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Effect of "Topotactic" Reduction Product of Tungsten Disulfide on Catalytic Activity of Metallocene Catalyst for Olefin Polymerization, Satoru YAMADA, Akihiro YANO*, Morihiko SATO*, Takahito ITOH : Journal of Molecular Catalysis A: Chemical 208, pp. 55-65, 2004

N,N-Dimethylanilinium ($\text{Ph}(\text{Me})_2\text{NH}^+$) salt of tungsten disulfide (WS_2) was developed as a novel cocatalyst for metallocene catalysts. The cocatalyst is composed of *N,N*-dimethylanilinium ion as a cationic part and "topotactic" reduction product of WS_2 , obtained by acquisition of an electron by the neutral host lattice of WS_2 without structural alteration, as an anionic part. Notable improvement of the catalytic activity for ethylene polymerization using the bis(indenyl)zirconium dichloride ($\text{Ind}_2\text{ZrCl}_2$)/triethylaluminum (Et_3Al) catalyst was observed upon the addition of the $\text{Ph}(\text{Me})_2\text{NH}^+$ salt of WS_2 . The addition of the corresponding molybdenum disulfide (MoS_2) one that had smaller crystallite size than the $\text{Ph}(\text{Me})_2\text{NH}^+$ salt of WS_2 showed the lower catalytic activity. The resultant poly(ethylene) prepared by the $\text{Ind}_2\text{ZrCl}_2/\text{Et}_3\text{Al}/\text{Ph}(\text{Me})_2\text{NH}^+$ salt of WS_2 possessed similar properties like narrow polydispersity to that prepared by conventional metallocene type catalysts. The Zr loadings on the precipitate of the $\text{Ind}_2\text{ZrCl}_2/\text{Et}_3\text{Al}$ catalyst activated by the $\text{Ph}(\text{Me})_2\text{NH}^+$ salt of WS_2 increased with a decrease in the crystallite size of the $\text{Ph}(\text{Me})_2\text{NH}^+$ salt of WS_2 . However, the catalytic activities in ethylene polymerization decreased drastically, indicating that the decrease of the crystallite size led to the significant increase of inactive species for ethylene polymerization.

Spontaneous Polymerization Mechanism of 7,7-Dicyanobenzoquinone Methide with *p*-Methoxystyrene, Yukihiro MITSUDA, Shuji KAWAGUCHI, Takahiro UNO, Masataka KUBO, Takahito ITOH : Macromolecules 37, pp. 1251-1256, 2004

Spontaneous polymerization of 7,7-dicyanobenzoquinone methide (CQM) with *p*-methoxystyrene (MeOSt) was investigated. An alternating copolymer of CQM with MeOSt was obtained as the hexane-insoluble product, and a small amount of a 1:2 cycloadduct of CQM:MeOSt in addition to large amounts of unreacted CQM and MeOSt was obtained as the hexane-soluble product. To clarify an active intermediate in this reaction, spontaneous polymerizations of CQM with MeOSt were carried out in the presence of additives such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and acetic acid and in three solvents with different polarity. The spontaneous reaction in the presence of the TEMPO did not afford any products trapped by TEMPO. On the other hand, the reaction in the presence of acetic acid gave a 1:1:1 adduct of CQM:MeOSt:acetic acid in a quantitative yield. It was concluded from these results that the spontaneous polymerization of CQM with MeOSt might proceed via a zwitterionic intermediate, which has gauche and trans forms.

Crystal Structures and Topochemical Polymerizations of 7,7,8,8-Tetrakis(alkoxycarbonyl)quinodimethanes, Shinji NOMURA, Takahito ITOH, Hirofumi NAKASHO, Takahiro UNO, Masataka KUBO, Kazuki SODA*, Katsunari INOUE*, Mikiji MIYATA* : Journal of American Chemical Society 126, pp. 2035-2041, 2004

Highly conjugated monomers, 7,7,8,8-tetrakis(alkoxycarbonyl)quinodimethanes (methoxy (1a), ethoxy (1b), isopropoxy (1c), benzyloxy (1d), chloroethoxy (1e), and bromoethoxy (1f)), were synthesized. Recrystallizations of 1a, 1c, 1e, and 1f yielded two crystal forms (prisms (1a-A) and needles (1a-B), needles (1c-A) and plates (1c-B), prisms (1e-A) and plates (1e-B), and prisms (1f-A) and needles (1f-B)), which have different molecular packing modes by X-ray crystal structure analysis, indicating that the crystals are polymorphic. In the photopolymerizations of these monomer crystals in the solid state, 1a-A, 1e-A, and 1f-A polymerized topochemically to give crystalline polymers. For their thermal polymerizations in the solid state, in addition to 1a-A, 1e-A, and 1f-A, 1e-B and 1f-B polymerized, but polymers formed from the 1e-B and 1f-B were amorphous. The packing of quinodimethane molecules in the crystals was defined by four kinds of parameters, stacking distance (d_s), the distance between the reacting exomethylene carbon atoms (d_c), the angles formed between the stacking axis and longer axis of the monomer molecule (θ_1), and the shorter axis of the monomer molecule (θ_2), and then the polymerization reactivity of these quinodimethanes in the solid state was discussed on the basis of these parameters.

Ionic Conductivity and Mechanical Property of Cross-linked Hyperbranched Polymer Electrolytes for Lithium Secondary Batteries, Takahito ITOH, Seiji HORII, Shinya HASHIMOTO, Takahiro UNO, Masataka KUBO, Osamu YAMAMOTO* : Transaction of the Materials Research Society of Japan 29, pp. 1025-1030, 2004

Composite polymer electrolytes composed of cross-linkable hyperbranched polymer (HBP), poly[bis(triethylene glycol)benzoate] capped with acetyl and/or acryloyl groups in various ratios, poly(ethylene oxide), BaTiO₃ as an inorganic filler, and LiN(CF₃SO₂)₂ as a lithium salt were prepared by solvent casting, followed by thermal cross-linking, and their ionic conductivities and mechanical properties were investigated.

Preparation of Mechanically Cross-Linked Polystyrenes, Masataka KUBO, Naoki KATO, Takahiro UNO, Takahito ITOH : Macromolecules 37, pp. 2762-2765, 2004

This paper reports preparation of mechanically cross-linked polystyrenes using cyclic macromonomer as a nonbonding cross-linking agent. Emulsion and thermal self-initiated copolymerizations of styrene with a well-defined cyclic macromonomer based on a cyclic polystyrene were carried out to obtain mechanically cross-linked polystyrenes with high swellability. Mechanically cross-linked chloromethylated polystyrene was prepared by thermal self-initiated terpolymerization of the cyclic macromonomer, styrene, and 4-vinylbenzyl chloride.

Spontaneous Polymerization Mechanism of 7,7-Dicyanobenzoquinone Methide with 1,3-Cyclohexane, Shuji KAWAGUCHI, Yukihiro MITSUDA, Takahiro UNO, Masataka KUBO, Takahito ITOH : Kobunshi Ronbunshu 61, pp. 263-268, 2004

Spontaneous polymerization of 7,7-dicyanobenzoquinone methide (CQM) with 1,3-cyclohexane (CHD) was investigated. The spontaneous reactions gave alternating copolymers of CQM with CHD, where CHD units were incorporated in 1,2- and 1,4-addition structures, as

hexane-insoluble products and a Diels-Alder adduct of CQM with CHD as hexane-soluble product. Addition of acetic acid to the spontaneous polymerization system did not affect the composition and distribution of products. On the other hand, the spontaneous polymerization in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) gave a low molecular weight alternating copolymer with TEMPO at the terminal end as hexane-insoluble product and a 1:1:1 adduct as hexane-soluble product. It was concluded from these results that the spontaneous polymerization of COM with CHD proceeds via a diradical intermediate.

Influence of Hyperbranched Polymer Structure on Ionic Conductivity in Composite Polymer Electrolytes of PEO/Hyperbranched Polymer/BaTiO₃/Li Salt System, Takahito ITOH, Seiji HORII, Takahiro UNO, Masataka KUBO, Osamu YAMAMOTO* : *Electrochimica Acta* 50, pp. 271-274, 2004

The influence of the hyperbranched polymer (HBP) structure such as molecular weights, molecular weight distribution, chain-end, ethylene oxide (EO) chain lengths on the ionic conductivity of the composite polymer electrolytes composed of poly(ethylene oxide) (PEO), BaTiO₃ as a ceramic filler, LiN(CF₃SO₂)₂ as a lithium salt, and HBP as a plasticizer were investigated. The difference in the molecular weights of the HBP did not affect significantly the ionic conductivity. However, molecular weight distribution of the HBP might affect the ionic conductivity of the composite polymer electrolyte, which decreased with broadening of the molecular weight distribution. Further branching at the chain-end structure in the HBP led to a decrease in the ionic conductivity. The HBP with a longer EO chain length was effective to an enhancement of the ionic conductivity.

Spontaneous Polymerization Mechanism of Electron-Accepting Substituted Quinodimethane with Vinyl Ether and Cyclic Ketene Acetal, Yukihiro MITSUDA, Takashige FUJIKAWA, Katsumi NAKASAKA, Takahiro UNO, Masataka KUBO, Takahito ITOH, *Journal of Polymer Science: Part A: Polymer Chemistry* 42, pp. 3800-3811, 2004

The spontaneous reactions of 1-(2,2-dimethyl-1,3-dioxane-4,6-dione-5-ylidene)-4-(dicyanomethylene)-2,5-cyclohexadiene (QM-1) with a vinyl ether, butyl vinyl ether (BVE), and a cyclic ketene acetal, 2-methylene-1,3-dioxepane (MDOP), were investigated. The reaction of QM-1 with BVE produced a terpolymer composed of QM-1, 7-butoxy-8,8-dicyanoquinodimethane, and BVE units as a hexane-insoluble product and a one-to-one adduct of methylene Meldrum's acid and BVE as a hexane-soluble product. The spontaneous reaction of QM-1 with BVE produced, in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), a terpolymer carrying TEMPO units in the chain ends, and in the presence of methanol, a one-to-one-to-one adduct of QM-1, BVE, and methanol was isolated. The spontaneous reaction with bulkier, electron-donating MDOP produced a low-molecular-weight alternating cooligomer of QM-1 with MDOP. The spontaneous polymerization was proposed to proceed via a zwitterionic intermediate taking two forms, gauche and trans, depending on the bulkiness of the comonomer.

Asymmetric Anionic Polymerization of 2,6-Dimethyl-7-phenyl-1,4-benzoquinone Methide, Takahiro UNO, Masaya MINARI, Masataka KUBO, Takahito ITOH : *Journal of Polymer Science: Part A: Polymer Chemistry* 42, pp. 4548-4555, 2004

Asymmetric anionic polymerizations of 2,6-dimethyl-7-phenyl-1,4-benzoquinone methide (1) were performed with various chiral anionic initiators, and the specific rotations of the obtained polymers were investigated. Optically active poly(1)s with configurational chirality were obtained with all the initiators, and a complex of fluorenyllithium (FLi) with (-)-sparteine [(-)-Sp] produced poly(1) with the largest negative specific rotation ($[\alpha]_{435} = -26.8^\circ$). The specific rotations of poly(1)s obtained with FLi/(-)-Sp depended on the initiator concentration and the solvent polarity. The maximum specific rotations were obtained at an almost constant initiator concentration (ca. 0.03 mol/L), regardless of the monomer concentration, in toluene, whereas a higher initiator concentration was required in more polar solvents. These results suggested that the aggregation state of the propagating chain end significantly affected the specific rotation of poly(1).

Solid-State Polymerization of 7-Alkoxy-carbonyl-7-cyano-1,4-benzoquinone Methides, Takahito ITOH, Shinji NOMURA, Nagisa SAITOH, Takahiro UNO, Masataka KUBO, Kazuki SODA*, Katsunari INOUE*, Mikiji MIYATA* : *Macromolecules* 37, pp. 7938-7944, 2004

Thermal polymerizations and photopolymerizations of 7-alkoxy-carbonyl-7-cyano-1,4-benzoquinone methides (methoxy (2a), ethoxy (2b), propoxy (2c), isopropoxy (2d), butoxy (2e), and sec-butoxy (2f)) were investigated in the solid state. In the thermal polymerization in the solid state, 2a, 2c, 2d, and 2e polymerized to give glassy solids or a mass of crystals, but both 2b and 2f did not polymerize. In the photopolymerization in the solid state, all monomer crystals except for 2a polymerized to give corresponding polymers as needlelike solids. The needlelike polymer obtained by photopolymerization of highly reactive 2c was amorphous by powder X-ray diffraction measurement. Crystal structure of 2c was determined by single-crystal X-ray structure analysis, and the molecular packing in the crystals was discussed.

Molecular Oxygen Insertion Polymerization into Crystals of Tetrakis(alkoxy-carbonyl)quino-dimethanes, Takahito ITOH, Shinji NOMURA, Masaki OHTAKE, Takafumi YOSHIDA, Takahiro UNO, Masataka KUBO, Atsushi KAJIWARA*, Kazuki SODA*, Mikiji MIYATA* : *Macromolecules* 37, pp. 8230-8238, 2004

Solid-state alternating copolymerization took place by molecular oxygen insertion in the crystals of 7,7,8,8-tetrakis(ethoxy-carbonyl)quinodimethane (1a) and 7,7-bis(ethoxy-carbonyl)-8,8-bis(methoxy-carbonyl) quinodimethane (1b) to form highly crystalline needlelike white solids for 1a and amorphous ones for 1b. The polymer structures were confirmed by ^1H NMR, ^{13}C NMR, IR, elemental analysis, powder XRD, and TGA measurements. However, in vacuo polymerizations of 1a and 1b in the solid state with heating and photoirradiation did not take place. 7,7,8,8-Tetrakis(methoxy-carbonyl)quinodimethane (1c) did not undergo solid-state alternating copolymerization with oxygen even in the presence of oxygen, but instead it homopolymerized to form highly crystalline homopolymer. The difference in the solid-state polymerization reactivity was discussed on the basis of molecular packing in the crystals obtained by X-ray crystallography. In addition, it was found by ESR measurement that the solid-state alternating copolymerizations with molecular oxygen proceed by means of a radical mechanism.

Preparation of Mechanically Cross-Linked Poly(vinyl alcohol), Masataka KUBO, Naoki HAYAKAWA, Yuya MINAMI, Masashi TAMURA, Takahiro UNO, Takahito ITOH: Polymer Bulletin 52, pp. 201-207, 2004

A novel cyclic macromonomer based on a cyclic polystyrene was prepared. Its radical copolymerization with vinyl acetate was carried out to give a mechanically cross-linked poly(vinyl acetate) which was converted to a mechanically cross-linked poly(vinyl alcohol) with high swellability.

Polymer Electrolytes Plasticized With Hyperbranched Polymer For Lithium Polymer Batteries, Takahito ITOH, Seiji HORII, Shinya HASHIMOTO, Takahiro UNO, Masataka KUBO: Ionics 10, pp. 450-457, 2004

Hyperbranched polymers (HBPs) with different terminal groups and different ethylene oxide (EO) chain lengths were prepared, and the influence of the HBP structures including molecular weights and molecular weight distribution on the ionic conductivity and the mechanical property of the composite polymer electrolytes composed of poly(ethylene oxide) (PEO), HBP, BaTiO₃ as a ceramic filler, and Li(CF₃SO₂)₂ as a lithium salt were investigated. It was found that the molecular weights of the HBP do not affect significantly the ionic conductivity, but the molecular weight distribution might affect it, and also further branching at the terminals of the HBP led to decrease in the ionic conductivity. The HBP with longer EO chain length was effective for enhancement of the ionic conductivity in comparison with the HBP with shorter one. The increase in cross-linkable groups (acryloyl group) at the terminals of the HBP improved the tensile strength, but caused the ionic conductivity to decrease. Loosely cross-linked composite polymer electrolyte showed higher ionic conductivity and higher tensile strength than no cross-linked one.

Double Nucleophilic Addition of Azide and Tetraallyltin to the Latent α,β Unsaturated Aldehydes Using in situ Hydrolysis of the Imino Functionality Promoted by Tin(IV) Chloride Pentahydrate, Makoto SHIMIZU, Takafumi NISHI: Synlett, pp. 889-891, 2004

Double Nucleophilic Addition of Azide and Tetramethyltin to α,β Unsaturated Aldimines Promoted by Aluminum Chloride, Makoto SHIMIZU, Chiaki YAMAUCHI, Toshiki OGAWA: Chem. Lett. 33 (5), pp. 606-607, 2004

Synthesis of 5-Acetyl-2-pyridones via Nucleophilic Addition of β Keto Esters to Alkynyl Imines, Iwao HACHIYA, Kana OGURA, Makoto SHIMIZU: Synthesis, pp. 1349-1352, 2004

Stereodivergent Synthesis of (2*R*)-2,3-Diricinolein by Lipase-catalyzed Hydrolysis of Triricinolein, Iwao HACHIYA, Akihisa MAKINO, Makoto SHIMIZU, Masatsugu AKITA*, Takashi HAMAGUCHI*: Tetrahedron: Asymmetry 15 (16), pp. 2451-2454, 2004

Aza-Reformatsky-type Reaction of α -Iodomethyl Ketone *O*-Alkyl Oximes Promoted by Titanium Tetraiodide, Makoto SHIMIZU, Tadahiro TOYODA: *Org. Bio. Chem.* 2 (20), pp. 2891-2892, 2004

A Cation-Exchange Resin Promoted Imino Aldol Reaction, Leading to the Synthesis of 2-Isocephem and 2-Oxa-isocephem, Makoto SHIMIZU, Masanori TACHI, Iwao HACHIYA: *Chem. Lett.* 33 (10), pp. 1394-1395, 2004

An Improved Process for the Large-Scale Preparation of Antirheumatic Agent MX-68, Noriaki MARUYAMA, Hirohito SHIMIZU*, Takashi SUGIYAMA*, Masashi WATANABE*, Masahiro KATO*, Makoto SHIMIZU: *Organic Process Research & Development* 8 (6), pp. 883-888, 2004

Reductive Coupling of Aldehydes with Nitriles Promoted by Titanium Tetraiodide, Makoto SHIMIZU, Hiroshi GOTO: *Lett. Org. Chem.* 1 (4), pp. 346-348, 2004

3,4,6-Trisubstituted-2-pyrone Synthesis via the Nucleophilic Addition of 2-Alkyl Meldrum's Acid to Alkynyl Ketone, Iwao HACHIYA, Hitoshi SHIBUYA, Kazuma HANAI, Makoto SHIMIZU: *Lett. Org. Chem.* 1 (4), pp. 349-352, 2004

Double Nucleophilic Addition of Ketene Silyl Acetals to α,β -Unsaturated Imines: Factors Controlling the Regioselectivity, Makoto SHIMIZU, Hiroshi KUROKAWA, Atsushi TAKAHASHI: *Lett. Org. Chem.* 1 (4), pp. 353-356, 2004.

New Synthetic Reactions Using the Reducing Ability of Titanium Tetraiodide [in Japanese], Makoto SHIMIZU: *J. Synth. Org. Chem., Jpn.* 62 (3), pp. 205-213, 2004

Elimination-Addition Mechanism for Nucleophilic Substitution Reaction of Cyclohexenyl Iodonium Salts and Regioselectivity of Nucleophilic Addition to the Cyclohexyne Intermediate, Morifumi FUJITA*, Wan Hyeok KIM*, Yuichi SAKANISHI*, Koji FUJIWARA*, Sayaka HIRAYAMA*, Tadashi OKUYAMA*, Yasuhiro OHKI*, Kazuyuki TATSUMI*, Yasunori YOSHIOKA: *J. Am. Chem. Soc.* 126 (24), pp.7548-7558, 2004

The reaction of 4-substituted cyclohex-1-enyl(phenyl)iodonium tetrafluoroborate with tetrabutylammonium acetate gives both the *ipso* and *cine* acetate-substitution products in aprotic solvents. The isomeric 5-substituted iodonium salt also gives the same mixture of the isomeric acetate products. The reaction is best explained by an elimination-addition mechanism with 4-substituted cyclohexyne as a common intermediate. The cyclohexyne formation was confirmed by deuterium labeling and trapping to lead to [4 + 2] cycloadducts and a platinum-cyclohexyne complex. Cyclohexyne can also be generated in the presence of some other mild bases such as fluoride ion, alkoxides, and amines, though amines are less effective bases for the elimination. Kinetic deuterium isotope effects show that the anionic bases induce the E2 elimination ($k_H/k_D > 2$), while the amines

allow formation of a cyclohexenyl cation in chloroform to lead to E1 as well as S_N1 reactions ($k_H/k_D \approx 1$). Bases are much less effective in methanol, and methoxide was the only base to efficiently afford the cyclohexyne intermediate. Nucleophiles react with the cyclohexyne to give regioisomeric products in the ratio dependent on the ring substituent. The observed regioselectivity of nucleophilic addition to substituted cyclohexynes is rationalized from calculated LUMO populations, which are governed by the bond angles at the acetylenic carbons: The less deformed carbon has a higher LUMO population and is preferentially attacked by the nucleophile.

Vibrational Analysis with the Symmetrically Combined Morse Potential Model for Antisymmetric Stretching in [CIDCl] Formed by Photodissociation of (DCI)₂, Masaki MITANI, Yasunori YOSHIOKA, Dock-Chil CHE*, Toshio KASAI* : J. Phys. Chem. A 108 (24), pp.5220-5225, 2004

We estimate the line spacing between vibrational levels for the antisymmetric stretching in [CIDCl] to elucidate the origin of the oscillating structure on the translational energy distribution of the terminal D atom released by the photodissociation of (DCI)₂. The vibrational analysis with the symmetrically combined Morse potential model is performed for linear hydrogen-bonding [CIDCl] and the dependence of change in vibrational levels on the Cl-Cl distance is examined. It is found that the calculated assignment and observed spacing show good correspondence for $R_{ClCl} = 3.65$ or 3.70 \AA , and it is therefore strongly suggested that the oscillation of dissociated D translational energy reflects the antisymmetric stretching vibration in the [CIDCl] counterpart.

Effect of Aging on Conductivity of Yttria Stabilized Zirconia, Masatoshi HATTORI*, Yasuo TAKEDA, Yoshinori SAKAKI*, Akihiro NAKANISHI*, Satoshi OHARA*, Kazuo MUKAI*, Jin-Ho LEE*, Takehisa FUKUI*: Journal of Power Sources 126, pp.23-27, 2004

Effect of Annealing on the Electrical Conductivity of the Y₂O₃-ZrO₂ System, M. HATTORI*, Y. TAKEDA, J. -H. LEE*, S. OHARA*, K. MUKAI*, T. FUKUI*, S. TAKAHASHI*, Y. SAKAKI*, A. NAKANISHI*: Journal of Power Sources 131, pp.247-250, 2004

The Effect of Doped Elements on the Electrochemical Behavior of Hexagonal Li_{2.6}Co_{0.4}N, Yu LIU, Kumi HORIKAWA, Minako FUJIYOSHI, Nobuyuki IMANISHI, Atsushi HIRANO, Yasuo TAKEDA: Journal of the Electrochemical Society 151(9), pp. A1450-A1455, 2004

Lithium Transition Metal Nitrides with the Modified Morphology Characteristics as Advanced Anode Materials for Lithium Ion Batteries, Y. LIU, T. MATSUURA, N. IMANISHI, T. ICHIKAWA, A. HIRANO, Y. TAKEDA: Electrochemistry Communication 6, pp.632-636, 2004

Silicon/Carbon Composites as Anode Materials for Li-Ion Batteries, Y. LIU, K. HANAI, J. YANG*, N. IMANISHI, A. HIRANO, Y. TAKEDA: Electrochemical and Solid-State Letters 7(10), pp.A369-A372, 2004

Study of the Capacity Fading Mechanism for Fe-Substituted LiCoO₂ Positive Electrode, Victoria L. MCLAREN*, Anthony R. WEST*, Mitsuharu TABUCHI*, Akiko NAKASHIMA*, Hikari TAKAHARA*, Hironori KOBAYASHI*, Hikari SAKAEBE*, Hiroyuki KAGEYAMA*, Atsushi HIRANO, Yasuo TAKEDA: *Journal of the Electrochemical Society* 151(5), pp. A672-A681, 2004

Novel Composite Anodes Based on Layered Lithium Transition Metal Nitrides for Lithium Secondary Batteries, Y. LIU, K. HORIKAWA, M. FUJIYOSHI, T. MATSUURA, N. IMANISHI, Y. TAKEDA: *Solid State Ionics* 172, pp.69-72, 2004

Electrical and Thermal Properties of Dense Ce_{1-x}RE_xO_{2-δ} Electrolyte Using Low-Temperature Sinterable Powder (0 ≤ x ≤ 0.2, RE=Y, Sm, Gd), Eisaku SUDA*, Bernard PACAUD*, Yvan MONTARDI*, Masashi MORI*, Yasuo TAKEDA: *Transactions of the Materials Research Society of Japan* 29(5), pp.2317-2320, 2004

Impedance Spectroscopy of Perovskite Air Electrodes for SOFC Prepared by Laser Ablation Method, N. IMANISHI, T. MATSUURA, Y. SUMIYA, K. YOSHIMURA, A. HIRANO, Y. TAKEDA, D. MORI*, R. KANNO*: *Solid State Ionics* 174, pp.245-252, 2004

Effects of Charge Disproportionation on the Phonon Density of State in Fe Perovskites, Jobu MATSUO*, Makoto SETO*, Shinji KITAO*, Yasuhiro KOBAYASHI*, Rie HARUKI*, Takaya MITSUI*, Atsushi FUJIMORI*, Yasuo TAKEDA, Shuji KAWASAKI*, Mikio TAKANO*: *Journal of the Physical Society of Japan* 73 (10), pp.2768-2770, 2004

Modification of Carbon Nanotubes by Laser Ablation of Copper, Akira. KOSHIO, Mitsuru SHIRAISHI, Yuuji KOBAYASHI, Masatou ISHIHARA*, Yoshinori KOGA*, Syunji BANDOW*, Sumio IJIMA*, Fumio KOKAI: *Chem. Phys. Lett.* 396, pp.410-414, 2004

Multi-wall carbon nanotubes (MWNTs) were modified by laser ablation of Cu in the presence of He gas. Quasi-spherical particles with diameters of 200 nm to 2 μm were sparsely deposited on as-grown MWNTs. Agglomerated nanoparticles with sizes of 1-10 nm covered ultrasonically-treated MWNTs. Both particles were oxidized. The interaction of nanoparticles with the surface of the ultrasonicated MWNTs, due to small charge transfer to carbon atoms of the MWNTs upon adsorption of Cu, was suggested. We discuss the size distribution and morphology of the particles from cluster and particle formation in gas-phase and the surface properties of the two MWNTs.

Compression of Polyhedral Graphite up to 43 GPa and X-ray Diffraction Study on Elasticity and Stability of the Graphite Phase, Atsuko NAKAYAMA*, Sumio IJIMA*, Yoshinori KOGA*, Katsuya SHIMIZU*, Kaori HIRAHARA*, Fumio KOKAI: *Appl. Phys. Lett.* 84, pp. 5112-5114, 2004

The crystal structure of polyhedral graphite particles (“G balls”) has been investigated under pressure up to 43 GPa and at room temperature by x-ray powder diffraction measurements. The polyhedra maintain the graphite phase under pressure higher than 40 GPa. A 29% compression in volume at 43 GPa involves an unusual decrease in the interlayer distance of 25%. The polyhedra recover their original crystal structure by releasing the pressure. A closed and solid structure of the polyhedra, suppressing a transition into another phase, causes them to become metallic under pressure higher than 20 GPa.

Three Nanostructured Graphitic Particles and their Growth Mechanisms from High-Temperature Carbon Vapor Confined by Ar Gas, Fumio KOKAI, Akira KOSHIO, Daisuke KASUYA*, Kaori HIRAHARA*, Kunimitsu TAKAHASHI*, Atsuko NAKAYAMA*, Masatou ISHIHARA*, Yoshinori KOGA*, Sumio IJIMA*: Carbon, 42, pp.2515-2520, 2004

CO₂ laser vaporization of graphite was carried out in the presence of high pressure Ar gas up to 0.8 MPa. We compared transmission electron microscope images and Raman spectra of deposited particles and luminous laser plumes of vaporized and clustered carbon species. We discuss the growth mechanisms of three graphitic carbon particles, a single-wall carbon nanohorn aggregate, a platelet graphite particle, and a polyhedral graphite particle, grown depending on the confinement of the Ar atmosphere. The formation of graphitic sheet or shell structures, dependent on resident carbon densities and their temperature gradient, is thought to begin from supersaturated hot carbon vapor up to about 3000°C and lead to the growth of the three graphitic particles.

Optimization of Solar Photocatalytic Degradation Conditions of Bisphenol A in Water Using Titanium Dioxide, Satoshi KANECO, Mohammad A. RAHMAN, Tohru SUZUKI, Hideyuki KATSUMATA, Kiyohisa OHTA: J. Photochem. Photobiol. A: Chem. 163, pp. 419–424, 2004

Solar Photocatalytic Degradation of Bisphenol A in Water with ZnO, Mohammad A. RAHMAN, Satoshi KANECO, Tohru SUZUKI, Hideyuki KATSUMATA, Kiyohisa OHTA: Photo/Electrochem. Photobiol. Environ. Energy Fuel 3, pp. 199–205, 2004

Determination of Silver in Waters by Tungsten Wire Preconcentration Method - Electrothermal Atomic Absorption Spectrometry, Mohammad A. RAHMAN, Satoshi KANECO, Md N. AMIN, Tohru SUZUKI, Kiyohisa OHTA: Talanta 62, pp. 1047–1050, 2004

Separation of Zinc Compounds by Sequential Metal Vapor Elution Analysis with Atomic Absorption Detection, Mohammad A. RAHMAN, Satoshi KANECO, Tohru SUZUKI, Hideyuki KATSUMATA, Kiyohisa OHTA: Talanta 64, pp. 989–992, 2004

Slurry Sampling for Direct Analysis of Lead in Bangladeshi Vegetable Samples by Molybdenum Electrothermal Atomizer Atomic Absorption Spectrometry, Mohammad A. RAHMAN, Satoshi

KANECO, Tohru SUZUKI, Hideyuki KATSUMATA, Kiyohisa OHTA: ITE Lett. Batt. New Technol. Med. 5, pp. 363–368, 2004

Leaching Behavior of Lead Compounds in Atmosphere Fine and Coarse Particles, Kunihiro FUNASAKA*, Takeji MIYAZAKI*, Toshikazu KAMIURA*, Joji FUKUYAMA*, Hideyuki KATSUMATA, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA: ITE Lett. Batt. New Technol. Med. 5, pp. 577–580, 2004

Development of Sintering Preparation Technology of Porous Materials from Sea Bottom Sediments for Waste Water Treatment, Satoshi KANECO, Takuya HARADA, Ahmed H.A. DABWAN, Tohru SUZUKI, Hideyuki KATSUMATA, Kiyohisa OHTA: ITE Lett. Batt. New Technol. Med. 5, pp. 467–471, 2004

Electrochemical Reduction of CO₂ at Alloy Electrode in Methanol, Satoshi KANECO, Hiroki YAMAUCHI, Hideyuki KATSUMATA, Tohru SUZUKI, Kiyohisa OHTA: Stud. Surf. Sci. Catal. 153, pp. 277–282, 2004

Reduction of Carbon Dioxide Using Metal Powders, Hideyuki KATSUMATA, Kouichirou MATSUSHITA, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA: Stud. Surf. Sci. Catal. 153, pp. 55–60, 2004

Long Term Sampling Method for PCDD/Fs in Atmosphere by Adsorption onto Economical Materials, Hideyuki KATSUMATA, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA: Chem. Lett. 33, pp. 1618–1619, 2004

Effect of Metal Nitrates on the Formation of PCDD/Fs during Newspaper Combustion, Hideyuki KATSUMATA, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA: Bull. Environ. Contamn. Toxicol. 73, pp. 479–486, 2004

Removal of Humic Substances and Their Metal Complexes by Adsorption with Bone Char, Hideyuki KATSUMATA, Satoshi KANECO, Haruna KASAI, Kumiko ITOH, Kazuaki MASUYAMA*, Tohru SUZUKI, Kunihiro FUNASAKA*, Kiyohisa OHTA: Environ. Eng. Sci. 21, pp. 341–348, 2004

Microbial Metabolism of Di-*n*-Butyl Phthalate by Bacterium *Bacillus Natto*, Aleya BEGUM, Hideyuki KATSUMATA, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA: Chem. Lett. 33, pp. 682–683, 2004

Removal of Heavy Metals in Aqueous Solution by Adsorption onto Oyster Shell, Hideyuki

KATSUMATA, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA, Yoshihiro YOBIKO: Photo/Electrochem. Photobiol. Environ. Energy Fuel 3, pp. 165–172, 2004

Removal of Heavy Metals in Water by Adsorption onto Sintering Porous Materials from Sea Bottom Sediments, Hideyuki KATSUMATA, Takuya HARADA, Satoshi KANECO, Ahmed H.A. DABWAN, Tohru SUZUKI, Kiyohisa OHTA: ITE Lett. Batt. New Technol. Med. 5, pp. 573– 576, 2004

Preconcentration of Phthalic Acid Esters in Water Samples by *Saccharomyces cerevisiae* Immobilized on Silica Gel, Hideyuki KATSUMATA, Aleya BEGUM, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA: Anal. Chim. Acta 502, pp. 167–172, 2004

Degradation of Bisphenol A in Water by the Photo-Fenton Reaction, Hideyuki KATSUMATA, Shinsuke KAWABE, Satoshi KANECO, Tohru SUZUKI, Kiyohisa OHTA: J. Photochem. Photobiol. A: Chem. 162, pp. 297–305, 2004

Nucleotide Sequence Analysis of *p10* Gene of *Antheraea pernyi* Nucleopolyhedrovirus and Construction of Two Transfer Vector Plasmids, Kenichi MAEGAWA, Xie T. WANG*, Jun KOBAYASHI*, Tetsuro YOSHIMURA: International Journal of Wild Silkworm and Silk 9, pp. 53-60, 2004

Development of Orally Administrated Liposome Vaccines against Bacteria- and Virus-Infectious Diseases in Cultured Fishes: Tetsuro YOSHIMURA, Takeyoshi TAKAGI, Kanta TSUMOTO, Masayuki SHONO, Teruo MIYAZAKI: Immunology 2004, pp. 225-228, 2004

Ligand-Printed Ion Pore Composed of Polypeptide Assembly in a Lipid Bilayer Membrane, Masahiro HIGUCHI, Tomoyuki KOGA*, Yoshiaki KOBUKE*, Takatoshi KINOSHITA*, Masami KAWAGUCHI: Trans. MRS-J. 29, pp. 3143-3146, 2004

A simple and novel approach for the preparation of a synthetic ligand-gated ion channel was investigated. The ligand-induced formation of an amphiphilic polypeptide assembly acts as an ion channel in lipid bilayer membrane. Various functional groups, which bind to the specific site on the ligand (X), were introduced at the amino terminal of α -helical polypeptide. The interaction between the ligand (X) and the terminal groups of the polypeptides induced the specific location of the α -helical polypeptide rods. Removing of the ligand (X) provided the ligand-printed ion pore in the membrane, while re-binding of the ligand (X) closed the pore. Another ligand (Y) was inactive to the ligand (X)-printed ion pore, *i.e.*, it did not close the channel. This ligand-printed polypeptide assembly may permit a novel and easier production of the ligand-gated ion channel, which will give a novel approach for the construction of signal transduction molecular devices.

Viscous Fingering of Silica Suspensions Dispersed in Polymer Fluids, Masami KAWAGUCHI: ACS Symposium Series No. 869 Nonlinear Dynamics in Polymeric Systems, pp. 250-261, 2004

Experimental studies of the viscous fingering of shear thinning silica suspensions in a radial Hele-Shaw cell and shear thickening silica suspensions in a linear Hele-Shaw cell were performed by the injection of air. For the shear thinning silica suspensions, the instability, namely changes in the viscous fingering pattern, was strongly related to the polymer concentration in the dispersant rather than the silica concentration. For the shear thickening silica suspensions, the imposed shear rate at which the instability was first observed, was close to the critical shear rate of the corresponding silica suspension. The finger velocities of the shear thinning silica suspensions were in agreement with the modified Darcy's law, while those of the shear thickening silica suspensions with the silica concentrations higher than 7.5 wt% were much lower than the prediction of the modified Darcy's law.

Rheo-Optical Properties of Silicone Oil Emulsions in the Presence of Polymer Emulsifiers, Masami KAWAGUCHI, Kenji KUBOTA: Langmuir 20 (4), pp. 1126-1129, 2004

Oil in water emulsions were prepared by dispersion of silicone oils into an aqueous solution of hydroxylpropyl methyl cellulose (HPMC) or poly(ethylene oxide) (PEO)-poly(propylene oxide) (PPO)-PEO block copolymers. The emulsions were characterized by measurements of steady-state shear viscosities, dynamic moduli, and stress-strain sweep curves coupled with optical microscope observation. The emulsions emulsified by HPMC showed solid-like viscoelastic responses, while the emulsions prepared by the block copolymers indicated liquid-like viscoelastic behavior. The simultaneous optical microscopic observation showed that the emulsions stabilized by HPMC did not flow below the yield stress, while those by the block copolymers did flow.

Viscous Fingering Instabilities in an Oil in Water Emulsion, Masami KAWAGUCHI, Sayaka YAMAZAKI, Tadayo KATO: Phys. Fluids 16 (6), pp. 1908-1914, 2004

Viscous fingering of silicone oil emulsion stabilized by hydroxylpropyl methyl cellulose (HPMC) in water was performed by the injection of water and an aqueous solution of HPMC as a function of the injection rate. The pressure imposed at the finger tip was simultaneously monitored. Changes in the viscous fingering patterns from a crack-like pattern to a ramified one through a cups-like one were observed with an increase of the injection rate, irrespective of the injected fluid. Such a pattern transition was strongly related to rheological properties of the emulsion. Moreover, the finger velocities of the emulsion were in agreement with the modified Darcy's law

Structure Study of Binary Titanophosphate Glasses Prepared by Sol-Gel and Melting Methods, Anjiang TANG, Tadanori HASHIMOTO, Tetsuya NISHIDA, Hiroyuki NASU, Kanichi KAMIYA: Journal of the Ceramic Society of Japan 112(9), pp. 496-501, 2004

The $70\text{TiO}_2 \cdot 30\text{P}_2\text{O}_5$ (mol%) glass was prepared by the sol-gel method. Its structure was examined by means of IR, Raman spectroscopy and X-ray radial distribution function analysis, and was compared with the corresponding melt-derived glass. It was found that average coordination number of Ti^{4+} ions was almost 6 and Ti^{4+} ions formed predominantly TiO_6 octahedra in the

sol-gel-derived glass, while Ti^{4+} ions were present in the 4, 5 and / or 6-fold coordination states to give average coordination number in-between 4 and 5 in the melt-glass. The preference of high coordination state of Ti^{4+} ions in the sol-gel glass was consistent with higher refractive index and density than the melt-glass.

Effective Deposition of Nano-Sized Silver Particles on Silica to Develop a Sensitive Local Plasmon-Based SPR Sensor, Noritsugu HASIMOTO*, Tadanori HASHIMOTO, Koichi MORI, Hiroyuki NASU, Kanichi KAMIYA: Journal of the Ceramic Society of Japan, Supplement 112-1, PacRim5 Special Issue 112(5), pp. S576-S578, 2004

Nano-sized silver particles-deposited silicas were prepared by (a) the sol-gel method, the evaporation-condensation of silver on (b) silica glass and (c) sol-gel derived silica film. Optical absorption peak due to surface plasmon resonance (SPR) of silver particles was measured using UV-VIS spectrophotometer. When the films were immersed in liquid, SPR absorption peak of the films (b) and (c) was shifted toward longer wavelength with the increase of the refractive index of the liquid, suggesting that these films can be used as optical sensors. On the other hand, SPR absorption peak of the film (a) was little shifted. The sensitivity to the refractive index change for the film (b) was 81.4 nm, and that of the film (c) made by depositing silver particles on the sol-gel silica was large as 90.2 nm, which may be attributed to less coverage of silver particles with silica matrix than the film (a) and less aggregate of them than the film (b).

Optical Properties of Ti^{3+} -Free Ternary Titanophosphate Glasses, Tadanori HASHIMOTO, Hiroyuki NASU, Kanichi KAMIYA: Proceedings of the XX ICG in Kyoto, Sep.27th-Oct.1st, O-07-085, 2004

The Ti^{3+} -free binary TiO_2 - P_2O_5 glasses containing TiO_2 up to 74 mol% prepared by the melt-quenching and a long-term post-annealing around the glass transition temperature in the air possess high transparency, high-index, high-dispersion and low density, and are expected as novel eco-optical glasses. In the present study, the effect of third and fourth components on the time of post-annealing to remove Ti^{3+} ions, and linear and nonlinear optical properties was examined. The substitution of K_2O for P_2O_5 in binary glasses shortened the post-annealing time and decreased the thermo-optic coefficient. The addition of a small amount of SnO_2 to binary glasses was found to be effective for removing Ti^{3+} ions, or decoloration of glasses with maintaining high-index, and also for stabilizing laser pulses. In addition, quaternary Li_2O - ZnO - TiO_2 - P_2O_5 glasses were expected as high-index molding glasses.

Structure Study of TiO_2 - P_2O_5 Glasses Prepared by Sol-Gel Method, Anjiang TANG, Tadanori HASHIMOTO, Hiroyuki NASU, Kanichi KAMIYA: Proceedings of the XX ICG in Kyoto, Sep.27th-Oct.1st, O-10-021, 2004

The $xTiO_2 \cdot (100-x)P_2O_5$ ($x = 70-95$ mol%) glasses with refractive indices as high as 2.1-2.3 were prepared by the sol-gel method. The refractive index was higher in the sol-gel-glass than in the melt-glass at $x = 70$. Heat-treated compositions with $x = 90$ and 95 were considered to be composites of 13-15 mass% nano-sized anatase and glass matrices with x slightly smaller than nominal values,

but were highly transparent. It was found by IR and Raman techniques that 6-fold coordinated Ti^{4+} ions are predominant in the glass phase, while 4 or 5, and 6-fold ones are coexisting in the melt-glass of $x = 70$. These results were consistent with very high refractive index of the sol-gel glasses.

Influences of Nanocrystal-Size and Matrix on Third-Order Optical Nonlinearity for Thin Films Prepared by RF-Sputtering, Hiroyuki NASU, Akimasa TANAKA, Tadanori HASHIMOTO, Kanichi KAMIYA, Kenji KAMADA*: Proceedings of the XX ICG in Kyoto, Sep.27th-Oct.1st, O-16-017, 2004

CdSe microcrystals with various size was successfully embedded in various glass matrices by magnetron Rf sputtering technique. The mean size of microcrystals was controllable by changing the relative surface ratio of CdSe pellets to the matrix in the target, and increased with increasing the relative area. The negative real part of the third-order optical susceptibility was seen for the all present films, and magnitude of the absolute value of real part in the same glass matrix increased with decreasing microcrystal size. On the other hand, the increase of the dielectric constant of the matrix increase the magnitude. Therefore it is interpreted that the strengthening the quantum size effect increase the magnitude of the real part of the third-order optical nonlinearity. Furthermore, even taking account of the imaginary part, it is evident that the strengthening the quantum size effect increases total third-order optical nonlinearity.

Electroluminescence from CdSe Nanocrystal-Doped ITO Films on SiO_2 Glass Substrates, Hiroyuki NASU, Yasuhiro Matsuzaki, Tadanori HASHIMOTO, Kanichi KAMIYA: Proceedings of the XX ICG in Kyoto, Sep.27th-Oct.1st, O-16-025, 2004

Electroluminescence was observed in CdSe microcrystal-doped indium tin oxide (ITO) thin films on SiO_2 glass substrates by Rf-sputtering method. The size of CdSe microcrystals was changed by altering the relative surface area of the CdSe pellets on the ITO target. ITO was well crystallized on SiO_2 glass substrates. Emission spectra shifted from red to yellow with decreasing CdSe microcrystal size. The shift was considered to result from the blue shift of the absorption edge caused by the quantum confinement effect of CdSe microcrystals.

Review of Combination of Peritoneal Dialysis and Hemodialysis as a Modality of Treatment for End-stage Renal Disease, H. FUKUI*, S. HARA*, Y. HASHIMOTO*, T. HORIUCHI, M. IKEZOE*, N. ITAMI*, M. KAWABE*, H. KAWANISHI*, Y. KIMURA*: Ther Apher Dial 8, pp. 56-61, 2004

Because the contribution of residual renal function (RRF) to total solute clearance is often significant in continuous ambulatory peritoneal dialysis (CAPD), loss of RPF over time can lead to inadequate dialysis if appropriate prescription management strategies are not pursued. Additionally, declines in ultrafiltration caused by increases in peritoneal permeability may limit continuation of CAPD therapy. Peritoneal dialysis and hemodialysis (PD + HD) combination therapy (complementary dialysis therapy) is an alternative method. This therapy allows the patient to maintain daily activities, as with CAPD, while undergoing once-a-week HD supplements for the insufficient removal of solutes and water. This therapy allows for the continuation of PD without shifting to total HD in PD patients who continue to have uremic symptoms even after individualization of the PD prescription.

This treatment option is psychologically more acceptable to patients and may be expected to provide such accompanying beneficial effects as peritoneal resting, improvement of QOL and reduction in medical cost.