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Ethane oxidative dehydrogenation over boron oxides supported on yttria stabilized zirconia

Kiyoshi Otsuka, Ten Ando, Setiadi Suprapto, Ye Wang, Kohki Ebitani, Ichiro Yamanaka

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguroku, Tokyo 152, Japan

Abstract

The role of yttria stabilized zirconia (YSZ) as a carrier in the catalytic oxidation of ethane and methane over B_2O_3/YSZ has been investigated. The electrochemical pumping of oxygen through YSZ to the B_2O_3/YSZ catalyst enhanced the conversion of ethane but had no effect on that of methane. The addition of boron oxide to YSZ greater than 10 wt.-% accelerated only the conversion of ethane very specifically. The XPS studies suggested the formation of peroxide ions as a result of the strong interaction between boron oxide and the carrier. Very similar results have been obtained for B_2O_3/Al_2O_3 catalysts. The role of YSZ has been suggested to increase the concentration of the surface peroxide ions that is responsible for the activation of ethane.

1. Introduction

There are many reports and patents [1–8] concerning prospective catalysts for the oxidative dehydrogenation of ethane (ODE reaction). Otsuka et al. have suggested that the compound oxide or mixed oxide of boron is one of the candidate catalysts for partial oxidation of ethane [6,9–11]. Among the boron oxides supported on various carriers tested so far, boron oxides on yttria stabilized zirconia (donated as B_2O_3/YSZ hereafter) was most active and selective for the oxidative dehydrogenation of ethane at 773–873 K [12]. The carrier YSZ was suggested to play an important role for supplying reactive oxygen to the catalytic active sites through oxygen anion conduction in the solid electrolyte. Boron peroxide on the surface has been suggested to be the reactive oxygen for ethane activation [6,12]. However, further studies are needed to verify these speculations.

It is natural to expect that the catalyst effective for the activation of ethane is active as well for the conversion of methane. However, preliminary experiments have indicated that this is not true.

In this report, we study the role of YSZ carrier in the catalysis of B_2O_3/YSZ for oxidative dehydrogenation of ethane using an electrochemical technique. Comparing the conversions of methane and ethane, we discuss the active sites and activation mechanisms for these light alkanes. The catalytic active sites on B_2O_3/YSZ for ethane conversion are investigated using XPS.

2. Experimental

The B_2O_3/YSZ catalysts were prepared by the wet impregnation method using YSZ powder and aqueous solutions of H_3BO_3. The catalysts were calcined in air for 2 h at 573 K and further for 2 h

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at 873 K. The YSZ powder and YSZ plate were supplied from Nippon Shokubai Kagaku Ind. Most of the reagents used in this work were purchased from Wako Chemical Co.

The catalytic tests were performed using a fixed-bed continuous flow reactor (quartz) operated at atmospheric pressure. The standard reaction conditions were as follows; W = 0.50 g, T = 823 K, $P(C_2H_6) = P(CH_4) = P(O_2) = 20$ kPa, F(total) = $50 cm^3 \cdot min^{-1}$ and the balance to atmospheric pressure was provided with He. The reactants and products were analyzed by using a Hitachi 263–30 gas chromatograph.

The electrocatalytic cell used for oxygen pumping experiments was prepared from the YSZ plate (14 × 20 × 0.4 mm) with silver electrodes deposited on both sides of the plate. The B_2O_3(10 wt.-%)/YSZ catalyst was deposited on either of the silver electrodes. The cell thus prepared was calcined in a flow of air at 1073 K for 2 h before the experiments. The electrical connection between both electrodes was performed using a gold wire. The cell was suspended in a flow of the gas mixture of ethane (or methane), oxygen and helium. Oxygen pumping through the solid electrolyte (YSZ plate) from the cathode (Ag) to the anode (B_2O_3/YSZ/Ag) was controlled by changing the applied voltage using a potentiostat.

XPS measurements for the catalysts were conducted by a FISONS Surface Instrument ESCALAB 220-1 with MgKα X-rays (1253.6 eV). The binding energy was calibrated, using a C_{1s} peak (284.6 eV). The background subtraction and peak separation were carried out on an ECLIPSE Data System. Before the XPS measurements, the sample was degassed at 653 K.

3. Results and discussion

We have tested more than 20 metal oxides as carriers for B_2O_3 catalysts [12]. Neither the basic metal oxides, amphoteric nor acidic metal oxides are favorable as the carriers of B_2O_3 for oxidative dehydrogenation of ethane. Yttria stabilized zirconia (YSZ) was most favorable since the YSZ showed a remarkable catalytic activity for this reaction. YSZ is well known as a solid electrolyte in which conduction is due almost entirely to oxygen ion transport in a lattice with anion vacancies. In the presence of reductant such as ethane, a partially reduced surface which is electronically conductive may be formed at the interface of B_2O_3 particle and YSZ. Around these boundaries, we can assume the generation of active oxygen (O^*) on the B_2O_3 surface which is enhanced by oxygen transport through the bulk of YSZ as schematically demonstrated in Fig. 1. We have suggested that the role of YSZ carrier is to increase the number of O^* that is responsible for the activation of ethane over B_2O_3/YSZ [12].

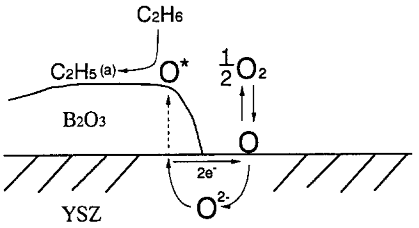

Fig. 1. A model for the formation of active oxygen (O^*) on B_2O_3/YSZ.

3.1. Effect of oxygen pumping through YSZ

In order to ascertain the above hypothesis, we have designed an electrocatalytic cell schematically indicated in Fig. 2. The cell was suspended in a flow of ethane and oxygen at 900–950 K. The oxygen was electrochemically pumped from the

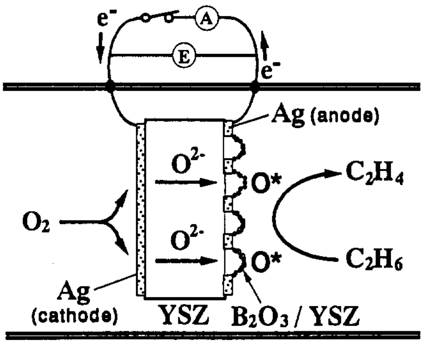

Fig. 2. Effect of oxygen pumping through YSZ. Schematic design of the cell.

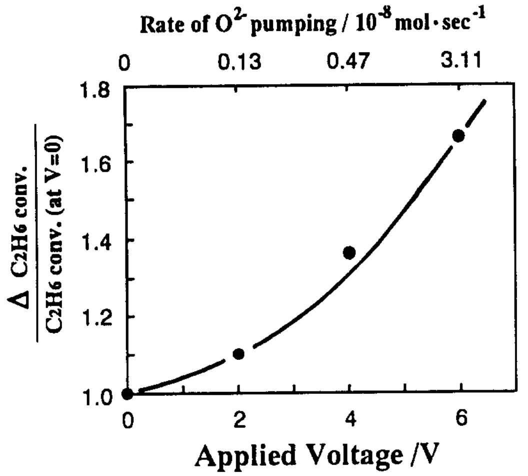

Fig. 3. The increased conversion as functions of applied voltage or O^{2-} pumping rate. Experimental conditions: T = 948 K, $P(C_2H_6)$ = 10 kPa, $P(O_2)$ = 5 kPa, F(total) = 100 cm^3/min, amount of catalyst = 2 mg.

left to the B_2O_3/YSZ catalyst through the YSZ membrane. By this procedure we can expect the enhancement in the formation of active oxygen O* suggested in Fig. 1.

Fig. 3 shows the effect of oxygen pumping on the rate of ethane conversion. The ratio of the increased rate of ethane conversion and that obtained under the open-circuit conditions is plotted as functions of the applied voltage or the pumping rate of O^{2-}. The rate of ethane conversion increased considerably with the pumping of oxygen. If B_2O_3/YSZ catalyst was not present at the anode, the oxygen pumping to the Ag anode did not influence the rate of ethane conversion. These observations support the speculation that the formation of O* is enhanced by the transfer of oxygen from the bulk of YSZ to B_2O_3.

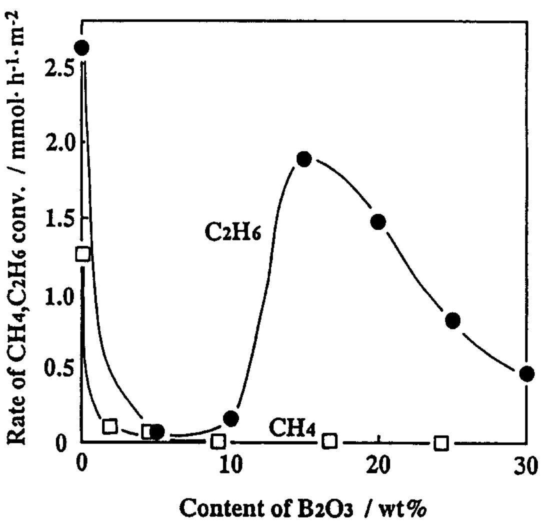

Fig. 4. Conversion rates of CH_4 and C_2H_6 vs. B_2O_3 content on YSZ. Experimental conditions: $P(C_2H_6) = P(CH_4) = P(O_2)$ = 20 kPa, T = 823 K (●), 923 K (□).

It is interesting to examine the effect of the applied voltage on the conversion of methane in comparison with the results for ethane conversion using the same procedure in Fig. 2. The experiments were performed at the temperatures 973–1023 K and under the applied voltage of 0 to 6 V. In conclusion, no enhancing effect on the rate of methane conversion was observed within experimental error.

3.2. Effect of B_2O_3 content on the methane and ethane activations

Fig. 4 shows the specific rates of conversion of methane and ethane as functions of the content of B_2O_3 supported on YSZ. The YSZ without B_2O_3 catalyzed both methane and ethane conversions mainly into CO and CO_2. These deep oxidation reactions were depressed sharply with addition of a small amount of B_2O_3 as can be seen in Fig. 4. However, further addition of B_2O_3 to YSZ increased the conversion of ethane specifically. The selectivity to ethylene was higher than 70% for the catalysts with a B_2O_3 content greater than 10 wt.-%. Surprisingly, activation of methane did not take place for the sample with a B_2O_3 content greater than 10 wt.-%. These results strongly suggest that the active site effective only to the ethane activation is generated for the B_2O_3/YSZ catalyst at a large content of B_2O_3.

3.3. XRD and XPS analyses for B_2O_3/YSZ

X-ray diffraction analysis for the samples of B_2O_3/YSZ indicated that no compound oxide between B_2O_3 and YSZ was formed. Only the diffraction peaks due to YSZ crystals were observed even for the B_2O_3(30 wt.-%)/YSZ sam-

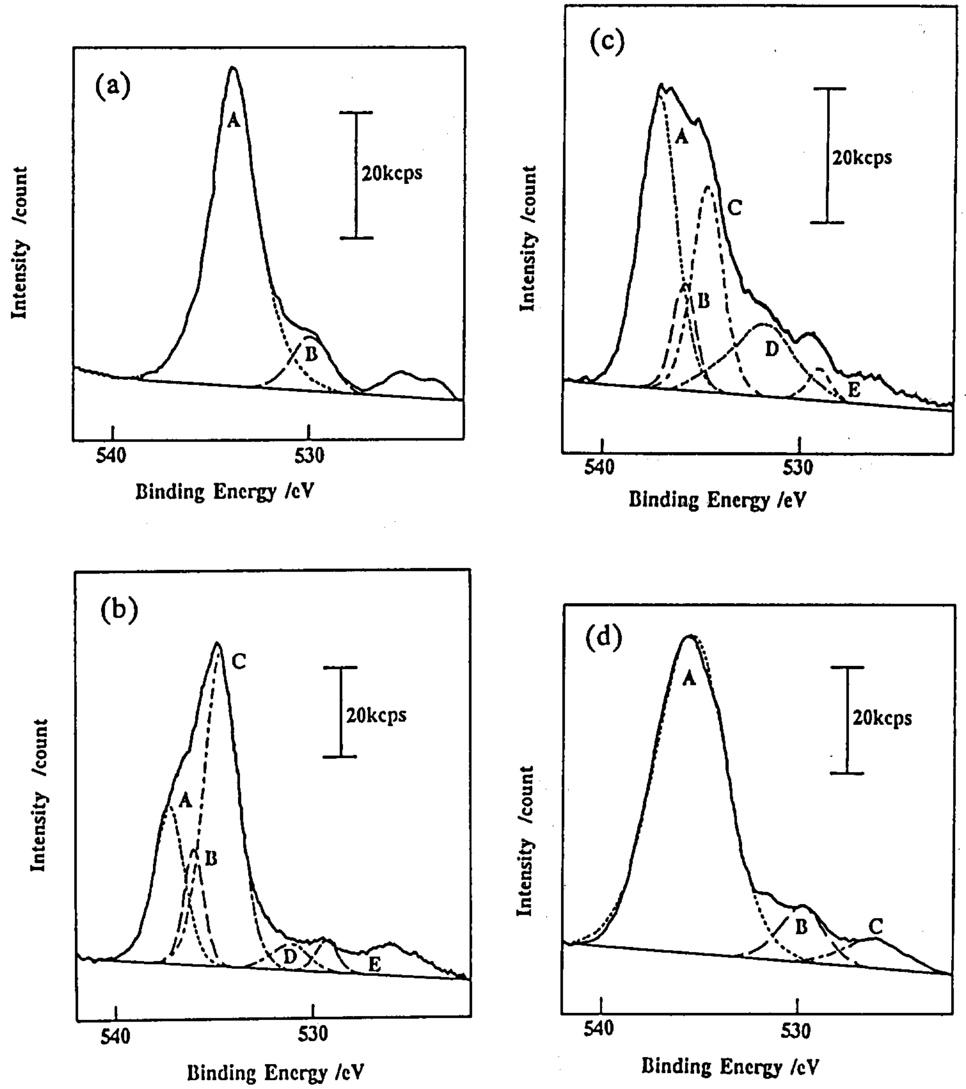

Fig. 5. O_{1s} XPS spectra for (a) YSZ, (b) B_2O_3(5 wt.-%)/YSZ, (c) B_2O_3(15 wt.-%)/YSZ and (d) pure B_2O_3.

ple, suggesting that the boron oxide added may exist in an amorphous state on the YSZ surface.

The O_{1s} XPS spectra obtained for pure YSZ, B_2O_3(5 wt.-%)/YSZ, B_2O_3(15 wt.-%)/YSZ and pure B_2O_3 are shown in Fig. 5a–d. The pure YSZ and B_2O_3 samples showed only one symmetric peak at a binding energy greater than 532 eV. Spectra (b) and (c) indicate that the addition of B_2O_3 to YSZ generates several kinds of oxygen species probably due to the interaction between YSZ and the boron oxide. Although these oxygen species have not been identified at the moment, the O_{1s} peak at the binding energy of 531–532 eV can be ascribed to a surface peroxide species by referring to the literature [13].

The relative intensity of this peak against the peak ascribed to YSZ alone increased sharply with a rise in the amount of B_2O_3, showing a maximum at ca. 15 wt.-% of B_2O_3. It should be noted that pure B_2O_3 does not show the peroxide peak. These observations suggest that a strong interaction between the added boron oxide and the support is essential for the formation of peroxide. This peroxide may be responsible for the activation of

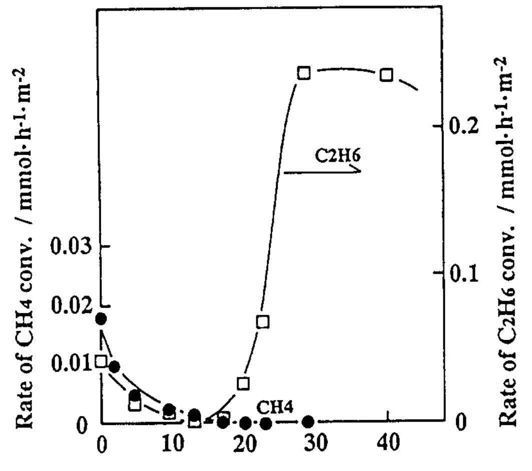

Fig. 6. Conversion rates of CH_4 and C_2H_6 vs. B_2O_3 content on Al_2O_3. Experimental conditions: $P(C_2H_6) = P(CH_4) = P(O_2) = 20$ kPa, T = 823 K (□), 923 K (●).

ethane on the B_2O_3/YSZ catalyst in Fig. 4. The acceleration in the rate of ethane conversion observed under the applied voltage in Fig. 3 may be ascribed to the enhancement in the concentration of this surface peroxide.

3.4. *Oxidation of methane and ethane on B_2O_3/Al_2O_3 and B_2O_3/Sm_2O_3*

One of the authors has studied the partial oxidation of ethane over B_2O_3-added Al_2O_3 [6] and B_2O_3-added Sm_2O_3 [12]. It is interesting to compare the results for these catalysts with those of B_2O_3/YSZ under the same experimental conditions.

Fig. 6 shows the effects of B_2O_3 content on the specific conversion rates of methane and ethane over the B_2O_3/Al_2O_3 catalysts. The specific rate of ethane conversion was one order of magnitude less than that for B_2O_3/YSZ. It should be noted that the results in Fig. 6 indicate that the addition of boron oxide to the Al_2O_3 carrier enhance only the activation of ethane. The XPS studies on the oxygen species for B_2O_3/Al_2O_3 catalyst clearly suggested the formation of peroxide species as can be seen in the XPS spectra (O_{1s}) in Fig. 7.

The rates of conversion of methane (at 973 K) and ethane (at 823 K) over B_2O_3/Sm_2O_3 decreased monotonously with increasing addition of B_2O_3 from 0 to 35 wt.-%. The conversion of ethane was not enhanced at a B_2O_3 content above 20 wt.-%, thus no newly formed active site was suggested. The XRD studies on the B_2O_3/Sm_2O_3 catalysts indicated the formation of compound oxide $SmBO_3$ which did not improve but decreased the activity of the catalyst. The XPS studies for the B_2O_3/Sm_2O_3 catalysts with B_2O_3 content of 15 and 30 wt.-% did not give the oxygen peak at ca. 531 eV, indicating the absence of peroxide species on these catalysts.

The results obtained for the B_2O_3/Al_2O_3 and B_2O_3/Sm_2O_3 support a close correlation between the formation of peroxide species and the specific enhancement in the rate of ethane conversion at a boron content > 20 wt.-%.

3.5. *Role of YSZ and the activation of ethane*

The results obtained for the B_2O_3/Al_2O_3 catalysts suggest that the generation of active sites for the specific activation of ethane is not a unique phenomenon to YSZ. The strong interaction of the catalyst (boron oxide) with the carriers (YSZ, Al_2O_3) may enhance the formation of active oxygen species (peroxide). However, we believe that

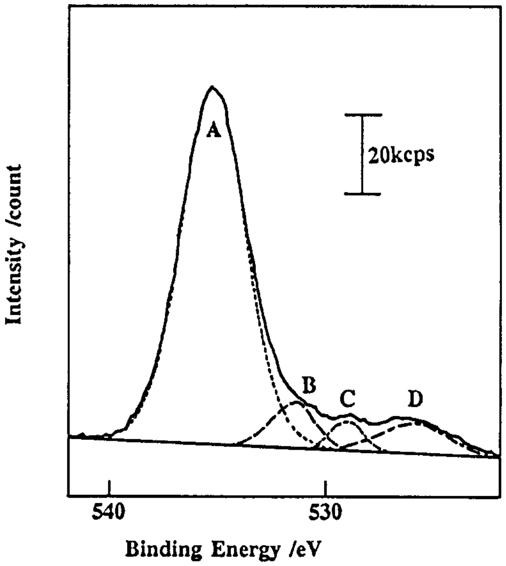

Fig. 7. O_{1s} XPS spectrum for B_2O_3 (30 wt.-%) / Al_2O_3.

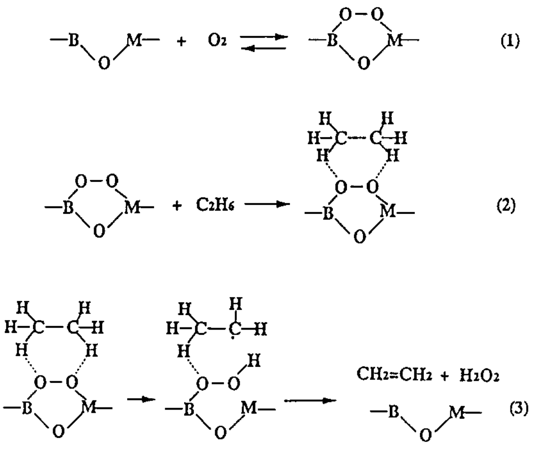

Fig. 8. Reaction mechanism of C_2H_6 oxidation.

the highest catalytic activity observed for the B_2O_3/YSZ must be ascribed to the nature of the solid electrolyte which promotes the generation of the surface peroxide as schematically demonstrated in Fig. 1. The results of oxygen pumping in Fig. 3 have supported this consideration.

Concerning the active sites specifically effective to the oxidative dehydrogenation of ethane, we tentatively suggest the activation mechanism of ethane on the peroxide as demonstrated in Fig. 8. The ethyl intermediate in reaction (3) of Fig. 8 may either be converted on the catalyst into ethylene or desorb into the gas phase for subsequent reactions. The larger C–H bond energy of methane than that of ethane as well as the high distortion energy required for the methane to coordinate to the two oxygen atoms of the peroxide might make it impossible to activate methane.

4. Acknowledgement

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