論文 / 著書情報
Article / Book Information

題目(和文)	窒化物担持ニッケル触媒のアニオン欠陥によるアンモニア分解
Title(English)	Decomposition of ammonia by anion-vacancy site of nitride-supported Ni-based catalysts
著者(和文)	小笠原気八
Author(English)	Kiya Ogasawara
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料系 材料	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（工学）
学生氏名： Student's Name	小笠原 気八		指導教員（主）： Academic Supervisor(main)	北野 政明 教授	
			指導教員（副）： Academic Supervisor(sub)	原 亨和 教授	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In recent years, hydrogen has attracted much attention as alternative energy carrier to conventional fossil fuels such as natural gas, coal, petroleum to reduce the carbon dioxide emission that contribute to global warming. Ammonia decomposition reaction has been regarded as a promising technique for on-site hydrogen production toward the realization of hydrogen energy society. Transition metal (e.g. Ru, Fe, Co, Ni) supported on oxide is typically used as a catalyst for ammonia decomposition reaction. Among these catalysts, Ru-based catalysts have a much higher catalytic activity due to its optimum nitrogen-binding energy. On the other hand, we have focused on Ni as an alternative catalyst to Ru-based catalysts for practical application because of its high dehydrogenation ability and cost advantage. However, the ammonia decomposition performance of Ni-based catalysts is still not sufficient under relatively low-temperature region (400−500°C). It is well known that the anion vacancy site (e.g. O^{2-}, S^{2-}, H^- vacancy) over various support materials (e.g. oxide, sulfide, hydride) often functions as an adsorption and/or active site for the catalytic reaction. From this point of view, nitrogen-containing materials with chemically active nitrogen species have a significant potential for support of ammonia decomposition catalysts because ammonia molecule is likely adsorbed on their nitrogen vacancy site. We previously demonstrated that nitrogen vacancy sites over lanthanide nitride such as CeN and LaN efficiently enhance the ammonia synthesis activity of Ni-based catalysts. In this thesis, CaNH, h-$BaTiO_{3-x}N_y$, and lanthanide nitrides (LnN: CeN and LaN) were applied as support material of Ni catalyst in ammonia decomposition.

Chapter 1: Hydrogen energy society, the research background of ammonia decomposition catalysts, and the objectives of this thesis were outlined.

Chapter 2: The role of NH^{2-} vacancy over CaNH support for ammonia decomposition reaction was investigated. We found that Ni/CaNH catalyst exhibited much higher ammonia decomposition performance than conventional oxide-supported Ni catalysts (Ni/Al_2O_3, Ni/CaO). The hydrogen production rate of Ni/CaNH with a higher surface area (ca. 39 m^2g^{-1}) reached 267.2 $mmol_{H2}g_{Ni}^{-1}min^{-1}$ at 60,000 $mL_{NH3}g_{cat.}^{-1}$ min^{-1}, which is much higher than those for state-of-the-art Ni-based catalysts. $^{15}NH_3$ decomposition test for Ni/CaNH catalysts demonstrates that the lattice NH^{2-} in the CaNH support participate in ammonia decomposition reaction. Experimental results and DFT calculation reveal that lattice NH^{2-} at Ni-CaNH interface is easily desorbed as N_2 and H_2 to form the NH^{2-} vacancy site with two anionic electrons. The anionic electrons at NH^{2-} vacancy site

can convert NH_3 molecules into NH^{2-} intermediates and H_2 even at 50°C, which indicates the high reactivity of NH^{2-} vacancy site. Therefore, these findings demonstrated that a NH^{2-}-vacancy-mediated Mars−van Krevelen mechanism was a key to developing a highly active Ni-based catalyst for ammonia decomposition.

Chapter 3: The role of lattice N^{3-} in the transition metal nitride (TMN TM: Ce, La, Y, Zr, Hf) for ammonia decomposition reaction was explored. Among the TMN, the lanthanide nitride (LnN Ln=Ce, La) significantly enhances the ammonia decomposition activity of Ni-based catalysts. These LnN compounds exhibited ammonia decomposition activity in the absence of Ni metal. Notably, the ammonia decomposition performance of bare CeN is almost comparable to that of Ni/oxide catalysts (Ni/CeO_2, Ni/La_2O_3), indicating that CeN surface contributes to catalytic reaction. The N_2-TPD measurement and DFT calculation revealed that nitrogen vacancy formation property of TMN is the dominant factor for the catalytic activity of Ni/TMN in ammonia decomposition.

Chapter 4: The water-durable hexagonal-$BaTiO_{3-x}N_y$ was developed as a support material for efficient Ni-based ammonia decomposition reaction. The h-$BaTiO_{3-x}N_y$ was successfully prepared by nitridation of h-$BaTiO_2H_{0.97}$, and the chemical composition of obtained oxynitride sample can be expressed as h-$BaTiO_2N_{0.34}$. Introduction of N^{3-} anion into the h-$BaTiO_{3-x}$ framework drastically increases the ammonia decomposition activity of Ni-based catalysts. The apparent activation energy of Ni/h-$BaTiO_{3-x}N_y$ is 20-30 $kJmol^{-1}$ lower than that of Ni/h-$BaTiO_{3-x}$ and Ni/t-$BaTiO_3$, indicating that lattice N^{3-} efficiently reduces the energy barrier of catalytic reaction. The Ni supported h-$BaTiO_{3-x}N_y$ catalyst can be reused as efficient catalyst without noticeable degradation of activity, even though h-$BaTiO_{3-x}N_y$ has similar promotion ability to CaNH support. Therefore, replacement of O^{2-} site of stable oxide framework by N^{3-} is effective method for developing the water-durable and efficient support material of ammonia decomposition catalysts.