

Calcination temperature effect on silica supported Pt catalyst for low temperature ethylene oxidation

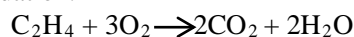
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Introduction

Ethylene is a plant maturation hormone released from fruits and vegetables. Trace amount of ethylene can accelerate their aging even at low temperature. In order to avoid food loss during storage and transport, complete and continuous elimination of ethylene at low temperature is an important issue. Despite several reports of heterogeneous catalysts [1], none of them were applicable for practical use. Our group has successfully reported complete oxidation of trace amount of ethylene at 0°C using a mesoporous silica supported metal catalyst [2]. In this study, we studied the effect of hydrophobicity of mesoporous silica support on the activity of supported Pt catalyst for ethylene oxidation.



Experimental

We used mesoporous silica (SBA-15) [3] and nonporous SiO₂ (AEROSIL-380, Evonik) as silica supports. Calcination of SBA-15 and SiO₂ at different temperatures (700, 800 and 900 °C) for 16 h was conducted to control hydrophobicity of their surfaces. Pt nanoparticle on the supports can be formed by an impregnation of Pt cations (1 wt%) with an aqueous (NO₂)₂(NH₃)₂Pt·HNO₃ solution, followed by thermal reduction of the Pt cation-loaded

Table 1. Structural properties and catalytic activities of supported Pt catalysts.

Catalyst	S _{BET} ^a / m ² g ⁻¹	Volume ^b / mL g ⁻¹	D _{Pt} ^c / nm	Conv. ^d (%)	Yield ^e (%)
Pt/SBA-15	867	1.04	3.9	28	13
Pt/SBA-15(700)	723	0.89	3.3	51	18
Pt/SBA-15(800)	572	0.76	5.0	45	28
Pt/SBA-15(900)	252	0.30	4.1	31	15
Pt/SiO ₂	392	0.39	2.4	30	11
Pt/SiO ₂ (700)	325	0.32	2.7	35	16
Pt/SiO ₂ (800)	313	0.32	2.7	35	17
Pt/SiO ₂ (900)	240	0.26	2.7	37	18

^aBET surface area, ^bMesopore volume estimated by BJH theory,

^cAverage diameter of Pt nanoparticles evaluated by CO-pulse titration,

^dEthylene conversion, ^eCO₂ yield

samples under H₂ flow. The resulting catalysts were denoted Pt/SBA-15(cal. temp.) or Pt/SiO₂ (cal. temp.). Ethylene oxidation at 0 °C was performed in a stainless steel fixed-bed reactor under an atmospheric pressure at a space velocity of 1500 mL h⁻¹ g⁻¹. Ethylene conversion and CO₂ yield were estimated at a steady state (300 min).

Results and Discussion

Table 1 summarizes structural properties and catalytic activities of supported Pt catalysts with different calcination temperatures. In the case of mesoporous silica, calcination treatment gave a positive effect on both the conversion and the yield despite no large difference in average diameter of Pt nanoparticle (3.0-5.0 nm) among these catalysts. Pt/SBA-15(800) showed high ethylene conversion (45%) and CO₂ yield (28%). H₂O adsorption experiment indicated that hydrophobicity of SBA-15 continuously increases with the increase in calcination temperature. Hydrophobic environment is highly beneficial to enhance desorption of evolved water from catalyst surface, leading possibly to high activity in ethylene oxidation. However, calcination at 900 °C accompanied degradation of original mesoporous structure and decreased largely BET surface area and mesopore volume, which suggested that most of Pt particles would be embedded outside of mesopores.

Catalytic activity of Pt/SiO₂ was comparable to that of Pt/SBA-15. While calcination treatment of SiO₂ at high temperature also increased hydrophobicity of its surface, there was no significant change in original catalytic activity of Pt nanoparticle embedded on hydrophobic SiO₂. In these cases, Pt nanoparticles are simply distributed on flat and hydrophobic SiO₂ surface, which results in no positive influence on ethylene oxidation. In conclusion, high catalytic activity of Pt/SBA-15(800) could therefore be explained by the stabilization of Pt nanoparticles within hydrophobic mesopores preventing deactivation with water.

References

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