学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Low Temperature Oxidation of Ethylene by Silica-Supported Platinum Catalysts

(シリカ担持白金触媒によるエチレンの低温酸化)

Ethylene is a plant hormone which plays an important role in ripening of fruits and vegetables. Despite its role as a natural ripening agent, production of ethylene has made it difficult for fruits and vegetables to be stored for a long term storage and transportation leading to decay and food waste – one of the challenges being faced by the society. Heterogeneous catalysts have been recognized to stride their way in the field of ethylene oxidation for its benefit of being able to mitigate food spoilage and are used practically in refrigerators as a model catalyst for decomposition of trace ethylene. Such kind of catalysts have excelled in terms of durability and conversion of ethylene at low temperature. Despite this excellent phenomenon, systematic study of ethylene oxidation at low temperature using Pt/mesoporous silica is yet to be done.

The author has demonstrated a detailed study of ethylene oxidation over Pt supported on mesoporous silica, SBA-15, reporting both the ethylene conversion and CO_2 yield. Such kind of oxidation reactions at low temperatures are prone to deactivation due to formation of water molecules and stabilization of carbon species on catalyst surface. This led the author to study in detail effect of water on the activity of the catalyst and an attempt to increase the activity of the catalyst at such low temperature, 0 °C. An approach was also taken in order to account for the carbon balance of the reaction. Kinetics and FTIR study were done in detail to understand the behavior of this reaction and identify the surface species.

In Chapter 1, the purpose of this dissertation and background of the study have been described in detail.

Chapter 2 shows the synthesis and detailed characterization of mesoporous silica, SBA-15 and metallic Pt incorporated in SBA-15. This Pt/SBA-15 showed complete conversion of ethylene for 90 minutes and gradually decreased to ca. 30 % and the CO_2 yield was around 15%. The difference between the conversion and yield was explained by the formation of carbon species on catalyst surface which were collected in the form of CO_2 on heating under inert condition, thus achieving carbon balance. Flowing water vapor on catalyst surface along with ethylene mixture gas showed deactivation of the catalyst which was again reactivated on stopping the water vapor flow. Besides this, amorphous silicas supporting Pt also proved to be useful as supports for this low temperature reaction.

In Chapter 3, specific control of hydrophobicity of the mesoporous silica was brought about in order to prevent the active Pt sites from water poisoning. Simple calcination treatment was done to SBA-15 and amorphous Aerosil-380 (A380) (for control experiment). Pt nanoparticles were impregnated on the calcined support and characterized in detail using low and wide angle XRD, N_2 adsorption isotherm, CO-pulse measurement and TEM. Study of water adsorption isotherm showed marked increase in hydrophobicity of the

Pt/mesoporous silica calcined at higher temperatures unlike that of A380 which remained identical. Ethylene oxidation at 0 °C showed an increase in ethylene conversion and CO_2 yield at the steady state of the reaction for Pt/SBA-15 calcined till 800 °C. However in the case of the calcined aerosils, the activity remained the same. Addition of water vapor followed by stopping its flow to catalyst surface of Pt/SBA-15 and Pt/SBA-15 calcined at 800 °C revealed faster recovery of the calcined sample due to smooth desorption of water. ^{29}Si NMR spectroscopy revealed presence of decreased amount of SiOH on surface of Pt/SBA-15(800) where the Pt nanoparticles are tightly encapsulated inside the hydrophobic mesopores unlike the Pt dispersed on flat SiO_2 for Pt/A380. Hence water generated are smoothly released from the hydrophobic Pt/SBA-15(800) resulting in increase in ethylene conversion and CO_2 yield.

In Chapter 4, kinetic study of ethylene oxidation at 0 - 40 °C was conducted which revealed the activation energy of the reaction. CO oxidation was carried out over the Pt/SBA-15 which reacted at a faster rate compared to that of ethylene oxidation. Comparison of these studies with literature excluded the chances of CO or epoxide formation to be present in the rate determining step. HPLC and ^{1}H NMR study revealed the presence of acetic acid on catalyst surface. FTIR study of ethylene oxidation at 0 and 30 °C revealed the presence of formate, acetate and acetic acid. FTIR study of adsorption and oxidation of formaldehyde, formic acid and acetic acid and further comparison confirmed CH_3COOH as spectator. Few possible pathways were suggested based on the above data.

Chapter 5 shows the summary of all the important results discussed in the above chapters. Ethylene removal from agricultural products at low temperature is extremely important to decrease food loss. This dissertation introduces the use of Pt/SBA-15 catalyst in the oxidation of ethylene at low temperature which has proved to be durable. The hydrophobicity of mesoporous silica has aided in the increase in catalytic activity at such low temperature 0 °C. Kinetics and in-situ FTIR study have provided an insight to the possible intermediates and spectator species involved during this low temperature oxidation reaction. The results obtained in this study provide a platform for better knowledge about the low temperature oxidation reaction. The author believes, it would offer a wide range of possibilities to be explored in the field of agriculture from the perspective of reducing food loss.