研究部門)

Mechanistic Studies on Diphenyl Carbonate Formation  
via Oxidative Carbonylation

YASUDA Hiroyuki, AIST

Phenoxy carbonyl palladium complex,  $\text{PdCl}(\text{CO}_2\text{Ph})(\text{PPh}_3)_2$ , which should be one of the key intermediates in the palladium-catalyzed oxidative carbonylation of phenol, has been synthesized by oxidative addition of phenyl chloroformate to  $\text{Pd}(\text{PPh}_3)_4$ . The complex thermally decomposes to form diphenyl carbonate (DPC), especially in the presence of additional triphenylphosphine. On the other hand, the DPC formation is not promoted by a nucleophilic attack of phenol.

### A-19

#### ポリ( $\epsilon$ -カプロラクトン-*block*-エチレングリコール)と ポリ乳酸のブレンドの相溶性

羅 亮皓, 帥 心涛, 井上 義夫 (東工大院生命理工)

Miscibility of Blends of Poly( $\epsilon$ -caprolactone-*block*-ethylene glycol)  
with Polylactide

Tokyo Institute of Technology

Thermal analyses of PCL-*b*-PEG/poly(L-lactide) (PLLA) and PCL-*b*-PEG/poly(DL-lactide) (PDLLA) blends demonstrated that the PEG phase of the block copolymer is miscible with PLA; on the contrary, the PCL phase of the copolymer is still immiscible with PLA. The improvement in the mechanical properties of the blends containing PCL-*b*-PEGs showed that PCL-*b*-PEGs are suitable for compatibilizing the immiscible PCL/PLA blends.

### A-20

#### 微生物産ポリ(3-ヒドロキシブタン酸-*co*- 3-ヒドロキシペンタン酸)の化学組成分布と物性

王 易, 山田 しの, 浅川 直紀, 吉江 尚子, 井上 義夫 (東工大院生命理工)

Comonomer Compositional Distribution and Thermal and Morphological  
Characteristics of Bacterial Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)s  
with High 3-Hydroxyvalerate Content

Tokyo Institute of Technology

The comonomer compositional distribution and thermal and morphological characteristics

were investigated for five bacterially synthesized poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) [P(3HB-*co*-3HV)] samples with 3HV content of 45, 49, 70, 80 and 96mol%. The 3HV content dependences of the thermal properties and crystalline structures were investigated for bacterial poly(3-hydroxybutyrate) [P(3HB)] and a series of compositionally well-fractionated P(3HB-*co*-3HV) samples with 3HV content ranged from 14mol% to 98mol% by DSC, WAXD and solid-state <sup>13</sup>C NMR.

## A-21

### DSC と FT-IR により示された 4,4' -チオジフェノールと ポリヒドロキシアルカン酸の水素結合

李 劍春・何 勇・石田 一樹・井上 義夫(東工大院生命理工)

The Hydrogen-Bonding Interactions between 4,4'-Thiodiphenol and Some Poly(hydroxyalkanoic acid)s Revealed by DSC and FT-IR Spectroscopic Analysis

Tokyo Institute of Technology

The specific intermolecular hydrogen-bonding interaction between some poly(hydroxyalkanoic acid)s (PHAs) and 4,4'-Thiodiphenol (TDP) were studied by DSC and FT-IR. Strong intermolecular hydrogen bonds existed between PHAs and TDP. The content of hydrogen bonds was influenced by both the content of TDP and the crystallizability of PHAs. TDP has more ability to form the self-hydrogen-bond of TDP-HO · · · HO-TDP type than the inter-hydrogen-bond of PHA-C=O · · · HO-TDP type.

## A-22

### アミノ基固定化 FSM-16 触媒によるアルデヒドの ビニルケトンへの直接的 1,4-付加反応

清水 研一・鈴木 浩正・萩原 久大・北山 淑江(新潟大院自然)

Direct 1,4-addition of Aldehydes to Vinylketones on  
*N*-methyl-3-aminopropyleted FSM-16 Catalyst  
SHIMIZU Ken-ichi, Niigata Univ.

Substituted 5-ketoaldehydes (**3**), which are important synthones for synthesis of natural products such as terpenoids, have been prepared mainly by multistage reactions and separations including the 1,4-addition of masked aldehydes. Here, we report that direct

1,4-conjugate addition of naked aldehydes to vinylketones, which cannot be catalysed by ordinary oxidic solid bases, is catalysed efficiently by *N*-methyl-3-aminopropyleted FSM-16 mesoporous silica.

## A-23

### シリカ系光触媒による化学合成

-メタン光カップリング、プロピレン光メタセシス、酸素によるプロピレンエポキシ化-  
吉田寿雄、加藤裕子、稲木喜孝、村田千津、服部 忠 (名古屋大学大学院工学研究科応用化学専攻)

Photocatalytic synthesis on silica-based materials - Methane coupling,  
metathesis of propene, epoxidation of propene by molecular oxygen -

YOSHIDA Hisao, Nagoya Univ.

We have developed some heterogeneous photocatalytic reactions over silica-based materials at room temperature such as photoinduced non-oxidative methane coupling, photometathesis of propene, and photoepoxidation of propene by molecular oxygen.

## A-24

### グリーンケミストリーからみたポリ(フェニレンオキシド)の解重合

齋藤 敬、益山 亨、小柳津研一、西出宏之 (早大理工)

Depolymerization of Poly(dimethylphenyleneoxide) under  
a Mild Oxidative Condition

SAITO kei, Waseda Univ.

Poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) is formed by the oxidative polymerization of 2,6-dimethylphenol in the presence of a copper-pyridine catalyst. The polymerization is known to involve redistribution and rearrangement of a quinone ketal intermediate as elementary steps. Since this reaction is reversible, PPO could be depolymerized under suitable oxidation conditions, to yield oligomeric products which can be repolymerizable. Driving force that governs the equilibrated system will be discussed from the viewpoint of green chemistry.

## A-25

### 二酸化炭素を一原料とする有機合成反応

佐々木義之、富永健一（産総研・環境調和技術研究部門）

## Utilization of carbon dioxide as a C1 building block

SASAKI Yoshiyuki, AIST

The incorporation of CO<sub>2</sub> into useful organic compounds is of industrial importance, for not only the CO<sub>2</sub> emission itself may be reduced to some extent but also it can replace the conventional processes that frequently use more toxic carbonyl carbon sources such as CO or phosgene and therefore require the additional investment for safety. The CO<sub>2</sub> fixation processes so far reported can be classified into five categories according to the oxidation state of the carbon atom in the product originating from CO<sub>2</sub>. Among these processes, those in which CO<sub>2</sub> is not so much reduced are preferable from the viewpoint of energy consumption.

### A-26

## メソポーラスシリカによる汚染重金属オキシ アニオンの環境調和型除去

横井俊之\*、辰巳 敬\*\*、吉武英昭\*（横国大院 環境情報\*・工\*\*）

Environmentally Benign Removal of Pollutant Heavy Metal Oxyanions  
by Using Mesoporous Silica  
YOKOI Toshiyuki, Yokohama National Univ.

Molecular adsorption sites for oxyanions were synthesized in the pores of mesoporous silicas by coordinating proton or metal cations on the terminal amino group of silane fixed on the surface in advance. Selective adsorptions of arsenate occur on the metal-centered sites in the aqueous solutions containing abundant sulfate ions. We propose that cation-anchored amino groups on the surfaces of mesoporous silica would work as excellent adsorbing sites of heavy metal oxyanions, pollutants in the groundwater causing environmental problems.

### A-27

## MCM-22 触媒を用いたシクロペンタノールの高選択的な合成

呉 鵬，辰巳 敬（横国大院工）

Clean Production of Cyclopentanol by MCM-22 Catalyst  
Duangamol Nuntasri, Yokohama National Univ.

The use of solid acid catalysts in place of mineral acids is expected to lead to greener processes.

In this respect, the selective synthesis of cyclopentanol through the liquid-phase hydration of cyclopentene has been attempted on solid acid catalysts. Zeolite MCM-22, converting cyclopentene to cyclopentanol with selectivity up to 99 %, exhibits much higher shape selectivity than ZSM-5, beta and the others. The cyclopentene conversion is effectively increased to high as 10 % by increasing the water/olefin ratio. The extremely high selectivity is presumed due to the sinusoidal 10-membered ring (MB) channels of MWW structure.

## A-28

### ほしいものを選択的につくる触媒開発 - 酸化反応を例にとって -

関根 泰・三宅 徹・菊地 英一・松方 正彦 (早稲田大学)

Catalyst survey for selective oxidation process.

SEKINE Yasushi, Waseda Univ.

It is important to develop new catalyst for selective oxidation process. We tried to conduct acetoxylation of p-xylene, and selective oxidation of ethylene glycol. Active carbon was employed for the catalyst, and it had some good features such as low-cost, disposable.

## A-29

### Pd系燃焼触媒の八二カム担持とメタン燃焼特性

菊地隆司, 江口浩一 (京都大学大学院 物質エネルギー化学専攻)

前田真吾, 佐々木一成 (九州大学大学院 物質理工学専攻)

小沢 靖 (電力中央研究所 横須賀研究所)

Low-temperature oxidation of methane over oxide-supported

Pd catalysts on honeycombs

EGUCHI Koichi, Kyoto Univ.

Catalytic combustion has been regarded as one of the key technologies that help minimize the environmental impact by conversion and use of energy, because of high combustion efficiency as well as low emission of air pollutants such as CO, NO<sub>x</sub>, and unburned hydrocarbons. Development of catalytic materials, which are highly active for oxidation of hydrocarbons at low temperatures, is of importance for high-temperature applications such as in gas turbine systems.

## A-30

### 中性テンプレートを用いたマイクロポーラス酸化ニオブの合成

リ ビョンジン・魯 大凌・原 亨和・野村 淳子・堂免 一成 (東工大資源研・CREST)

Preparation of microporous niobium oxide with neutral template

Tokyo Institute of Technology

Highly ordered microporous niobium oxide was prepared using a nonionic template. While templates are known to be removed by acid treatment or calcination, a nonionic template was also removed by water washing. The product showed higher surface area than the calcined sample. Transmission electron microscopy observation revealed the highly ordered microporous structure.

## A-31

### ソフト溶液プロセスより合成される 2次元金属酸化物シートの固体酸としての応用

高垣 敦・吉田 猛美・魯 大凌・高田 剛・野村 淳子・原 亨和・  
堂免 一成\*(東工大資源研・CREST\*)

Application of 2-dimensional metal oxide sheets as solid acid catalysts  
prepared by soft solution processing

TAKAGAKI Atsushi, Tokyo Institute of Technology

In general, layered metal oxides cannot work as solid acids for large organic molecules because of the narrow interlayer spaces. However, aggregated metal oxide sheets prepared by exfoliation and aggregation of some layered metal oxides such as HTiNbO<sub>5</sub> worked as efficient solid acid catalysts for the cracking of cumene and the liquid phase of ethyl acetate.

## A-32

## 赤外プローブ分子による固体酸触媒のキャラクタリゼーション

依田英介・西谷良子・野村淳子・若林文高<sup>††</sup>・堂免一成 (東工大資源研・国立科博<sup>††</sup>)

Characterization of solid acid catalysts studied by IR probe molecules

YODA Eisuke, Tokyo Institute of Technology

A detailed understanding of solid acid-catalyzed reaction requires knowledge on the surface acidity. For the investigation of acidic property, IR observation of adsorbed basic molecules such as CO and pyridine is employed. Although the assignments of adsorbed molecules on Brønsted and Lewis acid sites were reported, the relation among different basic probes and the quantitative analysis have not investigated. Therefore, the adsorption of pyridine and CO on solid acid catalysts are interpreted and compared.

### A-33

## パラジウム膜反応器を用いるフェノールの直接合成

水上富士夫・丹羽修一・伊藤直次・イワムラフミツミ・アヅハラジ (産業技術総合研究所)・

庄司宏 (丸善石油化学株式会社)・難波竹巳 (NOK 株式会社)

Green One-Step Process of Benzene to Phenol Using a Palladium Membrane

MIZUKAMI Fujio, AIST

To solve different problems in the existing phenol production processes, an efficient process using a shell-and-tube reactor, in which a gaseous mixture of benzene and oxygen is fed into a porous alumina tube coated with a palladium thin layer and hydrogen fed in the shell, was created. Here hydrogen dissociated on the palladium layer surface permeates onto the back, and reacts with oxygen to give active oxygen species, which attack benzene to produce phenol. This one-step process attained phenol formation selectivities of 80-97 % at benzene conversions of 2-16 % below 250 °C (phenol yield: 1.5 kg/kg<sub>Cat</sub>·h at 150 °C).

### A-34

## 化石資源枯渇防止のためのプラスチックのモノマー回帰。ポリカーボネートをホスゲン等価体として用いるジアミン、チオール等との反応

畑 宗平、後藤紘子、奥 彬 (京都工芸繊維大学工芸学部)

Monomer Recycling of Plastics as a Tiny Solution for the Conservation of Fossil Oil. Reaction of PC with Diamine, Dithiol, and Mixed Difunctionality using PC as a Phosgene Equivalent.

HATA Sohei, Kyoto Institute of Technology

Methods for the chemical recycling of poly(carbonate) wastes (PC) in the forms of bisphenol A and carbonate derivatives, such as *N,N*-dimethylalkylene ureas (DMI, DMP), 1,3-dithiane-2-one (EDTC), and mixed cyclic carbonate derivatives, were investigated to prove that PC can be utilized as an effective phosgene equivalent for industrial purposes.

**A-35**

**化石資源枯渇防止のためのプラスチックのモノマー回帰技術・ポリカーボネートをホスゲン等価体として利用するポリオールとの反応**

岩河康子、畑 宗平、奥 彬（京都工芸繊維大学工学学部）

Monomer Recycling of Plastics, a Tiny Solution for the Conservation of Fossil Resource. Reaction of Polyols Using Poly(carbonate) as a Phosgene Equivalent.

IWAKO Yasuki, Kyoto Institute of Technology

Methods for the chemical recycling of poly(carbonate) wastes (PC) in the forms of bisphenol A and a diol monomer, i.e. bis(hydroxyethyl) ether of bisphenol A (BPA), or cyclic carbonate derivatives, i.e. 4-hydroxymethyl-1,3-dioxorane-2-one, were investigated. Treatment of PC in ethylene glycol (EG) with a base catalyst produced bishydroxyethyl ether of BPA in quantitative yields (99%) (Eq 1). Analogously, PC was effectively utilized as a phosgene equivalent for quantitative production of industrially useful cyclic carbonates in the reaction with polyols (Eq 2).

**A-36**

**グリーンケミストリーを指向した  
新規不均一系ヒドロキシアパタイト固定化Pd触媒の開発**

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## Development of Hydroxyapatite-bound Palladium Catalysts with the aim of Green Chemistry

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The treatment of hydroxyapatites with  $\text{PdCl}_2(\text{PhCN})_2$  gave two new types of hydroxyapatite-bound Pd complexes, which act as effective heterogeneous catalysts for aerobic alcohol oxidation and for the Heck reaction, respectively. Moreover, the catalysts were recyclable with keeping their high catalytic performances, which contribute to the development of environmentally benign chemical processes.

### A-37

#### 新規ケミカルリサイクルシステムの構築： ポリカルボシランのケミカルリサイクルポリマーとしての可能性

池永 和敏、 泰永茂伸、隈部章愛、山本勝也（崇城大学・工学部・応用化学科）

#### A New Chemical Recycle System: The possibility of Polycarbosilanes for Chemical Recycle Polymers

IKENAGA, K., YASUNAGA, S., KUMABE, F., and YAMAMOTO, K. (Sojo University)

The developments of the catalytic, clean, and ecological decompositions of engineering polymers offer the possibility for new chemical recycle systems. Herein, we wish to report that the decomposition of polycarbosilanes by the catalytic amount of trifluoromethanesulfonic acid (TfOH). Polycarbosilane (1) was perfectly decomposed by the treatment of 40-60 mol% of TfOH in clued toluene at room temperature within practical reaction times, to give biphenyl in quantitative yield. The postulated mechanism of the decomposition of C(sp<sup>2</sup>)-Si bond was shown in Scheme 1.

### A-38

#### 担持 Pd-In 触媒上での NO の CO による還元反応

小澤義幸、関戸孝幸、宮尾敏広、内藤周弼\*（神奈川大学工学部応用化学科）

#### Catalytic Reduction of NO by CO over Supported Pd-In Catalysts

OZAWA, Y., SEKIDO, T., MIYAO, T. and NAITO, S.\* (Kanagawa University)

The mechanism of NO-CO reaction over Pd-In/SiO<sub>2</sub> catalysts at elevated temperature region

was studied by kinetical investigation as well as infrared spectroscopy during the reaction. Observed maximum and minimum of the reaction rates against reaction temperatures were explained by the switching of bimolecular complex mechanism with unimolecular redox mechanism.

### **A-39**

#### **担持 Pd 触媒上での NO の直接分解反応**

川上郁夫、岩橋麻衣、宮尾敏広、内藤周式（神奈川県工学部応用化学科）

#### Direct Decomposition of NO over Supported Pd Catalysts

KAWAKAMI, I., IWAHASHI, M., MIYAO, T. and NAITO, S.\* (Kanagawa University)

Direct decomposition of NO was studied over SiO<sub>2</sub> and BeO supported Pd catalysts. Pd/BeO catalysts exhibited one order of magnitude higher TOF than SiO<sub>2</sub> supported one. The TOF over BeO supported catalysts increased with the decrease of Pd loading. TPD studies after NO decomposition indicated that the excellent TOF observed over Pd/BeO catalysts resulted from the decrease in the desorption temperature of adsorbed oxygen species on the catalyst.

### **A-40**

#### **モリブデン-ケイ素錯体による触媒的二酸化炭素固定化反応**

湊 盟（横浜国立大学大学院）

#### Catalytic Carbon Dioxide Fixation Utilizing a Molybdenum-silyl Complex

MINATO, M. (Yokohama National University, Yokohama)

We previously reported the synthesis of a novel molybdenum-silyl complex, [MoH<sub>3</sub>{Si(Ph)[Ph<sub>2</sub>PCH<sub>2</sub>C(H<sub>2</sub>P(Ph))C<sub>6</sub>H<sub>4</sub>-o]<sub>2</sub>}. We explored catalytic activity of this complex toward CO<sub>2</sub> fixation. A toluene solution of the complex was allowed to react under CO<sub>2</sub>/H<sub>2</sub> pressure in the presence of dimethylamine at 110 °C affording 115 equivalents of *N,N*-dimethylformamide with respect to the complex. To our knowledge, this complex is the first molybdenum compound which can catalyze the transformation of CO<sub>2</sub> into dialkylformamide effectively.