

学 位 論 文 題 名

Catalytic Conversion of Butenes over Acid-Strength- and Amount-Controlled Silica-Supported 12-Tungstosilicic Acid

(酸強度と酸量が制御されたシリカ担持12-タングストケイ酸触媒による
ブデン転化反応に関する研究)

学位論文内容の要旨

In petroleum refinery and chemical industry, a large number of acid-catalyzed reactions are still carried out using conventional liquid acids, which are typically associated with a series of serious problems, such as high toxicity, corrosion, large cost of catalyst disposal, difficulty to separate from products and hardship of recovery, and thus brought out a large impact on environmental burden by producing catalyst waste and waste fluid. In contrast, use of solid acid catalysts has many advantages and can contribute to save energy and environmental protection. Being a different phase to reactants, solid acid catalysts are easily separated from heterogeneous system by filtration and could be reused. In addition, they can avoid corrosion, provide a safe operation and generate less waste. Therefore, replacement of liquid acids with solid acids is strictly necessary for building a sustainable society. In order to achieve the replacement, developing in high efficient solid acid catalysts is indispensable through the precise control of the acid strength and acid amount to meet the target reactions.

Catalysis by heteropolyacids and related compounds is a field of increasing importance worldwide because heteropolyacid including $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ is a molecular metal oxide cluster and its supported forms such as $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ are promising solid acid catalysts. Since acidic properties of the supported heteropolyacids change depending on the loading levels of the heteropolyacids and alkaline metal-modification, the quantitative understanding and consequent control of them must result in the high efficient solid acid catalysts. However, the changes in the acidic properties of the outermost surface have still been unclear. Until now systematic studies on acidic properties are few due to lack of suitable methods for assessing the acidic properties of supported heteropolyacids.

Based on the backgrounds, two objectives were established in the present thesis: (1) assessing the changes in the acidic properties of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ on the loading level and alkaline metal-modification by using mainly temperature-programmed desorption of benzonitrile and (2) elucidating the relationship between acidic properties and catalytic performance of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ in two typical but industrially important reactions: skeletal isomerization of *n*-butene to isobutene and preferential

oligomerization of isobutene in 1-butene and isobutene mixture.

The author found that the acidic properties of outermost surface for supported heteropolyacids greatly changed with the loading level and alkaline metal-modification. Strong Brønsted acid sites were formed on $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ with high loadings, while only medium strong acid sites exist on the low loading catalysts. Acid amount increased to a maximum and then decreased with the increase in loading level of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ on SiO_2 . The acid amount maximum appears at 60 wt% loading for strong acid sites and at 40 wt% loading for medium strong acid sites. The modification of alkaline metals including Na attenuated the acidic properties of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ and selectively poisoned the strong acid sites.

For the skeletal isomerization of *n*-butene to isobutene in the presence of water vapor, 40 wt% $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ showed the highest activity due to the large amount of acid sites located on the outermost surface. Another phenomenon was not observed for the solid acid catalysts other than supported heteropolyacids that the presence of water vapor in the reaction mixture minimizes the decrease in the activity with time on stream while maintaining high selectivity of over 80% toward isobutene. Activity and stability were greatly improved by the addition of water vapor because acid sites were avoided from poisoning by coke. Therefore, the stable conversion in the presence of water vapor was twice higher than that in the absence of water vapor.

Preferential oligomerization of isobutene in 1-butene and isobutene mixture with a molar ratio of 1 to 1 was studied over $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ and alkaline metal-modified $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ to search for an efficient catalyst that can selectively convert isobutene from the mixture. The reason is not only because the separation between isobutene and *n*-butene in industries is still hard and low efficiency, which made an effective catalyst with high selectivity, activity and long lifetime to be searched as soon as possible, but also because the oligomerization products from isobutene are important materials for chemical industry. It was found that selectivity increased with the decrease in loading amount of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ due to the absence of strong acid sites. In addition, the modification of alkaline metal for $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ further improved the selectivity. On the outermost surface, strong acid sites were eliminated while the amount of medium strong acid sites decreased a little. Therefore, the maximum selectivity being 98% was attained over 15 wt% $\text{Na}_3\text{HSiW}_{12}\text{O}_{40}/\text{SiO}_2$.

Based on these findings, the author concluded that precise control of acidic properties of $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$ by loading adjustment and alkaline metal-modification leads to high catalytic performance in butenes conversions. The author believes strongly that this can contribute to the environmental protections.

学位論文審査の要旨

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液酸を用いた化学プロセスが多く稼働しているが、大量の廃酸や酸廃水が発生するため環境負荷が大きい。これらの化学プロセスを固体酸触媒プロセスへと転換できれば、環境負荷を大幅に低減できる。この実現には、高性能な固体酸触媒の開発は不可欠である。酸量と酸強度は固体酸触媒の性能支配因子であり、それらの精密制御は高性能触媒の開発に繋がる。強酸性酸化物クラスターの12-タングストケイ酸をシリカに担持した触媒は種々の酸触媒反応を促進すること、また12-タングストケイ酸の担持量によって触媒性能が大きく変化することが知られている。担持量による触媒性能の変化は酸性質の変化と関連すると考えられているが、それを定量的に調べた研究はない。本学位論文は、担持量変化およびアルカリ金属に修飾によるシリカ担持12-タングストケイ酸触媒の酸性質変化をベンゾニトリル昇温脱離法により定量的に評価することを第一の目的に、また工業的に重要な2つの酸触媒反応 (*n*-ブテン骨格異性化反応、*iso*-ブテン選択的オリゴマー化反応) を例に、シリカ担持12-タングストケイ酸触媒の酸性質と触媒性能との関連性を明らかにすることを第二の目的として行われた。

学位申請者は、シリカ担持12-タングストケイ酸触媒の酸性質を評価できるベンゾニトリル昇温脱離法を確立し、この手法により反応に重要なシリカ担持12-タングストケイ酸触媒の最外表面の酸量と酸強度を定量的に測定した。また、高担持量の12-タングストケイ酸をシリカに担持すると、極めて強い酸点が発現することを見出した。さらに、シリカ担持12-タングストケイ酸触媒をアルカリ金属で修飾することで、この強い酸点が選択的に被毒されることを明らかにした。

40重量%の12-タングストケイ酸を担持したシリカ担持12-タングストケイ酸触媒

が*n*-ブテン骨格異性化反応に高い活性を示し、この性能は最外表面酸量が多いことに起因することを明らかにした。また、水蒸気を共存させて反応を行うと触媒表面へのコークの蓄積が抑制され触媒寿命が延長されることを、触媒の酸性質変化と関連づけて説明した。

iso-ブテン選択的オリゴマー化反応に対しては、低担持量のシリカ担持12-タングストケイ酸触媒が高い選択性を示し、これは触媒上に強酸点が存在しないことによることを明らかにした。さらに、アルカリ金属による触媒の修飾が選択性のさらなる向上に有効なことを示した。

以上、学位申請者はシリカ担持12-タングストケイ酸触媒の酸性質を定量的に評価し、かつ酸性質と触媒性能との関係を明確に与えた。ここで得られた結論は、合理的な固体酸触媒の設計とその開発に繋がることが期待される。審査委員一同は、これらの成果を高く評価し、また研究者として誠実かつ熱心であり、大学院博士課程における研鑽や修得単位などもあわせ、申請者が博士（環境科学）の学位を受けるのに十分な資格を有するものと判定した。なお、審査委員の一人である松橋博美（北海道教育大学）は、書面により本学位論文を審査した。