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研究課題名（和文）Synthesis of active and stable bifunctional nanocluster catalysts and their application in Carbondioxide insertion reaction

研究課題名（英文）Synthesis of active and stable bifunctional nanocluster catalysts and their application in Carbondioxide insertion reaction

研究代表者

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研究成果の概要（和文）：この研究の目的は、CO2を活性化する可能性を有し、穏やかな反応条件下で1つのポット多成分結合反応に適用することができる複数の活性化部位を有する高活性で安定した新しい触媒を設計することである。本研究では、イミダゾール系リガンドを用いた安価なシリカの機能化を通じて、異種の二官能性SiO2系触媒を合成することができた。イミダゾリニウム塩は、基材およびCO2用金属および活性化剤のリガンドとして作用した。この二官能系では、環状炭酸塩を軽度反応条件下でプロパルギルアルコールを用いて調製した。有機塩基や無機塩基などの添加剤を使わずに、この反応にグリーンルートを提供した。

研究成果の学術的意義や社会的意義
The catalyst developed by this research made the synthesis of cyclic carbonates and carbamates possible by utilizing CO2 which is a “green” perspective to the synthesis of value added compounds with easy recovery and reusability of the novel catalyst for its applicability in chemical industry.

研究成果の概要（英文）：The purpose of this research is to design highly active and stable new catalyst with multiple activation sites that possess potentiality to activate CO2 and can be applied for one pot multicomponent coupling reaction under milder reaction condition. In this context, we could synthesize heterogenous bifunctional SiO2 based catalyst through functionalization of cheap silica with imidazole-based ligand. The imidazolinium salt acted as ligand for metal and activator for substrate and CO2. With this bifunctional system, cyclic carbonates were prepared using propargyl alcohols under mild reaction condition. Our system provided green route for this reaction without any additive such as organic and inorganic bases.

研究分野：Heterogenous catalyst

キーワード：Heterogenous catalyst　carbondioxide　Silver complex　Synthetic methods　bifunctional catalyst

１．研究開始当初の背景

Chemical fixation of CO_2 to useful chemicals has attracted much attention because it is a non-toxic feedstock for carbon-based materials such as carboxylic acids, cyclic carbonates, carbamates and lactones. Although CO_2 is used in many well-established reactions, attractive and straightforward procedures for the direct carboxylation of carbon nucleophiles with CO_2 as the electrophile remain largely underdeveloped. Cyclic carbonates and carbamates are valuable chemicals. A numerous reaction catalyzed by transition-metals homogenous and heterogeneous catalyst systems have been explored recently, however, they need to use high pressure of CO_2, high temperature, small-membered ring compounds, organometallics, or other higher energy starting materials, ligands; and usually suffer from catalyst deactivation by agglomeration due to irreversible reaction between reagents or side products with the active sites of the catalyst.
For activating such a highly stable CO_2, some of the efficient Cu, Ni or Ag; and MOF (metal-organic framework) based heterogeneous catalysts have been developed which help in adsorption and activation of CO_2 as shown by experiment and DFT calculations. However, such heterogeneous catalysts are very few and applied to CO_2 insertion in active substrates such as terminal alkynes or boronic acids. In addition, investigation over CO_2 activation on catalyst surface is limited to theoretical study only. Hence, new catalysts still need to be developed which can activate multiple sites at once to carry out multicomponent reaction with CO_2. Through this proposed research we expect to design highly active and stable new catalyst with multiple activation sites that possess potentiality to activate CO_2 and can be applied for one pot multicomponent coupling reaction under milder reaction condition.

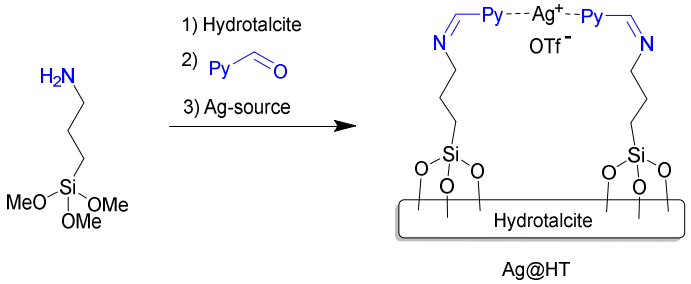
２．研究の目的

This proposed plan constitutes the design and synthesis of highly active and stable bifunctional catalysts for the multicomponent coupling reactions using CO_2 as C1 source and its utilization in the production of useful chemicals and materials through multiple site activation of substrate molecule to form carbonates and lactones by CO_2 insertion reaction. It is expected that only heterogenous bifunctional catalyst possesses such a capacity of multiple site activation of substrate and CO_2 through its high surface area and reaction on the surface without additional strong oxidant or reductant to carry out one pot multicomponent reaction with CO_2.

３．研究の方法

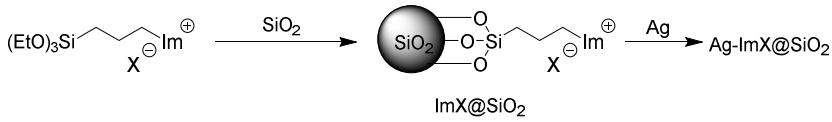
(1) Preparation of bifunctional catalyst

Our proposed plan involves both the effect of solid support and ligand to prepare highly active and stable bifunctional catalyst with high surface area, Lewis acid and basic sites, and an affinity for carbon dioxide to carry out multicomponent coupling reaction. For such purpose, metal oxides (MgO, Al_2O_3 and SiO_2) and electron donating ligands are applied as stabilizer.
①Here, based on our previous result (Tetrahedron 2018, 74, 948), highly active and stable Mg/Al-hydrotalcite (HT) supported pyridine-Ag catalyst was prepared (scheme 1) to use carbon dioxide in multicomponent coupling reaction.



Scheme 1. Synthesis of HT-supported pyridine-Ag catalyst

②We prepared bifunctional SiO_2 based Ag-catalyst through functionalization of cheap silica (aerosil-300) having high surface area with imidazole-based ligand (scheme 2) which acted as very effective capping agent for metal and activator for activation of substrate and CO_2. Simple nucleophilic substitution reaction was applied for functionalization.



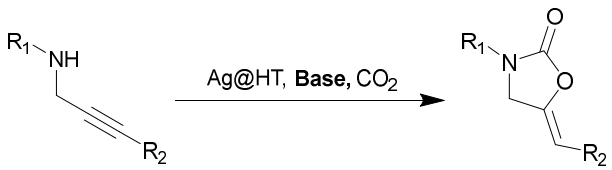
Scheme 2. Synthesis of SiO_2-supported Imidazole-based Ag catalyst

(2) Catalytic reactions through multiple site activation of substrate using bifunctional catalyst

The activity of bifunctional-catalyst for multicomponent one pot reactions were tested by reacting with different substrates such as propargyl alcohols and amines with CO_2. With these bifunctional catalysts, cyclic carbonates and carbamates were prepared using propargylic alcohols under mild reaction condition.

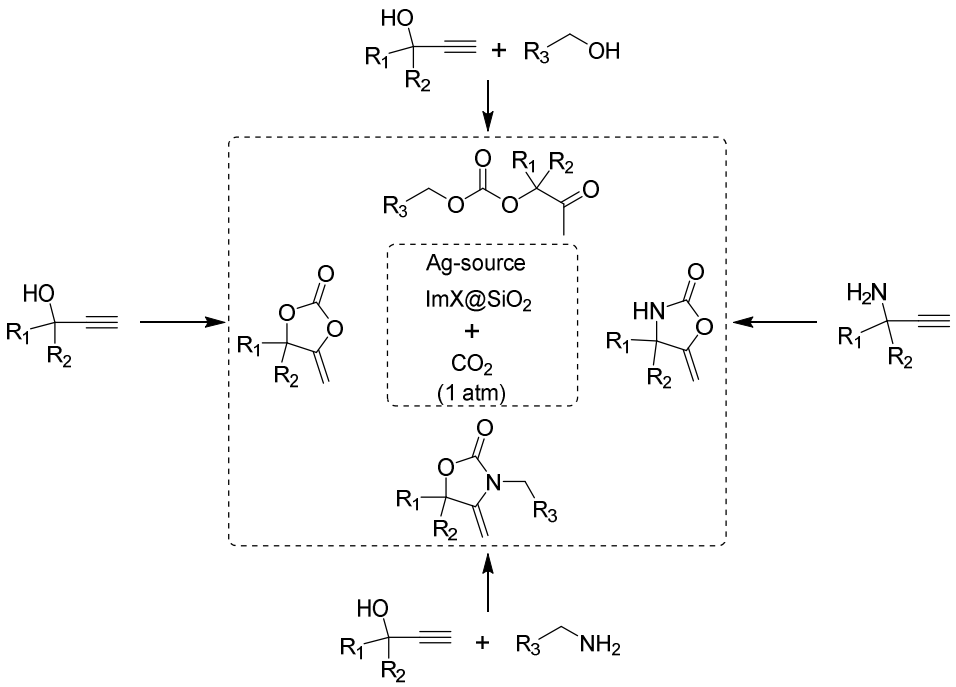
4．研究成果

(1) After successful synthesis of pyridine-Silver catalyst on functionalized hydrotalcite, the catalytic system containing ionic silver stabilized on functionalized hydrotalcite was applied in the cyclization of propargyl amines with CO_2 forming a wide variety of Oxazolidinone derivatives in atmospheric CO_2 and room temperature (Scheme 3). The catalyst prepared was quite stable, versatile and could be stored without the need of protective atmosphere.



Scheme 3. Ag@HT catalyzed cyclization of propargyl amines

(2) The silica-supported bifunctional heterogenous catalytic system based on imidazolinium salt ($Im^+X^-@SiO_2$) as an activator was found to activate both Ag-catalyst and substrate for carboxylative cyclization reaction of alcohols by efficient utilization of CO_2. Our catalytic system not only performed very well for the two-component reaction of propargyl alcohols/amines with CO_2, but also three-component reaction of propargyl alcohols, CO_2 and other alcohols/amines with excellent yields of the corresponding carbonates and carbamates under mild reaction condition (scheme 4). This system secures the advantages of both homogeneous and heterogeneous catalysis of ammonium salts with good activity, easy isolation of the product and recovery of the catalyst.



Scheme 4. Catalytic application of Ag-ImX@HT for synthesis of carbonates and carbamates

５．主な発表論文等

〔雑誌論文〕　計7件（うち査読付論文　7件／うち国際共著　0件／うちオープンアクセス　2件）

１．著者名 Tomohiro Tsutsumi, Sangita Karanjit, Atsushi Nakayama, Kosuke Namba	４．巻 21
２．論文標題 A Concise Asymmetric Total Synthesis of (+)-Epilupinine	５．発行年 2019年
３．雑誌名 Organic Letters	６．最初と最後の頁 2620～2624
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.orglett.9b00607	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Atsushi Nakayama,Hideo Sato, Shuji Nagano, Sangita Karanjit, Hiroshi Imagawa, Kosuke Namba	４．巻 67
２．論文標題 Asymmetric Total Syntheses and Structure Elucidations of (+)-Eurotiumide F and (+)-Eurotiumide G	５．発行年 2019年
３．雑誌名 Chemical and Pharmaceutical Bulletin	６．最初と最後の頁 953～958
掲載論文のDOI（デジタルオブジェクト識別子） 10.1248/cpb.c18-00948	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

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２．論文標題 Synthesis and Antimicrobial Evaluation of Side-Chain Derivatives based on Eurotiumide A	５．発行年 2020年
３．雑誌名 Marine Drugs	６．最初と最後の頁 92～92
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/md18020092	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Tomohiro Tsutsumi, Arisa Saitoh, Tomoyo Kasai, MengYue Chu, Sangita Karanjit, Atsushi Nakayama, Kosuke Namba	４．巻 61
２．論文標題 Synthesis and evaluation of 1,1,7,7-tetramethyl-9-azajulolidine (TMAJ) as a highly active derivative of N, N-dimethylaminopyridine	５．発行年 2020年
３．雑誌名 Tetrahedron Lett.	６．最初と最後の頁 152047～152047
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.tetlet.2020.152047	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Sangita Karanjit, Ayumu Tamura, Masaya Kashihara, Kazuki Ushiyama, Lok Kumar Shrestha, Katsuhiko Ariga, Atsushi Nakayama, Kosuke Namba	４．巻 10
２．論文標題 Hydrotalcite-Supported Ag/Pd Bimetallic Nanoclusters Catalyzed Oxidation and One-Pot Aldol Reaction in Water	５．発行年 2020年
３．雑誌名 Catalysts	６．最初と最後の頁 1120～1120
掲載論文のDOI（デジタルオブジェクト識別子） 10.3390/catal10101120	査読の有無 有
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１．著者名 Atsushi Nakayama, Tenta Nakamura, Toshihiro Zaima, Saho Fujimoto, Sangita Karanjit, Kosuke Namba	４．巻 60
２．論文標題 Concise Total Synthesis of Tronocarpine	５．発行年 2021年
３．雑誌名 Angew. Chem. Int. Ed.	６．最初と最後の頁 635～639
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/anie.202009966	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

１．著者名 Atsushi Nakayama, Tenta Nakamura, Tabassum Ara, Tatsuya Fukuta, Sangita Karanjit, Takeshi Harada, Asuka Oda, Hideo Sato, Masahiro Abe, Kentaro Kogure, Kosuke Namba	４．巻 74
２．論文標題 Development of a novel antioxidant based on a dimeric dihydroisocoumarin derivative	５．発行年 2021年
３．雑誌名 Tetrahedron Letters 2021, 74, 1531762	６．最初と最後の頁 1531762～1531762
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.tetlet.2021.153176	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計2件（うち招待講演　2件／うち国際学会　0件）

１．発表者名 Sangita Karanjit
２．発表標題 Stabilization and Immobilization of Colloidal Metal Nanoparticles: Organic Bond Transformations under Mild Condition
３．学会等名 CSJ Asian International Symposium（招待講演）
４．発表年 2020年

１．発表者名 Sangita Karanjit
２．発表標題 World Chemistry Forum 2021 (WCF-2021)
３．学会等名 Hydrotalcite supported Heterogeneous Catalysts for Reactions under Mild Conditions（招待講演）
４．発表年 2021年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関