

論文 / 著書情報
Article / Book Information

題目(和文)	調製手法の改良による金属含有ゼオライト触媒の高性能化
Title(English)	Improvement of catalytic performance of metal-containing zeolites by modification of synthesis method
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12878号, 授与年月日:2024年9月20日, 学位の種別:課程博士, 審査員:横井 俊之,山中 一郎,多湖 輝興,松本 秀行,青木 才子
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12878号, Conferred date:2024/9/20, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

論文要旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 応用化学	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（工学）
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要旨（和文 2000 字程度）

Thesis Summary (approx.2000 Japanese Characters)

This dissertation explores the understanding and optimization of metal-containing zeolites, specifically TS-1 and Sn-MWW zeolites, through various modification methods. Key findings include the beneficial impact of oxalic acid as an additive in the hydrothermal synthesis of TS-1 zeolites, which enhances catalytic efficiency by controlling crystallization and preventing unwanted phases. Additionally, post-synthetic defect healing treatments effectively remove silanol defects, improving the hydrophobicity and catalytic performance of TS-1 zeolites. The research also highlights the critical role of solvent environments in catalytic processes, optimizing conditions for high-yield propylene glycol production from propylene using Ti-MWW catalysts. Furthermore, both direct and post-synthesis methods for Sn-MWW catalysts have been developed, particularly for biomass applications.

Chapter 2

This chapter demonstrates that adding oxalic acid as an additive facilitates a more controlled crystallization process of TS-1 zeolites by reducing the pH, resulting in larger crystals with higher catalytic efficiency. The optimal amount of oxalic acid accelerates the crystallization rate, adjusts the coordination states of titanium species, and effectively inhibits the formation of undesirable anatase TiO₂. This method provides a detailed investigation of the impact of alkalinity on the formation mechanism of the zeolite framework structure, titanium species, and the catalytic activity of the synthesized TS-1 catalysts. The optimized TS-1 catalyst showed significantly higher catalytic activity in the epoxidation of 1-hexene using H₂O₂ as an oxidant compared to conventional TS-1 zeolites. The findings suggest that using a green additive like oxalic acid can shorten hydrothermal synthesis times, offering a promising approach for efficiently producing TS-1 catalysts.

Chapter 3

This chapter details the successful preparation of TS-1 zeolites without silanol defects through post-synthetic defect healing treatment. The treatment involved using a pore-filling organic structure-directing agent, where silanol defect healing was induced by fluoride species in TS-1 samples prepared with various TPAOH and water ratios. Post-treatment analyses indicated that samples with TPAOH concentrations higher than 0.5 showed negligible changes in crystallinity, morphology, particle size, and titanium coordination and content. FT-IR spectroscopy confirmed the removal of silanol defects, and static water vapor adsorption isotherms supported the significant improvement in the hydrophobicity of all defect-healing-treated samples. Catalytic tests of alkene epoxidation demonstrated considerable improvements in the performance of defect-healed TS-1

catalysts with TPAOH ≥ 0.5 . These improvements were attributed to the removal of silanol defects and the reduced number of isolated Si–OH groups. This work highlights the importance of defect healing in enhancing the catalytic activity of TS-1 zeolites, providing valuable insights for future catalytic processes.

Chapter 4

This study explores the crucial role of solvent environments in the catalytic conversion of propylene (PE) to propylene glycol (PG) using titanosilicate catalysts. The Ti-MWW catalyst, synthesized via a post-synthesis method, was selected for its high yield of propylene oxide, which can be subsequently converted into propylene glycol. A thorough investigation of various solvents, including polar and non-polar types, was conducted to assess their impact on the efficiency and selectivity of the catalytic process. The findings revealed that the choice of solvent significantly influences the process outcomes. Specifically, a mixture of methanol and water in a 25:75 ratio was identified as the most effective solvent environment for achieving higher yields of propylene glycol in a one-pot process. This solvent mixture provided the highest yield percentage, demonstrating its suitability for industrial applications.

Chapter 5

This chapter discusses the synthesis of stannosilicates with MWW topology using a direct method with various Si/Sn ratios in an alkali medium. The study found that sodium cations play a crucial role in the crystallization process of Sn-MWW. Low alkali gels resulted in amorphous products, even with adjustments or increases in the organic structure-directing agent (OSDA), indicating that this approach was ineffective. In contrast, Sn-MWW synthesized via a post-synthesis method exhibited better catalytic performance in both Baeyer–Villiger oxidations and the conversion of fructose to methyl lactate. These findings emphasize the superiority of the post-synthesis method over the direct method for producing more effective Sn-MWW catalysts.

Summary

Overall, this dissertation underscores the immense potential of zeolite-based catalysts in various chemical reactions. Chapter 2 highlights the use of oxalic acid to synthesize TS-1 zeolites without anatase form and enhance their catalytic performance. Chapter 3 emphasizes the significance of defect healing treatment from various synthesis gel compositions. Chapter 4 elucidates the pivotal role of solvent environments in the catalytic conversion of propylene (PE) to propylene glycol (PG) using titanosilicate catalysts in a one-pot reaction. Finally, Chapter 5 demonstrates that the direct synthesis method for tin-containing MWW zeolites shows potential comparable to Sn-Beta zeolites in biomass applications, with sodium cations playing a crucial role in the crystallization process.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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