

Synthesis of metal free mesoporous CN_x materials and their applications as functional materials

(金属元素を含まない CN_x の合成とその機能性材料としての応用)

学位論文内容の要旨

Conventional organic syntheses are generally based on homogeneous catalysts. In homogeneous catalytic reactions, hydroxides, metal halides, alkoxides etc., are widely used. However, these homogeneous reactions suffer disadvantages in separation, regeneration, etc., and also produce large amount of metal salts as byproducts. From the viewpoint of green and sustainable chemistry, the use of heterogeneous catalysts is highly desirable to afford high yields and perfect selectivity towards the end products and avoiding the use of noxious substances, along with little or no undesired byproducts. As a consequence of this, synthesis of high quality solid acid-base catalysts is one of the important challenges in the sustainable catalysis field. However, the practical use of aforementioned catalysts restricts in the limited field. That restriction arises from the drawbacks such as their instability and partial dissolution into the reaction media. To overcome this problem, the development of new and stable metal free solid materials is required. On the other hand, this challenge has not been examined sufficiently, whereas several metal free nitride materials such as BN, BCN and CN materials have been reported in the literature.

Among the metal free nitride materials, the carbon nitride (CN) is a well-known and fascinating material that has attracted worldwide attention because the incorporation of nitrogen atoms in the carbon matrix can enhance the mechanical, conducting, and energy-storage properties. Since N-doping causes a Brønsted-basicity on the surface of CN including amine groups and structural nitrogen which consists of nitrogen doped carbon materials provides a Lewis-basicity on its surface, it is expected that porosity in the carbon nitride matrix will be able to extend the application possibilities in the enhancement of the development of base catalysts. In **chapter 1**, the research history and present status of N poor CN, C₃N₄ materials and their mesoporous materials science were introduced and above mentioned key points were summarized.

After the fabrication techniques and characterization methods were shown in **chapters 2**, synthesis and characterization of mesoporous SiO₂ templates which were used for the fabrication of mesoporous carbon nitride materials (MCNs) were also presented in **chapter 2**. In **chapter 3**, 3D body centered cubic N-poor bi modal mesoporous CN_x (Bi-MCN) having the C/N atomic ratio of 4.3 was successfully fabricated for the first time by using the 3D body centered cubic mesoporous silica KIT-6 as sacrificial hard template through a simple nanocasting technique. The obtained materials are structurally well ordered with a bimodal 3D porous structure, a high surface area and a large pore volume. It is also important to tune the pore diameter and the textural parameters such as specific surface area and specific pore volume, as these properties dictate the efficiency of these materials in large spectrum of practical applications. The pore diameter and the textural parameters tuning of 3D N poor mesoporous carbon nitride (MCN-6) materials was also shown by simply changing the pore diameter of the parent KIT-6 silica template. The pore diameter, specific surface area and the specific pore volume of the 3D-MCN-6 materials increases with increasing pore diameter of the hard template. FT-IR and XPS results reveal that samples contain CN network with a lot of free NH₂ groups which are originated from ethylenediamine and can offer the basic sites. The temperature programmed desorption of CO₂ suggests that the surface of samples are basic in nature and the basicity of the sample is 0.195mmol of CO₂ g⁻¹. The performance of 3D-MCN-6 materials were tested in the base-catalyzed Knoevenagel condensation of benzaldehyde and malononitrile. The 3D-MCN-6 catalysts exhibit excellent activity and afford a high yield of the corresponding α,β-unsaturated nitrile in a short reaction time even at a room temperature. In addition, these catalysts are highly stable

and can be recyclable several times without affecting their activity.

The performance of the MCN materials crucially depends on the amount of nitrogen incorporated in the carbon matrix and its mode of integration. Several researchers have devoted their energies to the work which functional properties of these materials are improved by increasing nitrogen content in the MCN materials. However, nobody has reported the N-rich mesoporous carbon nitride materials which C/N atomic ratio is lower than that of the theoretically predicted C_3N_4 nanostructure with ordered porous structure. It is because the nitrogen in the carbon matrix has poor thermodynamic stability at high temperatures. Here, in **chapter 4**, diaminotetrazine based N rich 2D hexagonal and 3D body centered cubic mesoporous carbon nitride (MCN) materials having the C/N atomic ratio ca. 0.5 and tunable textural parameters were firstly fabricated by using the 2D hexagonal mesoporous silica SBA-15 and 3D body centered cubic mesoporous silica KIT-6 which have various pore diameters as sacrificial hard templates through the self condensation followed by polymerization of novel nitrogen rich aminoguanidine precursor at elevated temperature. This unique N-rich CN_x structure was assigned based on the data of FT-IR, XPS and chemical analysis of the components of N-rich mesoporous CN_x materials. The prepared N-rich mesoporous carbon nitride samples are structurally well ordered with 2D and 3D porous structure, a high surface area and a large pore volume with yellow in color and exhibits very good visible absorption properties with a band gap of 2.25eV. Further, the novel N rich mesoporous carbon nitrides are active catalysts in the Friedel-Crafts acylation of benzene using hexanoyl chloride as the acylating agent. Those activities were higher than that of the N poor MCN and N rich carbon nitride particles (i.e. Non-porous material). That catalyst affords a high yield to synthesis of hexanophenone which is one of important substituent for the fragrance aromatic compounds.

In **chapter 5**, the ability of the N rich MCN was described to act as the “reactive hard template” to make nanoporous GaN. The obtained GaN possesses nanoporous structure with high specific surface area and well crystallinity, this can be due to the N-rich mesoporous CN_x material with small amount of the interconnected micropores which provides the better confinement for the nanoporous GaN formation. Further, the nanoporous GaN is very high active catalyst in the Friedel-Crafts acylation of benzene using hexanoyl chloride as the acylating agent and the results are compared with the commercially available GaN and mesoporous carbon nitrides having different nitrogen contents. Among the materials examined, nano porous GaN showed better activity. To conclude why the activity of nanoporous GaN was higher than other samples, the surface basicity of the samples was examined. The CO_2 TPD experiment indicates that the nanoporous GaN showed the highest CO_2 adsorption capacity, although the N content in the N rich mesoporous CN_x is higher than that of the GaN. The most of N in the N rich mesoporous CN_x material exists in the aromatic ring, such N is bonded to the sp^2 hybridized carbon. Since aforementioned N is not highly basic in nature, the surface basicity of CN_x was not so high level. On the other hand, the N in GaN is bonded with sp^3 hybridized Ga, it provides the strong basic sites on the surface of the sample. The amount of basic temperature point on the surface of GaN was conspicuously increased on nano-porous GaN which was synthesized using reactive hard template approach.

As mentioned above, the textural parameters of the mesoporous CN_x materials were controlled by the control of porous structure of SiO_2 templates. Also, N-rich diaminotetrazine based mesoporous CN_x materials were synthesized for the first time in the present study. Since the N rich CN_x consists of unique bulk and surface structures, the nanostructured N rich CN_x matrix showed high catalytic activity for the activation of benzene in Friedel-Crafts type reaction. And, it is also clarified that the unique N-rich mesoporous CN_x templates with small amount of micropores makes the interconnection and participates in the reaction for fabrication of new nanoporous GaN. Also it is expected that the N-rich mesoporous CN_x reactive template approach will pave the way for the fabrication of new nanoporous nitride materials having high textural parameters, well crystallinity and enough amount of basicity for a design of new catalysts.

学位論文審査の要旨

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学 位 論 文 題 名

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近年、触媒担体や環境浄化用吸着剤などへの応用の観点から、新規メソポア材料に関する研究開発が盛んに行われている。従来のメソポア材料に関する研究は、主として、金属元素をカチオンとして用いる酸化物を中心にしたものであったが、金属カチオンを含まない炭窒化物のメソポア化合物に関する研究、特に、化学量論組成 (C₃N₄組成) に比して、窒素量が過少か、または過剰に含まれたメソポア炭窒化物に関する研究は、未開拓分野であり、今後の発展が大いに期待される分野である。

本学位論文では、こうした学術的背景をもとに、まず、3次元または2次元に細孔構造 (細孔径、細孔体積) が制御された、メソポアシリカをテンプレート (鋳型) として用いて、この細孔内に、有機物を挿入したのち、炭化させ、さらに、不要となった鋳型を取り除くハードテンプレート法により、従来、報告されたメソポア炭素のもつ、細孔構造 (細孔径、細孔体積) 特性を大きく上回るメソポア炭素材料を合成し、その合成条件の最適化に関する知見を整理した。

このように、これまでにない大きな細孔径と細孔体積を、2次元及び3次元的に、整然と配置したメソポア炭素材料の合成をおこなうことに成功したことで、これらを、さらに窒化することで、化学量論組成 (C₃N₄組成) に比して、窒素が過少または過剰な構造を有する新規メソポア炭窒化物の合成に、初めて成功し、その合成手法に関し得られた知見を系統的に整理して、学位論文としてまとめた。

さらに、得られた新規メソポア化合物の構造は、電子エネルギー損失分光 (Electron Energy Loss Spectroscopy: EELS) 法を用いて、バルク内における分子構造特有の炭素周囲の窒素の配位状態の解析を、赤外吸収分光 (Infrared absorption spectrometry: IR) 法と、光電子分光 (photoemission spectroscopy: XPS) 法を用いて、表面・界面の材料の特徴を精査し、合成した材料特有の構造の解析を行い、窒素過少及び窒素過剰な組成を有するメソポア炭窒化物の構造についての詳細な解析を行い、その結果についての整理を行った。

こうして得られた窒素過少ならびに、窒素過剰な組成を有する新規メソポア炭窒化物に関しては、その触媒活性を評価するとともに、その活性を、既存の触媒材料と比較することで、得られた新規メソポア炭窒化物の触媒材料としての機能の高さを示し、さらに、触媒反応活性発現機構に関する考察を、表面における固体塩基特性との関係により考察を行い、さらなる活性向上の方向性を示した。

加えて、得られた新規メソポア炭窒化物の大きく、連続した細孔構造を利用し、この細孔内に、ガリウム前駆体を挿入し、窒化処理を行うことで、新規メソポア炭窒化物から、メソポア窒化ガリウム多孔体が合成できることを、初めて見出し、その合成経路や最適合成条件に関するデータを系統的な実験を行うことで整理した。

従来、窒化ガリウムは、電子材料への応用が盛んに検討されていることから、高比表面積を有する窒化ガリウムの合成に関する研究は報告例がなく、触媒担体をはじめとした触媒材料への応用に関する分野は、未開拓状態であった。

そこで、窒化ガリウム表面に現れることが期待される、固体酸・塩基点と、これらを活性点として、期待される機能に関する考察をもとに、結晶性が良く、優れた3次元細孔構造をもつ、メソポア窒化ガリウム多孔体の合成に成功し、その合成経路や最適合成条件に関するデータも、他の新規メソポア炭窒化物同様に、系統的な実験を行うことで整理した。

こうして得られたメソポア窒化ガリウム多孔体の触媒活性は、既存の触媒や、多孔性に乏しい既存の窒化ガリウムと比較することで、その活性が優れたものであることを示した。

以上のように、新規なメソポーラス窒化炭素化合物の合成と、この材料をテンプレートとしたポーラス窒化ガリウムの合成に初めて成功し、その新規化合物の構造の決定を行い、あわせて、その表面を活用した触媒反応活性の向上を達成し、その活性発現機構を、窒化物表面が有する固体塩基性との関係で考察し、新たな窒化物触媒作成の指針を示した点が優れており、よって、本論文は、北海道大学博士(理学)の学位を授与される資格あるものと認める。