The Impregnated Boron Oxide Catalysts for The Reaction of Dehydrogenation of Ethane

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Abstract

The various material for catalyst systems were YSZ (yttria-stabilized zirconia), Al2O3, and Sm2O3 as catalyst supports with addition on each support by various boron oxide catalyst loadings. This study is intended to find the highest catalyst activity on each catalyst materials prepared (B2O3/YSZ, B2O3/Al2O3 and B2O3/Sm2O3) and to confirm the existence of peroxide species as an important role for mainly reaction of ethylene dehydrogenation reaction. The results showed that YSZ with the content of 15 % wt boron oxide showed the highest catalytic activity for the partial oxidation of ethane with the main product was ethylene. For B2O3/Al2O3 catalyst exhibited the highest activity obtained by addition 30 wt%B2O3 content. However, the catalytic activity of the various contents of boron oxide added to Sm2O3 showed that the increasing of boron oxide lead to the decreasing completely the catalyst activities for ethane oxidation reactions. The XPS studies on those catalyst systems exhibited the appearance peak at the binding energy 531 eV, which attributed to the formation of peroxide species at the interface of boron oxide and YSZ and Al2O3, in consistent to the results of catalytic reaction test is that the high intensity is by the highest active catalyst (15 % B2O3/YSZ and 30% B2O3/Al2O3). Moreover, the nothing peak at this binding energy for all the composition of the B2O3/Sm2O3 catalysts and no activities of those catalysts for ethane dehydrogenation strongly suggested that there is a strong correlation between the results of catalyst activities and the existence of the peroxide species detected on XPS spectra. So, the peroxide species is responsible for the dehydrogenation or partial oxidation of ethene, can be accepted as a high scientific argument.

Keywords: Peroxide species; B2O3/YSZ; B2O3/Al2O3; B2O3/Sm2O3; dehydrogenation reaction

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Introduction

Ethylene as a building block compounds is very important raw material for the petrochemical industry. This olefin compound can be processed into a variety of downstream petrochemical products like plastic, resin, fibre and others. The ethylene compound can be obtained from ethane compounds either through a catalytic reaction or non-catalytic (thermal cracking). B2O3/YSZ catalyst is a catalyst that is quite interesting and uncommon to employ a research. YSZ (yttria-stabilized zirconia) is solid zirconia, with added 8% yttria mole. B2O3 is considered acidic while the YSZ is a solid that can serve as a conductor of ions. Catalytic performance of B2O3/YSZ has been examined in the reaction of partial oxidation of methane (Setiadi, 2004). The existence of B2O3 in the surface of catalyst apparently can change the behaviour of the original high-performance catalysts in oxidation reactions of methane to become a partial oxidation catalyst. It turns out the oxide alloy also has high catalytic partial oxidation reactions of ethane into ethylene (Otsuka et al., 1995).

The synergy catalytic nature by integration of some oxides second oxide used as the total oxidation reaction and the reaction partial oxidation catalyst, subsequent development used in alloys catalyst B2O3/Al2O3, Al2O3 can be acidic nor alkaline (Setiadi, 2005). and turns alloy is also very active to partial oxidation, especially to a catalytic reaction dehydrogenation of ethane be ethylene. But the mixing with a metallic oxide Sm2O3 the results showed very far away. The oxide combination was totally not giving positive synergy catalytic properties in reaction in partial oxidation reaction for methane and ethane (setiadi, 1994). It suggests that strong alkaline properties metal oxides Sm2O3 make the reactions of
alkaline with the acidity of boron oxide in the surface. So it formed a salt compound to inhibit the partial oxidation reactions.

From the explanation above, the high activity of the catalyst for partial oxidation reaction mainly to, caused by high concentrations of active site catalyst for reaction of dehydrogenation ethane into ethylene. It should be strongly supposed that strongly that the active site of catalyst was a peroxide species in the surface, formed at the contact between the particles of B$_2$O$_3$ with the surface of YSZ or Al$_2$O$_3$. This is a consequently logic because the pure form of each component of Al$_2$O$_3$, B$_2$O$_3$, YSZ is obviously not active, because there is no peroxide and very difference to the reactivity of each its alloys. Therefore, this paper will expose about studying strategy of partial oxidation reaction of ethane by comparing their reactivity of each alloy catalyst B$_2$O$_3$/YSZ, B$_2$O$_3$/Al$_2$O$_3$ and B$_2$O$_3$/Sm$_2$O$_3$.

Model of the core active catalyst formed from the interaction of B$_2$O$_3$ with metal oxide (YSZ, Al$_2$O$_3$) in the field between the surface. The active core most likely is in the form of a peroxide species bound to atoms of B and M (Si, Al, or Y). More details can be seen in the illustration of Figure 1. These active nuclei have formed when the calcination result is a catalyst in the reaction between molecules of O$_2$ with boron are positively charged and the formed boron zirconia peroxide. In addition, the amount of the excess of B$_2$O$_3$ (B$_2$O$_3$ content%) then the longer active core will be getting buried by the particle on the surface of the catalyst B$_2$O$_3$, resulting in decreased activity of the catalyst in the reaction of dehydrogenation of ethane. The test results according to the activity that the nature of the catalyst leads to total ethane oxidation reactions.

In its role as the core of the active catalyst, peroxide molecule ethane species by tying 1 hydrogen atom on each atom C transition state forms compounds on the surface. Formation of ethylene molecule through the termination of C=H and formed H$_2$O molecules. At this stage the O$_2$ molecules needed a catalyst to reshape spec peroxide. In the reaction of dehydrogenation ethane use oxygen is also known as oxy-dehydrogenation reaction. Recurring cycle again after the boron atoms react with oxygen.

![Figure 1. Illustration of the existence of an active core model peroxide species in the reaction of dehydrogenation ethane to ethylene](image)

**Methodology**

Catalyst Preparation Material preparation of catalyst has been described in some previous papers (Setiadi, 1999; Setiadi, 2005). The Material used is the catalyst of YSZ solid, Al$_2$O$_3$ and Sm$_2$O$_3$. Boron oxide were obtained from boric acid (H$_3$BO$_3$) as a precursor of the oxide. Preparation of catalyst with impregnation method done by dissolving solids solid boric acid into the water free of minerals (de-ionized water) that is kept at a temperature of 75 °C so that the dissolved solids are perfect. Then solution used for impregnating each solid by means mixing and pouring at temperature 80 °C, dried until obtained solids. The solid resulted, was then at atmospheric conditions calcined sequentially at a temperature of 300 °C and 750 °C, respectively, for 2 hours. The calcination results are solid and can be used for characterization and tested for their catalytic properties on ethane dehydrogenation reaction.

Catalytic reaction technique in performance testing is conducted have also been described in various papers in advance. Dehydrogenation of ethane reaction was carried out at atmospheric pressure using fixed fluidized-continuous, made from quartz. Catalyst with certain weight was fixed in the reactor using quartz wool. Quartz material is glass-like material (transparent) and hold on high (300 °C). to customize the temperature, the reactor is put into an electric furnace with a cylindrical form attempted to position the right catalyst at a temperature of bonfire that is highest in the furnace. The temperature reaction/temperature measured by using a catalyst a thermocouple that is inserted in a pipe quartz mounted according to the depth of fixed bed of catalyst in the reactor. As seen in schematic diagram of catalytic test in Figure 2, to ensure the air free-condition, helium gas used as carrier and the inert gas was flowing for approximately 30 minutes to remove the air existing in pipe or equipment (purging).
Next temperature reactor raised according to the condition desired by means typeset temperature on control connected with a thermocouple submerged in catalyst. After pretreatment, purging done gaseous oxygen, with the manner of shutting the flows and let gas he still flows on the system reactor. The reaction was carried out with the first ethane flow gradually fed into reactor. Gas output connected in reactor on line with gas chromatography to do the analysis change.

![Diagram](image1)

**Figure 2.** Schematic Diagram for catalytic test and the Reactor Profile

**Results and Discussion**

Influence content on a catalyst B$_2$O$_3$/YSZ testing the nature of catalytic B$_2$O$_3$/YSZ to each content B$_2$O$_3$ reaction against dehydrogenation of ethane, the result was in this Figure 3 and 4.

![Diagram](image2)

**Figure 3.** Plot of B$_2$O$_3$ content vs. The Conversion rate of Ethane using (B$_2$O$_3$/YSZ) catalyst

![Diagram](image3)

**Figure 4.** Plot of B$_2$O$_3$ content vs. The Formation Rate of product in dehydrogenation of ethane using B$_2$O$_3$/YSZ catalyst

The condition of reaction carried on 823 k, temperature atmospheric pressure P$_{CH_4}$ = P$_O_2$ = 20 kpa and total gas rate of 50 ml/min. As it seems at the two Figures although performance solids YSZ (without B$_2$O$_3$ content) showing liveliness very high in converting ethane, compounds but its main product of CO$_2$ c.o.and namely is total oxidation product of ethane. The addition of B$_2$O$_3$ content to% uF0B1 5% weight, was able to decrease the activity of the catalyst is sharp, good views from the rate of conversion of ethane (Figure 3) and the rate of product formation (Figure 4). This gives the sense that the reduction of B$_2$O$_3$ ethane oxidation reactions can hit (inhibitor), which on the surface of YSZ. B$_2$O$_3$ destroyed/eliminated core active catalysts which play a role in the oxidation reaction of ethane. However, the addition of boron oxide in the range of 5% to 15%, it looks that any influence that sharp look with the
increasing conversion of ethane and the rate of product formation. In addition, the main product produced is in the form of ethylene, $\text{C}_2\text{H}_4$ (see Figure 4). The addition of $\text{B}_2\text{O}_3$ in this range results in a reaction process dehydrogenation of ethane as well as optimum levels of 15% $\text{B}_2\text{O}_3$, i.e. the weight which is the best catalyst. So the adding of $\text{B}_2\text{O}_3$ above 15% heavy, namely decline curves as it seems in all curves. It shows all the catalyst have content $\text{B}_2\text{O}_3$ decrease its activity resulting from the addition of the excessive of $\text{B}_2\text{O}_3$ content.

**Influence of catalyst on the content of $\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3$**

The catalytic properties Testing/Al$_2$O$_3$B$_2$O$_3$ for each content of dehydrogenation of ethane reaction against $\text{B}_2\text{O}_3$, the results shown in Figure 5 and 6.

![Figure 5](image5.png)

**Figure 5.** Plot of $\text{B}_2\text{O}_3$ content vs. the rate of Ethane Conversion using $\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst

As it seems at both the Figure, similar to the nature of catalytic $\text{B}_2\text{O}_3$/YSZ although performance solids Al$_2$O$_3$(without content $\text{B}_2\text{O}_3$) showing the reactivity in converting compound ethane, but products mainly in form of CO and CO$_2$ that is the product total oxidation ethane. But the addition of the $\text{B}_2\text{O}_3$ until 15% weight, new capable of lowering suppress the rate of the conversion of ethane at CO, an image or Figure of the rate of the formation of the product (6) being to YSZ, the addition of boron oxide in the range of 15% heavy is already reached the point of maximum.

The addition of boron oxide in the range of 15% to 40% u2013 $\text{B}_2\text{O}_3$ seem that the existence of significant influence by increasing the conversion rate of ethane is sharp and the rate of product formation towards ethylene as well as other useful chemical. In addition to the main product produced is in the form of ethylene, $\text{C}_2\text{H}_4$ (Figure 6), the addition of this range generate $\text{B}_2\text{O}_3$ a process of reaction dehydrogenation rate of ethane with optimal levels of $\text{B}_2\text{O}_3$ i.e. 30% weight and composition of the alloy is the best catalyst for catalytic systems/Al$_2$O$_3$B$_2$O$_3$. The addition of the levels above 30% weight $\text{B}_2\text{O}_3$ palpable decline curve, indicates that all of the catalyst which has an excess veins $\text{B}_2\text{O}_3$ content thus will reduce its activities.

A very important thing to be examined is the effect of the addition of the above 5% $\text{B}_2\text{O}_3$ on YSZ and 15% in weight of the alleged possibility of Al$_2$O$_3$ formation of new active core results of interaction between $\text{B}_2\text{O}_3$ and Al$_2$O$_3$ which acts to dehydrogenation
reaction. But if it was assumed that the core is active B₂O₃ catalyst, then:

- should the amount of the excess veins B₂O₃ above 15% weight to YSZ or above 30% Al₂O₃ Catalyst weight on will make the performance of the catalyst B₂O₃/YSZ/Al₂O₃B₂O₃ and getting high, but in fact declining.

- the result is not likely to happen should be optimum at 15% B₂O₃/YSZ and 30%/Al₂O₃B₂O₃.

- When associated with the influence of the addition of B₂O₃ with respect to surface area, the more does not support the assumption that the existence of B₂O₃ as an active core for dehydrogenation of ethane reaction. Because the surface area is precisely the decline with a large content of B₂O₃ (Setiadi, 1994).

So clearly that it is unlikely that compound B₂O₃ constituting the nucleus active to reaction dehydrogenation ethane. to strengthen assumption

that the establishment of new structures as the nucleus active catalyst for reactions dehydrogenation ethane, then tested activity alloy oxide B₂O₃/Sm₂O₃. Clear was in this Figure 7 and 8 that addition content boron oxide not at all provide positive effect and instead of catalytic getting high content boron oxide decreasing. It is strongly assumed that alloy second oxide is totally not formed structures peroxide as their interaction second oxide. Catalyst characterization of solids by using XPS (x-ray photo spectroscopy), then a typical peroxide species appear on the binding energy 531 eV (Setiadi, 1994). As shown in Figure 9 to 15% B₂O₃ catalyst/YSZ, speci peroxide appears to peak code D. The peak intensity is quite high compared to the catalyst with the levels of other B₂O₃ content. A similar case also looks at 30% B₂O₃ catalyst/Al₂O₃ (code B) although smaller intensities (Figure 10).

However the opposite peaks on binding energy 531 eV, not at all visible on catalyst B₂O₃/Sm₂O₃ (Figure 11 and 12).
The addition of \( \text{B}_2\text{O}_3 \) above 5% for catalyst \( \text{B}_2\text{O}_3/\text{YSZ} \) and above 15% \( \text{B}_2\text{O}_3/\text{Al}_2\text{O}_3 \) Catalyst for changing the nature of the catalyst became very active to dehydrogenation of ethane reaction. The best catalyst for \( \text{B}_2\text{O}_3/\text{YSZ} \) weight \( \text{B}_2\text{O}_3 \) is 15% and 30% for \( \text{Al}_2\text{O}_3/\text{B}_2\text{O}_3 \)/catalyst.

- Based on the results of the characterization of the catalyst XPS method turned out to be consistent with the results of the catalytic performance, strongly indicated that the active site of the catalyst for the reaction of dehydrogenation ethane is a peroxide species derived from the results of interaction between YSZ and \( \text{Al}_2\text{O}_3/\text{B}_2\text{O}_3 \) with on the contact between the surface area of the particles of the second.

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