

Syntheses of Dimethyl Carbonate and Urethane Directly from Carbon Dioxide

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The utilization of carbon dioxide as a *renewable* C₁ building block has been a challenge for synthetic chemists and is getting more important. Especially, utilization as a *phosgene alternative* is quite promising. We investigated the transformation of CO₂ under supercritical conditions in the presence of a catalytic amount of Bu₂SnO: (i) synthesis of dimethyl carbonate (DMC) by the reaction with methanol, and (ii) synthesis of urethane through the reaction with amine and alcohol.

Organic solvent-free synthesis of polyphenyleneoxide (PPO) in supercritical carbon dioxide

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Polyphenyleneoxide (PPO) is one of the important engineering plastics showing excellent mechanical, thermal, electrical and chemical properties at higher temperatures. In industry, PPO has been produced by oxidative-coupling reaction in toluene solvent and it has been pointed out that the solvent recovery plays an important role in determining the process feasibility. Additionally the viewpoint of green sustainable chemistry has brought the trend of solvent-free synthesis even for polymer industry. From these backgrounds, we have made an attempt of PPO synthesis in supercritical carbon dioxide (SC-CO₂) without using organic solvent. It is well known that SC-CO₂ can have solvent power of dissolving monomers but generally poor solvent for high molecular weight polymers. This was also found in our trial experiment of PPO synthesis in SC-CO₂. In this study, we propose a new synthetic technique for high molecular weight PPO via two-step polymerization with controlling reaction temperature in SC-CO₂.

Organic reactions with solid acid and base catalysts in supercritical water

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Recently, supercritical water (SCW) is becoming a green solvent for a several organic reactions. SCW can provide a high reaction activity, however sometimes requires catalysts for accelerating and controlling the reaction rate and selectivity. So far, a lot of experimental results for catalytic reactions in SCW have been

reported, but a limited studies can be found about a catalytic function of the catalyst in SCW. A metal oxide, which has both acidic and basic sites on the surface, has been known to work actively for reactions even in SCW. In this study, we propose a new green pH control technique with metal oxides in SCW, through the studies on 2-propanol, acetic acid, and glucose reactions .

A1-04

Lipase-Catalyzed Enantioselective Acylation in an Ionic Liquid Solvent

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Lipase-catalyzed transesterification of alcohols took place smoothly under reduced pressure when methyl phenylthioacetate was used as acyl donor in [bmim]PF₆, and we succeeded in obtaining the corresponding acylated compound in optically pure form; this makes it possible to use lipase repeatedly because there was no drop in the reaction rate despite three repetitions of the process.

A1-05

Fluorination Reactions in Ionic Liquids

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The utility of ionic liquids for fluorination using 2,2-difluoro-1,3-dimethylimidazolidine (DFI) is described. Especially, the carbonyl group of α,β -epoxy carbonyl compounds was converted to the difluoromethylene group smoothly.

A1-06

Degradation of 2,2-Difluoroethanol

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2,2-Difluoroethanol was accumulated by bacteria, giving difluoroacetic acid and so on. The conversion of 2,2,-difluoroethanol to difluoroacetic acid with a biological system is described.

A1-07

Microreactors for the Synthesis of Fluorinated Materials

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The utility of microreactor for the synthesis of afluoro-a,b-unsaturated esters by the Horner-Wadsworth-Emmons reaction of triethyl 2-fluoro-2-phosphonoacetate with aldehydes in the presence of base, is described.

A1-08

Chemical recycling of sulfur-cured natural rubber using SUPERCRITICAL CARBON DIOXIDE

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The recycling of rubber components in used rubber products, especially those in automobile tires, is one of the most important subjects for the rubber industry. In our study, supercritical CO₂ has been adopted for the devulcanization process of natural rubber (NR) vulcanizates as a reaction media. Supercritical CO₂ has a few advantages as a devulcanization reaction media. CO₂ is easily and rapidly removed by releasing pressure after the reaction and may also enhance the diffusion rate of a devulcanizing reagent into the rubber vulcanizate comprised of a 3-dimensional network polymer.

A1-09

Asymmetric Reactions in Supercritical Carbon Dioxide by Biocatalysts

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Two types of biocatalytic reactions in supercritical carbon dioxide were investigated: asymmetric reduction of ketones using alcohol dehydrogenase and kinetic resolution of alcohol using lipases. As a result, optically active alcohols were obtained with excellent enantioselectivities.

A1-10

Application of Ionic Liquids to Extractive Fermentation of Lactic Acid

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In order to investigate the application of ionic liquids to the extractive fermentation of lactic acid, we examined the toxicity of ionic liquids to lactic acid-producing bacteria, and conducted the extraction of lactic acid from the aqueous solution to ionic liquids. We found that two bacteria species survive in the presence of ionic liquids, and the extractability of ionic liquids is superior to that of conventional organic solvents.

A1-11

Isomerization of n-Butane under Supercritical Conditions over Solid Acid Catalysts

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The isomerization of n-butane under supercritical conditions over sulfated zirconia has been studied. We found that the under supercritical conditions the catalytic activity was higher than that of gas or liquid phase and the catalyst lifetime was greatly improved.

A1-12

Hydroformylation Using Carbon Dioxide Catalyzed by Ruthenium Complexes in Ionic Liquid

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Ruthenium complexes in ionic liquid effectively catalyze the hydroformylation of simple alkenes with carbon dioxide as a reactant.

A1-13

ENZYMATIC ESTERIFICATION IN GREEN SOLVENTS: APPLICATION OF IONIC LIQUIDS IN BIOCONVERSIONS

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Biocatalytic processes have already proven to be a useful tool for green chemistry, because the biocatalysts

(whole cells, enzymes) are biodegradable and selective. In addition to the catalyst and the products/reagents, one of the main source of pollution in industrial processes is the solvent, which constitutes the bulk of the reaction media. Most of the solvents are toxic, flammable and evaporable, which makes difficult their separation from the products considering solvent losses during procedures.

A1-14

Organic Carbonate Synthesis by Environmentally Benign Processes

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In order to design a highly active catalytic system for the palladium-catalyzed oxidative carbonylation of phenol, we elucidated the reactivity of possible intermediates such as $L_2Pd(OPh)_2$ and $L_2PdX(CO_2Ph)$. We also found an efficient heterogeneous catalysis of $SmOCl$ as well as a recyclable homogeneous catalysis of polyfluoroalkyl phosphonium iodides (R_fRPI) for the propylene carbonate (PC) synthesis from propylene oxide (PO) and CO_2 under supercritical CO_2 ($scCO_2$) conditions.

A1-15

Amine Catalyzed Carbon Dioxide Addition Reaction to Internal Oxiranes in Supercritical Carbon Dioxide

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In supercritical carbon dioxide, 10 mol% of benzylamine promoted the carbon dioxide addition reaction to methoxyoxirane to afford the corresponding cyclic carbonate in a good yield. For the carbon dioxide addition to cyclohexene oxide, amine catalysts were activated by addition of onium salts and the corresponding cyclic carbonate was obtained in good yields under high density carbon dioxide.

A1-16

Non-Covalent Derivatization: Solving Real World Problems At The Molecular Level With Green Chemistry

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Non-Covalent Derivatization is a method of manipulating the physical properties of materials by using intermolecular interactions. Using the phenol-amide hydrogen bond as the primary interaction, binary non-covalent derivative systems of hydroquinones have been constructed. One dimensional derivatives using bis (N, N-dialkyl) terephthalamides, two dimensional derivatives using tris (N, N-dialkyl)-trimesamides and three dimensional derivatives using tetrakis (4-(N,N-dialkylamido) phenyl) methane have been prepared. Using the Benzoin/Benzyl redox couple, we have investigated the control of several macroscopic properties. The synthesis of the amide components and phase diagrams will be presented along with a discussion of the intermolecular forces at work in these systems.

A1-17

Electrochemical Fluorination of Oxygen-Containing Heterocycles in Ionic Liquids

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Ionic liquids (ILs) are becoming widely recognized as solvents for green organic synthesis. In addition, the reuse of solvents is preferable in view of green chemistry. However, there have been only few papers dealing with electroorganic synthesis in ILs.

A1-18

MEASURING REACTION KINETICS OF ORGANIC REACTIONS IN SUPERCRITICAL HYDROFLUOROCARBON SOLVENTS.

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By far the most commonly used supercritical (sc) fluid is CO₂ because it is inexpensive, non-toxic, has low critical constants (T_c = 304.20 K, P_c = 72.8 bar) and is environmentally benign. The difficulty that arises with the use of CO₂ is its inability to dissolve many organic and metal complexes due to its low polarity.

A1-19

HYDROGEN BOND PROPERTIES OF SUPERCRITICAL HYDROFLUOROCARBONS

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Due to the low critical point, lack of toxicity and low cost, scCO₂ is so far the most commonly used supercritical fluid. Nevertheless scCO₂ is a non-polar solvent and many organic compounds and metal complexes have very limited solubility in scCO₂.

THE FISCHER INDOLE SYNTHESIS IN AN IONIC LIQUID

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Heterocyclic compounds form the bedrock of the invention of new drugs in the pharmaceutical industry. Consequently, improvements in the synthesis and reaction of heterocyclic compounds will have an important impact on industrial chemistry. The synthesis of heterocyclic rings often involves the heating of an aromatic precursor in a strong acid. Ionic liquids provide alternative, “greener” reaction condition for the Fischer indole reaction..

Green Carbohydrate Chemistry – Environmentally Benign Chemical Glycosidation Using Ionic Liquids as New Reaction Media

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Glycosidation reactions of a glycosyl phosphite and alcohols are conducted in an ionic liquid, hmim[NTf₂], containing a protic acid, HNTf₂, to give the corresponding glycosides in high yields. This novel method is greener than traditional protocols using Lewis acid and organic solvent, because of the environmentally benign properties of the ionic liquid and the reusability of the reaction system.