Low temperature ethylene oxidation over platinum based bimetallic catalyst supported on mesoporous silica

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Abstract: Aerobic oxidation of trace ethylene (50 ppm) at 0 ºC was studied using Pt-based bimetallic catalysts (Pt-*M*, *M*: Co, Ni, Fe, and Ru) loaded on a mesoporous silica support (SBA-15). Pt-Ru bimetallic catalysts afforded higher activities than Pt/SBA-15 and Ru/SBA-15. Other bimetallic catalysts were inferior to Pt/SBA-15 in terms of the period for initial 100% conversion and the steady state activity. Ru species introduced on pre-formed Pt/SBA-15 catalyst is effective for the reaction.
Keywords: Low temperature oxidation, trace ethylene, Pt-bimetallic catalyst

1. Introduction

Ethylene is a gaseous volatile organic compound that works as a plant hormone to inhibit or promote plant growth. Ethylene released from fruits, vegetable, and flowers can accelerate their aging and spoiling even at low temperature. Consequently, elimination of trace amount of ethylene at low temperature (ca. 0 °C) is imperative. Biotechnological techniques with soil bacteria, dry biobeds, and biofilters have been applied to ethylene removal. However, high cost for these biological compounds and their low efficiencies were serious drawbacks in practical application. We reported aerobic oxidation of trace ethylene (50 ppm) with a mesoporous silica-supported Pt catalyst at 0 °C.[1] In the present study, we studied Pt-based bimetallic catalysts loaded on a mesoporous silica support (SBA-15) for the development of a highly active catalyst for the reaction.

2. Experimental

Mesoporous silica SBA-15 was synthesized with an amphiphilic triblock copolymer P123 as a structure-directing agent.[2] Supported monometallic (Ru and Pt, 0.5 wt%) and bimetallic (Pt-*M*/SBA-15, *M*: Co, Ni, Fe, and Ru, Pt and *M* 0.5 wt% each) catalysts were synthesized by the combination of conventional impregnation using water-soluble metal salts and subsequent reduction with H_2. Here Pt or Ru nanoparticles (0.5 wt%) were introduced on pre-formed Ru/SBA-15 or Pt/SBA-15, respectively, to control the distribution of these secondary metals. The former and latter catalysts synthesized by sequential impregnation were denoted as Pt/Ru/SBA-15 and Ru/Pt/SBA-15, respectively. Catalytic oxidation of ethylene was carried out in a fixed bed flow reactor. Each catalyst in the granular form (355-500 μm, 400 mg) was loaded in a reaction tube and pretreated at 150 °C for 2 h under He flow (40 mL min^{-1}). A gas mixture of C_2H_4 (50 ppm), O_2 (20%), N_2 (5%) and He (75%) was fed to a catalyst bed at 0 °C under atmospheric pressure with space velocity of 1500 mL g^{-1} h^{-1}. The outlet gases were analyzed by an online gas-chromatograph.

3. Results and discussion

Figure 1 shows time on stream curves of ethylene oxidation over the supported metal catalysts at 0 ºC. They showed complete ethylene conversion at the initial stage, but the activities decreased during the course of the reactions. The conversion of monometallic Pt catalyst (Pt/SBA-15) decreased from 60 min and reached constant at 30% in 150 min. Most of bimetallic catalysts were inferior to Pt/SBA-15 in terms of the period for initial 100% conversion and the steady state activity at 150 min. Despite initial activity of monomeric Ru/SBA-15 comparable to that of Pt/SBA-15, steady-state activity at 150 min was quite low (7%). In contrast,

three Pt-Ru bimetallic catalysts afforded higher activities than Pt/SBA-15. Ru/Pt/SBA-15 had the period for 100% conversion for 110 min and steady state activity at 150 min of 25%, which indicated that the strategy for the introduction of Ru as a secondary component on Pt/SBA-15 is effective for the development of a highly active catalyst for this reaction. It was easily expected that the structural distribution of Ru and Pt species on SBA-15 support determines the catalytic activity.

Figure 2 shows the XRD patterns of SBA-15, Pt/SBA-15, Ru/SBA-15, and bimetallic Pt-Ru catalysts. Two diffraction peaks at 2θ = 40° and 46° clearly appeared in Pt/SBA-15, Pt-Ru/SBA-15, and Ru/Pt/SBA-15. They are assignable to (111) and (200) of crystalline Pt with face-centered cubic structure, respectively. No significant difference in the crystallite size of Pt for Pt/SBA-15, Pt-Ru/SBA-15, and Ru/Pt/SBA-15 estimated from Scherrer's equation to be 7.2, 7.2, and 6.3 nm, respectively. Contrary to Pt, no diffraction peak due to crystalline Ru was observed for any catalyst. This suggests the formation of fine particles of metallic Ru or amorphous RuO_x. No shift of the diffraction peaks due to the crystalline Pt for all bimetallic catalysts indicates that Pt and Ru separately existed without the formation of Ru-Pt alloy and Ru was highly dispersed on all the samples. High activity of Ru/Pt/SBA-15 is probably due to local structure of Pt nanoparticle. Ru species was distributed on both SBA-15 support and Pt nanoparticle, and the latter formed a core-shell structure (Pt core and Ru shell). Because such Ru species is more active than that formed on SBA-15, the resulting Ru/Pt/SBA-15 is effective for ethylene oxidation

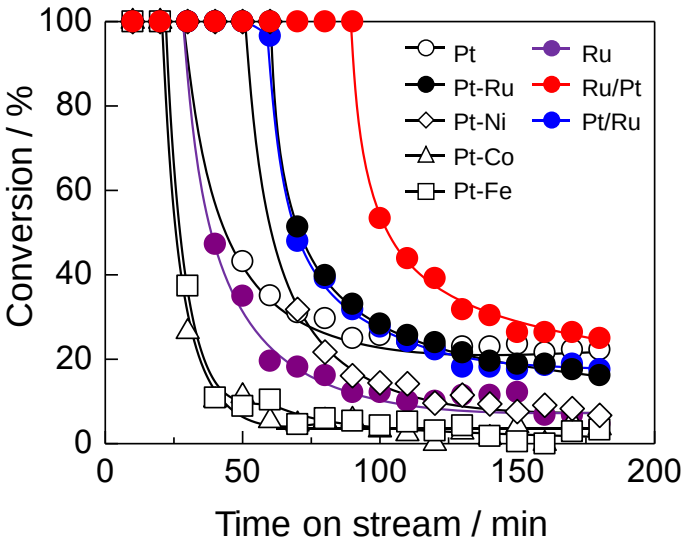

Figure 1. Time on stream curves of ethylene oxidation over various supported metal catalysts on SBA-15 at 0 ºC. Space velocity (SV); 1500 $mLh^{-1}g^{-1}$; catalyst: 400 mg; C_2H_4: 50 ppm; O_2: 20%; N_2: 5%; He: 75%.

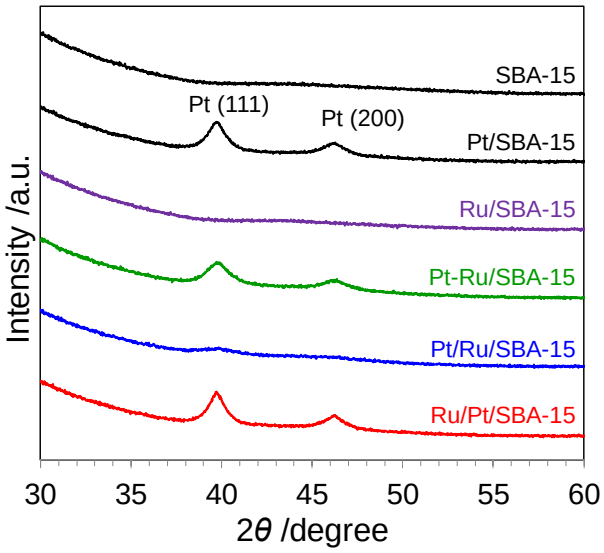

Figure 2. XRD patterns of Pt-Ru bimetallic catalysts.

4. Conclusions

We found that a supported Ru catalyst on pre-formed Pt/SBA-15 catalyzes aerobic oxidation of trace ethylene at 0 ºC more effectively than Pt/SBA-15, Ru/SBA-15, and other Pt-based bimetallic catalysts. Impregnation of Ru species on Pt/SBA-15 and subsequent reduction with H_2 forms an Ru-Pt bimetallic system possibly based on a core-shell-type structure.

References

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