Aerobic Oxidation of Trace Ethylene at Low Temperature over Platinum Nanoparticle on Hydrophobic Mesoporous Silica Support

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Abstract:

High temperature calcination of mesoporous silica SBA-15 has been found to produce a silica support of Pt nanoparticle for ethylene oxidation at 0 °C. Pt nanoparticle stabilized inside the hydrophobic mesopores of SBA-15 enable smooth desorption of physisorbed water evolved during the course of reaction whereas no significant effect was obtained for nonporous silica Aerosil-380. Hydrophobic silica surface and mesoporous structure are essential for the development of a supported Pt catalyst for this reaction.

Keywords: trace ethylene, mesoporous silica, hydrophobicity

1. Introduction

Ethylene is a natural ripening hormone produced by fruits and vegetables [1] which is physiologically active at extremely low temperature. However, undesirable deterioration of fresh agricultural products is caused with trace ethylene even at low temperatures, which results in food waste. Our group has recently reported aerobic oxidation of trace ethylene at 0 °C using a mesoporous silica-supported Pt catalyst [2]. FTIR studies revealed that Pt catalyst can oxidize ethylene to CO_2 and H_2O via HCHO and CO as possible intermediates. While initial activity of the supported Pt catalyst was decreased during the course of the reaction, original activity was completely recovered by heat treatment under inert conditions. This deactivation is probably derived from H_2O molecules that partially blocks Pt sites active for the reaction. In order to suppress the deactivation, we focused our attention on hydrophobicity of silica support simply controlled by calcination treatment. Mesoporous silica, SBA-15 [3] and non-porous silica, Aerosil-380 (A380) were used as silica supports in this study. Prior to the immobilization of Pt nanoparticle, calcination of SBA-15 and A380 was conducted at different temperatures (700, 800 and 900 ºC) for 16 h to increase in hydrophobicity of their surfaces.

2. Experimental

Impregnation of Pt cations (1.8 wt%) with an aqueous $Pt(NH_3)_2(NO_2)_2$ solution, followed by thermal reduction under H_2 flow formed Pt nanoparticles on SBA-15 and A380 (Evonik industries) supports with various calcination temperatures. The resulting catalysts were denoted Pt/SBA-15(700-900) or Pt/A380 (700-900). Ethylene oxidation at 0 ºC was performed in a stainless steel fixed-bed reactor under an atmospheric pressure at a space velocity of 1500 mL g^{-1} h^{-1}.

3. Results and discussion

All catalysts afforded complete conversion for 90-120 min. However, they decreased their initial activities gradually and reached constant apparently at 30–45% after 240 min. Table 1 summarizes structural parameters and ethylene conversion at 300 min of a series of Pt/SBA-15 and Pt/A380 samples. Pt/SBA-15 and Pt/A380 gave 30% toward ethylene conversion (entries 1 and 5), and their activities were improved after calcination at more than 700 ºC. In the case of SBA-15, ethylene conversion increases up to 45% at 800 ºC (entries 1–3), despite the decrease in surface area from 867 to 572 m^2 g^{-1}. Further increase in calcination temperature at 900 ºC leads to the decrease in the conversion (entry 4). This decrease is due to the loss of original mesoporosity (large surface area and pore volume) by thermal degradation of mesoporous structure. As a result, SBA-15 support calcined at 900 ºC can be regarded as a nonporous silica.

Table 1. Structural parameters and catalytic activities of Pt/SBA-15 and Pt/A380 samples.

Entry	Catalyst	S_{BET}[a] / m^2 g^{-1}	Volume[b] / mL g^{-1}	D_{Pt}[c] / nm	Conversion[d] (%)
1	Pt/SBA-15	867	1.04	6.9	30
2	Pt/SBA-15 (700)	723	0.89	5.9	39
3	Pt/SBA-15 (800)	572	0.76	9.2	45
4	Pt/SBA-15 (900)	252	0.30	7.3	31
5	Pt/Aerosil	392	0.39	4.3	30
6	Pt/A380 (700)	325	0.32	4.8	35
7	Pt/A380 (800)	313	0.32	4.9	35
8	Pt/A380 (900)	240	0.26	4.8	37

[a]BET surface area, [b]Mesopore volume estimated by BJH method, [c]Average diameter of Pt nanoparticles evaluated by CO-pulse titration, [d]Ethylene conversion at 300 min

In contrast, Pt/A380 (entries 6-8) showed no significant changes in ethylene conversion. Similar sizes of Pt nanoparticle for all samples (4.3-9.2 nm) estimated by CO-pulse measurement have no effect on catalytic activity. Focusing on SBA-15 and A380 calcined at 800 ºC, H_2O adsorption measurement and ^{29}Si MAS NMR analysis indicated the increase in hydrophobicity of silica surface in both supports. Ethylene conversion for Pt/SBA-15 (800) at steady state whereas Pt/A380 (calc. temp.) showed almost similar activities. Hence, Pt/SBA-15 and Pt/SBA-15 (800) were chosen to study the ethylene oxidation in the presence of water vapor to clarify the effect of physisorbed water on their catalytic activities (Figure 1). The reaction was performed at 28 ºC with relatively large SV of 9000 mL g^{-1} h^{-1} to prevent liquid water formation in the reactor and keep ethylene conversion at ca. 40-50% steadily. Ethylene conversion decreased gradually with time and reached constant at 15 h in both the catalysts. However, Pt/SBA-15 (800) exhibited higher catalytic activity than Pt/SBA-15 in the absence and presence of water vapor. It should be noted that Pt/SBA-15 (800) is clearly superior to Pt/SBA-15 in the recovery of the conversion more smoothly after stopping the supply of water vapor. In addition, this phenomenon was only observed for mesoporous silica supports. Therefore, hydrophobic silica surface of SBA-15 plays a decisive role for desorption of physisorbed water, which leads to efficient ethylene oxidation.

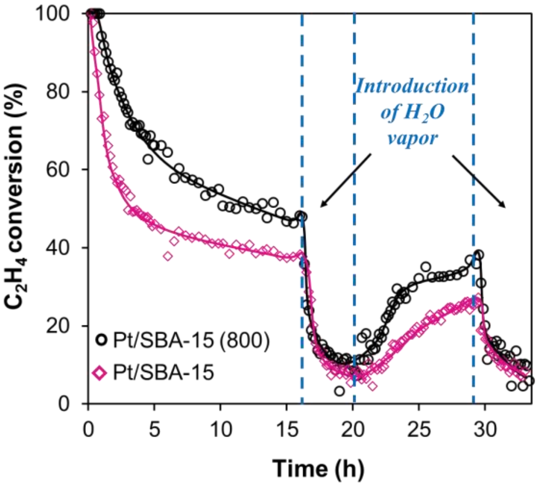

Figure 1. Effect of addition of water vapor on ethylene conversion of Pt/SBA-15 and Pt/SBA-15 (800). Reaction conditions: Pt loading, 1.8 wt%; SV, 9000 mL g^{-1} h^{-1}; reaction temperature, 28 °C; C_2H_4, 50 ppm; O_2, 20%; N_2: 5%; He, 75%; water vapor, 0.86%.

4. Conclusions

Supported Pt catalysts with hydrophobic SBA-15 supports calcined at 800 ºC showed higher ethylene conversion and CO_2 yield than original Pt/SBA-15 catalyst whereas calcination treatment was not effective for nonporous SiO_2 support. This enhancement can be explained by hydrophobic mesopores: water molecules formed on Pt nanoparticles tightly incorporated into hydrophobic mesopores are released outside the mesopores, which prevents Pt sites from deactivation with water.

References

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