Chemistry Letters Vol.37, No.1 (2008)

Complete Oxidation of Ethylene at Temperatures below 100 °C over a $Pt/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}/\gamma\text{-}Al_2O_3$ Catalyst

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A $Pt/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}/\gamma\text{-}Al_2O_3$ catalyst was prepared in order to establish complete oxidation of ethylene at temperatures below 100 °C. Ethylene was completely oxidized over the catalyst as low as at 65 °C, while over $Pt/\gamma\text{-}Al_2O_3$, which has been well known as an active oxidation catalyst, complete oxidation was achieved at 145 °C.

Ethylene, which is well known as an extremely important building block in the petrochemical industry, has a role in biology as a plant hormone that enhances ripening. It acts at trace levels throughout the life of the plant by stimulating or regulating the ripening of fruit, the opening of flowers, and the abscission (or shedding) of leaves.[1] Although the production rate is normally low, ethylene is produced from essentially all parts of higher plants. In high concentrations, however, it accelerates the spoilage of fruit and vegetables. The ethylene produced by fruit is especially harmful to vegetables. Thus, in order to keep such agricultural products fresh, it is necessary to remove excess ethylene. Application of adsorption materials is an effective way, but periodic exchange of the adsorption sheets is necessary as saturation occurs. On the contrary, catalytic conversion of ethylene by complete oxidation into carbon dioxide and water is a simple and clean alternative that is a highly selective and maintenance-free process. However, it is significantly difficult to realize complete oxidation of ethylene at low temperatures. For example, ethylene was completely oxidized over a 1 wt % Au/Co_3O_4 catalyst at 190 °C.[2]

In our laboratory, investigations have focused on new materials that can supply reactive oxygen molecules not only from the surface but also from the bulk, in order to develop a new oxide catalyst that can completely oxidize hydrocarbons, including ethylene, at low temperatures. As a result, it was found that a $Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}/\gamma\text{-}Al_2O_3$ (CZB/Al_2O_3) solid has remarkable oxygen storage and release abilities at low temperatures.[3,4] The well-established catalytic and redox properties of $Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}/\gamma\text{-}Al_2O_3$ make it a very promising material for obtaining well-dispersed platinum catalysts that have high activity for the oxidation of hydrocarbons.

In this study, a $Pt/Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}/\gamma\text{-}Al_2O_3$ catalyst was prepared, and complete oxidation of ethylene over the catalyst is discussed. The aim of this work is to establish complete oxidation of ethylene at temperatures below 100 °C.

The $Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}/\gamma\text{-}Al_2O_3$ support was prepared by the conventional wet impregnation method. A mixture of 0.1 mol L^{-1} aqueous solutions of $Ce(NO_3)_3$ (32 mL), $ZrO(NO_3)_2$ (8 mL), and $Bi(NO_3)_3$ (10 mL) was diluted with 20 mL of deionized water, and the solution was then impregnated on 4.41 g of commercially available $\gamma\text{-}Al_2O_3$ (Iwatani Chemical, RK-30), which was calcined in advance at 500 °C for 4 h. The CZB content was 17 wt %. The resulting sample was dried at 80 °C overnight, heated to 500 °C at a rate of 5 °C min^{-1}, and then calcined at this temperature for 1 h under an ambient atmosphere. A supported platinum catalyst ($Pt/CZB/Al_2O_3$) was also prepared by impregnation of platinum colloid stabilized with polyvinylpyrrolidone (Tanaka Precious Metals; Pt: 2 nm) on the CZB/Al_2O_3 support. After impregnation, the catalyst was dried at 80 °C overnight and then calcined at 500 °C for 4 h. The Pt content was 3 wt %. A Pt (3 wt %)/$\gamma\text{-}Al_2O_3$ catalyst (Pt/Al_2O_3) without CZB was also prepared by similar procedures as a reference.

X-ray fluorescence analysis (XRF; Rigaku, ZSX100e) was used to confirm the composition of the catalysts. X-ray powder diffraction (XRD) was measured on a Rigaku MultiFlex with monochromatic Cu Kα radiation (40 kV, 50 mA) in the 2θ range of 10–70°. BET specific surface area was measured using nitrogen adsorption (Micrometrics, FlowSorb II 2300).

The catalysts were pretreated at 200 °C for 2 h in a flow of Ar (20 mL min^{-1}). The ethylene oxidation activity was tested in a conventional fixed-bed flow reactor with a 10-mm diameter quartz glass tube by feeding a gas mixture of C_2H_4 (1 vol %), O_2 (4 vol %), and He (balance) at a rate of 100 mL min^{-1} over 0.5 g of catalyst. The feed rate of the reactant (W/F) was 0.3 g s mL^{-1}, where W and F are the catalyst weight and the gas flow rate, respectively, and the space velocity was 8000 h^{-1}. The catalytic activity of the catalyst was evaluated in terms of C_2H_4 conversion, and the gas composition was analyzed using a gas chromatograph with an activated charcoal column and a thermal conductivity detector (TCD).

Figure 1 shows the XRD patterns for Pt/Al_2O_3, CZB/Al_2O_3, and $Pt/CZB/Al_2O_3$. The XRD results for the CZB/Al_2O_3 support show only peaks corresponding to the fluorite structure phase and $\gamma\text{-}Al_2O_3$; no crystalline impurities were

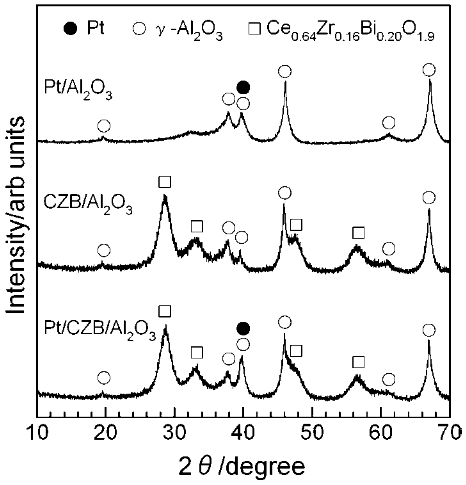

Figure 1. X-ray powder diffraction patterns of Pt/Al_2O_3, CZB/Al_2O_3, and $Pt/CZB/Al_2O_3$ catalysts.

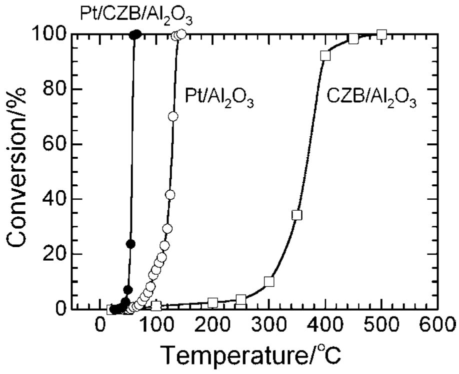

Figure 2. Conversion of ethylene over the Pt/CZB/Al_2O_3 (●), Pt/Al_2O_3 (○), and CZB/Al_2O_3 (□) catalysts.

observed. Introduction of platinum induces the appearance of a small peak of polycrystalline platinum. However, it is only discernible at $2\theta = 39.8°$, because the diffraction peaks of platinum at 39.8° and 67.5° overlap with the diffraction peaks of γ-Al_2O_3 at 39.9° and 67.0°, as identified in the XRD patterns for Pt/Al_2O_3. No changes in the structure of the CZB/Al_2O_3 support due to the introduction of platinum were detected. BET specific surface areas of Pt/Al_2O_3, CZB/Al_2O_3, and Pt/CZB/Al_2O_3 were 143, 130, and 132 $m^2\,g^{-1}$, respectively.

Figure 2 depicts the conversion of ethylene over the CZB/Al_2O_3, Pt/Al_2O_3, and Pt/CZB/Al_2O_3 catalysts as a function of temperature. Ethylene was oxidized into only carbon dioxide and water for all temperature ranges. The activity was increased with increasing reaction temperature. However, the CZB/Al_2O_3 catalyst was not so active, requiring high temperatures above 500 °C for the complete oxidation of ethylene.

In order to enhance the oxidation activity for complete oxidation of ethylene, platinum nanoparticles were dispersed onto the CZB/Al_2O_3 catalyst by the impregnation of colloidal particles. The loading of platinum nanoparticles was considerably effective, and the activity of Pt/CZB/Al_2O_3 was remarkably increased, compared with that of the CZB/Al_2O_3 catalyst. However, the catalytic activity was strongly dependent on the nature of the support. Although Pt/Al_2O_3 has been well known as an active oxidation catalyst, the activity of Pt/CZB/Al_2O_3 was significantly higher than that of the conventional Pt/Al_2O_3 catalyst. Ethylene was completely oxidized over the Pt/CZB/Al_2O_3 catalyst at temperatures as low as at 65 °C, while over the Pt/Al_2O_3 catalyst complete oxidation was achieved at 145 °C.

The clear differences observed between the oxidation activities of CZB-doped and nondoped alumina–platinum catalysts are enough to recognize the positive contribution of CZB. The CZB/Al_2O_3 support and the Pt/Al_2O_3 catalyst did not present remarkable catalytic activities, so that the observed activity must be ascribed to the platinum/CZB interface. It is well known that ceria and its related materials have oxygen release and storage properties, due to its particular ability to undergo deep and rapid reduction/oxidation cycles according to the redox reaction between Ce^{4+} and Ce^{3+}, correlating with the production of a reducing or oxidizing atmosphere around the catalyst.[5] In this way, CZB can control and induce the oxygen pullover from CZB to Pt, in order to enhance the oxygen mobility in the near surface region of the catalyst. Indeed, a remarkable reduction peak was observed at 76 °C in the temperature-programmed reduction profile of Pt/CZB/Al_2O_3 (see Supporting Information). This characteristic property leads to an increase in the catalytic activity, because it has been described that low-temperature catalytic combustion of volatile organic compounds (VOCs) involves lattice oxygen species in the near surface region.[6–9]

The effect of CZB in the Pt/CZB/Al_2O_3 catalyst is the enhancement of the catalytic oxidation activity due to its high lattice oxygen mobility. Therefore, the CZB-doped catalysts favor the deep oxidation of ethylene adsorbed on the support to CO_2 and H_2O. In good agreement with this consideration, Pt/CZB/Al_2O_3 started to produce CO_2 at lower temperatures than Pt/Al_2O_3, and no CO or ethylene oxide production was detected. Furthermore, in support of these effects, a similar strong synergistic effect between silver and CZB on alumina has also recently been evidenced in Ag/CZB/Al_2O_3 catalysts.[4]

In summary, the complete catalytic oxidation of ethylene was investigated on Pt (3 wt %)/$Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ (17 wt %)/γ-Al_2O_3 and Pt (3 wt %)/γ-Al_2O_3 catalysts prepared by the wet impregnation method. The catalytic results for these materials show that the $Ce_{0.64}Zr_{0.16}Bi_{0.20}O_{1.90}$ solid solution significantly promotes the activity of platinum particles in the oxidation of ethylene, probably by increasing the mobility of the lattice oxygen in the near surface region of the catalyst.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 19028041, "Chemistry of Concerto Catalysis") from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1 F. B. Abides, P. W. Morgan, M. E. Salvelt, *Ethylene in Plant Biology*, Academic Press, San Diego, **1992**.
2 H.-G. Ahn, B.-M. Choi, D.-J. Lee, *J. Nanosci. Nanotechnol.* **2006**, *6*, 3599.
3 N. Imanaka, T. Masui, K. Minami, K. Koyabu, T. Egawa, *Adv. Mater.* **2007**, *19*, 1608.
4 T. Masui, K. Koyabu, K. Minami, T. Egawa, N. Imanaka, *J. Phys. Chem. C* **2007**, *111*, 13892.
5 J. Kašpar, P. Fornasiero, M. Graziani, *Catal. Today* **1999**, *50*, 285.
6 M. A. Centeno, M. Paulis, M. Montes, J. A. Odrizola, *Appl. Catal., A* **2002**, *234*, 65.
7 S. Scirè, S. Minicò, C. Crisafulli, C. Satriano, A. Pistone, *Appl. Catal., B* **2003**, *40*, 43.
8 S. Minicò, S. Scirè, C. Crisafulli, R. Maggiore, S. Calvagno, *Appl. Catal., B* **2000**, *28*, 245.
9 M. Baldi, E. Finocchio, F. Milella, G. Busca, *Appl. Catal., B* **1998**, *16*, 43.

Published on the web (Advance View) December 1, 2007; doi:10.1246/cl.2008.42