

論文の内容の要旨

論文題目 **Studies on Novel Solid Acid Catalysts of Transition Metal Oxides with Mesoporous and Layered Structures**

(メソポーラス及び層状構造を有する新規固体酸触媒に関する研究)

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This thesis describes a development of novel solid acid catalysts. A number of metal oxide solid acids were evaluated in order to study the acid catalytic activity of various mixed metal oxides with different structures and compositions. Layered protonated metal oxides, exfoliated nanosheets and mesoporous structured metal oxides were studied as novel solid catalysts. The metal oxides examined in this study were mainly composed of group 5 (Nb, Ta) and group 6 (Mo, W) elements. The thesis consists of 13 chapters all written in English.

Chapter 1: A general introduction about solid acid catalysts is described.

Chapter 2: Nanosheet aggregates prepared from protonated layered tungstates HMWO_6 ($M = \text{Nb, Ta}$) were examined as potential solid acid catalysts. The nanosheet aggregates were formed by soft chemical processing of the layered compound using tetra(*n*-butylammonium) hydroxide, and the catalytic activity and acid strength of the aggregates were compared with those for HTiNbO_5 , HNb_3O_8 , and a range of conventional solid acids. The catalytic activity for the Friedel-Crafts alkylation of anisole in the presence of benzyl alcohol increased in the order $\text{HTiNbO}_5 < \text{HNb}_3\text{O}_8 < \text{HMWO}_6$ ($M = \text{Nb, Ta}$), consistent with the acid strengths determined by desorption measurements and nuclear magnetic resonance spectroscopy. Nuclear magnetic resonance spectroscopy indicated that the acid catalytic activity of the nanosheet aggregates was attributable to strong Brønsted acid sites, presumably $\text{M}(\text{OH})\text{M}'$ ($M = \text{Ti, Nb, Ta}$; $M' = \text{Nb, W}$).

Chapter 3: Layered HNbMoO_6 was found to function as a strong solid acid catalyst, exceeding the activity of zeolites and ion-exchange resins for Friedel-Crafts alkylation, acetalization and hydrolysis of saccharides. HNbMoO_6 also exhibited high catalytic

activity for esterification of hydrocarboxylic acid and hydration. The catalytic performance of layered HNbMoO_6 is attributed to the intercalation of reactants into the interlayer and the development of strong acidity.

Chapter 4: The acid properties and catalytic activity of layered and nanosheet aggregates of HNbMoO_6 for liquid-phase Friedel-Crafts alkylation were examined. ^{31}P MAS NMR spectroscopy using trimethylphosphine oxide as a probe molecule revealed that HNbMoO_6 possesses strong acid sites in the interlayer region. It was determined that benzyl alcohol was intercalated into the HNbMoO_6 interlayer during alkylation to form a monolayer configuration, allowing the strong interlayer acid sites to participate in the reaction.

Chapter 5: The intercalation and reaction process of layered HNbMoO_6 for liquid-phase Friedel-Crafts alkylation and esterification of lactic acid are examined. Different sized layered HNbMoO_6 with same acid properties, examined by NH_3 -TPD and FT-IR, reveal that not all of the strong acid sites in the interlayer region of layered HNbMoO_6 are efficiently used during reaction. It is determined that the reactions occur at the edge of the layered structures.

Chapter 6: Protonated, layered transition metal oxides $\text{H}_{1-x}\text{Nb}_{1-x}\text{Mo}_{1+x}\text{O}_6$ with various Nb and Mo ratios were examined as solid acid catalysts. Layered Nb-Mo oxides exhibited remarkable catalytic activity in Friedel-Crafts alkylation of toluene with benzyl alcohol and hydrolysis of cellobiose exceeding that of ion-exchange resins, and H-type zeolites, and this was attributed to the intercalation behavior and changes on solid acid properties for different ratios of Nb and Mo.

Chapter 7: Layered and nanosheet aggregates of HTaMoO_6 were examined as solid acid catalysts. The HTaMoO_6 aggregated nanosheets were formed by soft chemical processing of layered HTaMoO_6 using tetra(*n*-butylammonium) hydroxide. The catalytic activity and acid properties of the HTaMoO_6 compounds were compared with those of layered HNbMoO_6 and a range of conventional solid acids. The catalytic activity of HTaMoO_6 for Friedel-Crafts alkylation with benzyl alcohol, hydrolysis of disaccharides, and esterification of acetic acid and lactic acid increased after exfoliation and aggregation, consistent with the acid strengths determined by NH_3 temperature-programmed desorption and ^{31}P magic-angle spinning nuclear magnetic resonance spectroscopy measurements. HTaMoO_6 nanosheets possess additional strong acid sites on the oxide formed by exposure of a single layer, along with strong acid sites within the interlayer of the layered aggregate structure, resulting in higher acid catalytic activity than that of the original layered oxide.

Chapter 8: Mesoporous $\text{Nb}_x\text{W}_{(10-x)}$ mixed oxides with different Nb and W

concentrations prepared from NbCl_5 and WCl_6 in the presence of poly block copolymer surfactant Pluronic P-123 were examined as potential solid acid catalysts. Amorphous wormhole-type mesopores were observed for samples from $x = 3$ to 10 whereas W-rich samples ($x = 0$ to 2) formed a non-mesoporous structure with presence of crystallized tungsten oxide (WO_3). The acid-catalytic activity, acid strength and mesopore structure of mesoporous Nb-W oxides changed in order of W concentrations, exhibiting a very high activity for both Friedel-Crafts alkylation of anisole and hydrolysis of sucrose. The results were compared with those for non-porous $\text{Nb}_2\text{O}_5\text{-WO}_3$ and a range of conventional solid acids. Mesoporous Nb-W oxides obtained higher turnover rate than that of non-porous $\text{Nb}_2\text{O}_5\text{-WO}_3$ led to the strong acid sites and a mesoporous structure with a high surface area and easy reactant accessibility.

Chapter 9: Mesoporous Nb_3W_7 oxides were studied by changing the mesopore structure, using different block copolymers as structural directing agent and changing the alcohol solutions and calcination temperatures. The acid-catalytic activity and mesopore structure of mesoporous Nb_3W_7 oxides changed in order of pore size observed by both X-ray diffractions and N_2 desorption. The mesoporous Nb_3W_7 oxides with bigger pore size exhibited higher activity for Friedel-Crafts alkylation of anisole, hydrolysis of disaccharides and esterification of lactic acid led to the liquid diffusion limit, influencing negatively on acid reaction rates for small sized mesopores. And the mesoporous Nb_3W_7 oxides samples synthesized at different calcination temperatures (673–873 K) exhibited different acid property for NH_3 temperature-programmed desorption, forming stronger acid sites for mesoporous Nb_3W_7 oxides calcinated at higher temperatures obtaining higher reaction rate for both alkylation and hydrolysis reactions.

Chapter 10: Several mesoporous $\text{Ta}_x\text{W}_{10-x}$ mixed oxides prepared from TaCl_5 and WCl_6 in the presence of poly block copolymer surfactant Pluronic P-123 were examined as potential solid acid catalysts. Mesoporous Ta-W oxides (Ta:W = 3:7) with an amorphous wormhole-type mesoporous were found to be a highly active solid acid, exceeding the results obtained from non-porous $\text{Ta}_2\text{O}_5\text{-WO}_3$, HTaWO_6 nanosheets, ion-exchange resins (Nafion NR50 and Amberlyst-15) and zeolites (H-ZSM5 and H-Beta) in Friedel-Crafts alkylation and hydrolysis reactions. Mesoporous Ta-W oxides exhibited a higher turnover rate than non-porous $\text{Ta}_2\text{O}_5\text{-WO}_3$ and HTaWO_6 nanosheets, indicating that the mesoporous structure is an advantageous environment for the strong acid sites, because of the high surface area and easy reactant accessibility.

Chapter 11: Several porous $\text{Nb}_x\text{Mo}_{10-x}$ mixed oxides prepared from NbCl_5 and MoCl_5 in the presence of block copolymer surfactant Pluronic P-123 were examined as

potential solid acid catalysts. Amorphous mesoporous structures were observed in samples with x from 10 to 9, whereas samples with higher Mo concentrations ($x = 3-8$) formed large pores by inter-particle voids and a non-porous structures with crystallized molybdenum oxide (MoO_3) were observed in samples with x from 0 to 2. The acid strength increased with increasing the Mo content in $\text{Nb}_x\text{Mo}_{10-x}$ oxides, which was determined by NH_3 temperature-programmed desorption (NH_3 -TPD) and Fourier transform infrared (FT-IR) spectroscopy using pyridine as a probe molecule. Porous Nb_3Mo_7 oxide exhibited the highest acid-catalytic activity for the Friedel-Crafts alkylation of anisole due not only to mole ratio of Nb/Mo but also to pore structure.

Chapter 12: The results described in the Chapters 2-11 are summarized.

Chapter 13: General Conclusion of thesis is described.

Novel mixed transitional metal oxide solid acids were prepared in layered, aggregated and mesoporous structures. Each solid acid had a unique nature. Aggregated nanosheets make possible the usage of acid sites present in the interlayer. Layered HNbMoO_6 is the first case of a layered metal oxide with excellent solid acid reaction rates due to its intercalation ability. Mesoporous $\text{Nb}_x\text{W}_{(10-x)}$ oxide is the first mixed metal oxide mesoporous solid acid with high catalytic activity due to its high surface area mesoporous reaction field. This investigation is very important as a pioneering study on the development and characterization of different metal oxide based structured solid acids with unique characteristics with potential use in both the fine and commodity chemical sectors.

Therefore, this thesis is recognized as a Doctoral Thesis for Chemical System Engineering Course of The University of Tokyo..