Dehydrogenation of Propane Combined with Selective Hydrogen Combustion over Pt-Sn Bimetallic Catalysts

Shinji Kaneko*, [1], Tsuyoshi Arakawa, Masa-aki Ohshima, Hideki Kurokawa, and Hiroshi Miura
Department of Applied Chemistry, Saitama University, Sakura-ku 255, Saitama-shi, Saitama, Japan

[1]Current Address: Department of Chemistry, University of California, Riverside, CA 92507, USA
*Corresponding author: Tel.: +1-951-827-5736; fax: +1-951-827-4713
E-mail address: skane001@ucr.edu

Abstract

Dehydrogenation of propane combined with selective hydrogen combustion was studied over supported Pt-Sn bimetallic catalysts. A catalytic test for normal dehydrogenation was also carried out as part of the proposed process. Pt/Al_2O_3 modified with Sn and Zn was found to be suitable for both of these two reactions. In the normal dehydrogenation, conversions equal to the calculated equilibrium conversion were achieved with almost complete selectivity for propylene. Optimization of catalyst composition was done by addition of various amounts of Sn to Pt/Al_2O_3 and Pt/Zn-Al-O. For dehydrogenation combined with hydrogen combustion, selective hydrogen combustion was achieved over Pt-Sn bimetallic catalysts. Moreover, a stable conversion higher than that of equilibrium for normal dehydrogenation was obtained using Pt-Sn/Zn-Al-O under certain reaction conditions.

Keywords: dehydrogenation of propane; selective hydrogen combustion; Pt-Sn bimetallic catalysts; Zn-Al-O support

1. Introduction

As industrial demand for propylene grows, its production via dehydrogenation (DH) of propane is assuming greater importance. DH of propane (Scheme 1) has been carried out in the presence of inert gas, hydrogen or steam (normal dehydrogenation) [1, 2].

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad (1)$$

DH of propane is highly endothermic and therefore requires high reaction temperatures (around 600°C). As a consequence of these high reaction temperatures, the process suffers from poor economy and rapid catalyst deactivation due to coke formation. In order to overcome the restriction of thermodynamic equilibrium, oxydehydrogenation (ODH) of propane (Scheme 2) has been studied by many research groups, as documented in recent reviews [1, 2].

$$C_3H_8 + {}^1\!/_2 O_2 \rightarrow C_3H_6 + H_2O \qquad (2)$$

However, there has been no breakthrough in the search for catalysts that provide the necessary yield of propylene for commercial application.

As an alternative to ODH, a new method based on a combination of DH with selective hydrogen combustion (SHC) has been proposed. The reaction equilibrium can be shifted towards the desired products by selective combustion of hydrogen formed via DH. Moreover, the combustion of hydrogen, which is highly exothermic, can supply a large fraction of the heat required for the DH reaction.

This new reaction system has already been commercialized for DH of ethylbenzene (Lummus/UOP SMART SM^{TM} process). According to the US patents assigned to UOP Inc. [3, 4], this process employs modified Fe catalysts for DH and modified Pt, Pd, or Rh catalysts for SHC. However, it has not yet been industrialized for DH of small alkane molecules such as propane.

DH of propane combined with SHC has been studied by some research groups [5-9]. The most challenging aspect is the selective combustion of hydrogen in the presence of propane and propylene, which are both easily combustible. The majority of research groups have studied supported and/or unsupported oxide catalysts, including Bi_2O_3 [5, 6], In_2O_3 [5, 7, 8], and Cu/SiO_2/ZSM-5 [9], and considerably high SHC selectivity (85-95%) has been reported.

Some non-oxide-based catalysts have also been developed: Imai et al. [10] and Late et al. [11] reported that Pt-Sn bimetallic catalysts promoted selective combustion of hydrogen in the presence of propane and propylene. Pt-Sn catalysts are known for their high selectivity and stability in the propane DH reaction; they should therefore be able to catalyze both DH and SHC reactions. If both of these reactions proceed over the same catalyst, the process can be simplified and its efficiency improved substantially. However, it was not demonstrated that a conversion higher than that of equilibrium for normal DH was actually be achieved in their reports [11].

A recent study by Waku et al. [12] clearly indicated that conversions higher than that of normal DH equilibrium can be obtained by combining the reaction with SHC. However, the catalyst (Pt/Na-[Fe]ZSM-5) and the reactor (a recirculating reactor equipped with a quartz capillary for the introduction of air) they employed were so specific that at this time the reaction system seems far from practical application.

In this study, Pt-Sn catalysts supported on various oxides (mainly Al_2O_3 and Zn-Al-O) were tested for propane DH combined with SHC, as well as normal DH as part of a multi-stage DH process. Pt-Sn/SiO_2 was employed for comparison with the study done by Late et al. [11]. Optimization of catalyst composition was done by the addition of specific amounts of Sn to Pt/Al_2O_3 and Pt/Zn-Al-O. The equilibrium for normal dehydrogenation needs to be achieved in the first reactor without the production of a large amount of by-products to realize this process.

Therefore we employed high Pt loading (5 wt%) in this study so as to achieve the reaction equilibrium and to see if a high selectivity towards propylene can be obtained. A conventional fixed-bed reactor was employed for both of these reactions. Particular emphasis was placed on the ability of the catalyst to achieve a conversion higher than that of equilibrium for normal DH. The feasibility of the DH process combined with SHC was examined.

2. Experimental

2.1 Catalyst Preparation

Zn-Al-O support was prepared by a co-precipitation method using $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ as metal precursors and aqueous NH_3 as a precipitant. The resulting precipitate was dried at 130ºC overnight and then calcined at 300ºC for 2 h and 500ºC for 2 h under O_2 flow. The sample was further calcined at 600ºC for 3 h in a muffle furnace. In the first calcination step at 300ºC, nitrate residues were removed as NO_x.

Monometallic Pt catalysts and bimetallic Pt-Sn catalysts were prepared by impregnation and co-impregnation using $H_2PtCl_6 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$ as metal precursors, and Al_2O_3, SiO_2, and Zn-Al-O as oxide supports. Al_2O_3 and SiO_2 were supplied by Mizusawa Industrial Chemicals, LTD.. After drying at 130ºC overnight, the catalysts were calcined at 500ºC for 3 h, and reduced at 500ºC for 5 h under H_2 flow.

2.2 Characterization

CO adsorption measurements were conducted at 25 ºC to determine the number of surface Pt atoms based on the assumption that the ratio of adsorbed CO molecules and surface platinum atoms equals 1. Prior to the adsorption measurement, the samples were reduced under flowing H_2 at 500ºC for 1 hour and purged with He at the same temperature for 15 min.

BET surface areas were also determined. The samples were pretreated under flowing N_2 at 300 ºC for 15 min.

Additionally, RAD-B system (Rigaku Corporation) and FT/IR350 (JASCO Corporation) were employed for X-Ray Diffraction (XRD) measurements and Fourier-Transformed Infrared (FT-IR) measurements of adsorbed carbon monoxide.

2.3 Normal Propane Dehydrogenation

Normal propane dehydrogenation was carried out using a fixed bed flow system. The reactor was made of stainless steel (10 mm i.d., 300 mm length). The catalyst (0.05 - 0.50 g) was diluted with quartz sand to 3.00 g so that the reaction could be conducted isothermally as far as possible. The catalyst was pretreated under flowing H_2 at 500 ºC for 1 hour. The reaction temperature was 500ºC, the feed ratio of the reaction mixture was C_3H_8:He = 1:2, and the total feed rate was 90 ml/min. Thermal conductivity detection gas chromatography (TCD-GC) was employed for product analysis.

2.4 Propane Dehydrogenation Combined with Hydrogen Combustion

To simulate a two-stage DH and SHC process (described in section 3), the reaction was carried out using a single reactor as though the reaction were taking place in the second reactor after normal DH in the first reactor. The feed gas was a mixture of C_3H_8, C_3H_6, H_2, He, and air. The feed ratio was equal to the equilibrium composition of normal DH at 500ºC (C_3H_8:C_3H_6:H_2 = 0.72:0.28:0.28) and the O_2:H_2 feed ratio was 1:2 (stoichiometry for H_2 combustion) to 1:4. The total flow rate was fixed at 90 ml/min using He as a balance gas. A quartz reactor was used to prevent auto-oxidation. The amount of H_2O was not analyzed by GC, but calculated through mass balance of oxygen (the only other oxygen-containing products were CO and CO_2). The change in catalyst bed temperature recorded by thermocouple due to reaction heat was within 10ºC. The other reaction conditions were the same as normal propane dehydrogenation described above (see section 2.3).

3. Thermodynamic simulation of equilibrium conversions

The equilibrium conversions for normal DH and DH combined with SHC were calculated in order to evaluate experimental results. Calculations were done based on the thermodynamic parameters given in literature [13]. Fig. 1 shows the schematic of this two-phase process assumed in this study. The equilibrium shift due to hydrogen combustion was calculated based on the following assumptions:

1. The process is carried out in two isothermal sequential reactors.
2. In the first reactor, normal DH progresses to equilibrium (the composition of feed gas is C_3H_8:He = 1:2).
3. Between the two reactors, air is fed as an oxidant in the amount required to combust half or all of the hydrogen formed via DH in the first reactor.
4. In the second reactor, oxygen reacts only with hydrogen (SHC) and DH progresses toward the equilibrium conversion as shifted by SHC.

This simulation was done assuming selectivities toward DH and SHC were 100 %. Therefore, if the selectivity toward DH is below 100 % due to side reactions such as cracking, conversion of propane can exceed the calculated equilibrium value. On the other hand, if the selectivity toward SHC is below 100 % due to combustion of hydrocarbons, calculated equilibrium conversion can not be achieved. However, as we show in section 4.2 and 4.4, experimental selectivities toward both DH and SHC were above 99. 5 % in most cases, thus this assumption was found to be fairly reasonable for practical use.

4. Results

4.1. Properties of catalysts

Table 1 shows the catalytic properties of Pt/Al_2O_3 and various catalysts modified by Zn and Sn. All reported loadings are nominal values. The Zn/Al ratio chosen for the Zn/Al-O support was the optimal value for isobutane DH that we reported previously [14]. These additives led to a decrease in BET surface area and CO uptake. CO uptake is known to be largely equal to the number of surface Pt atoms due to the selective adsorption of CO on surface Pt atoms (CO/$Pt_{surface}$ ~ 1) [14-17]. It was confirmed that almost no CO adsorption was observed for Al_2O_3, Zn-Al-O, and Sn/Al_2O_3.

From XRD measurements, it was found that Zn-Al-O is a mixture of $ZnAl_2O_4$ spinel phase and γ-Al_2O_3 phase as we reported previously [14].

The addition of Sn in particular resulted in considerably lower CO uptake. It has been suggested by other research groups [15, 18-21] that the decrease in the ratio of surface Pt due to Sn addition results from Pt-Sn alloy formation and surface Pt dilution with Sn; surface Pt atoms are partially covered with Sn atoms due to the formation of Pt-Sn alloy particle, and as a result Pt ensembles are divided into separate atoms. The formation of Pt-Sn alloy phase was confirmed by XRD measurements of Pt-Sn catalysts (no data shown).

It has been reported that the decrease in CO uptake by addition of Zn can be attributed to strong metal support interaction (SMSI) effect; ZnO reduced due to high reduction temperature migrates and covers surface Pt sites [22-24].

The properties of Pt-Sn/SiO_2 are also shown in Table 1. This catalyst was also prepared by a co-impregnation method, which is similar to the preparation method employed by Late et al [11]. CO uptake of this catalyst was extremely small compared to other catalysts prepared by the same method. This can be attributed to the different surface properties of Al_2O_3 and SiO_2. Many researchers have compared the CO uptake of Pt-Sn/Al_2O_3 and Pt-Sn/SiO_2, and found that CO uptake was higher for the catalysts supported on Al_2O_3 in most cases [25-27]. However, Pt dispersion on SiO_2 is known to be heavily dependent on the preparation conditions, especially temperature [28]. Oxidation and reduction at lower temperature may result in a higher Pt dispersion of Pt-Sn/SiO_2.

4.2 Normal Propane Dehydrogenation

Normal propane DH was studied as the first part of the multi-stage process we propose. In order to fully utilize the effect of hydrogen combustion, the equilibrium for normal dehydrogenation should be achieved in the first reactor without the production of a large amount of by-products. Therefore, in this section, particular emphasis was put on whether the theoretical equilibrium conversion could be obtained while maintaining high selectivity for dehydrogenation. Catalytic stability was also evaluated. In addition, optimization of the amount of Sn loading was done.

Effect of Sn and Zn additions

Pt/Al_2O_3 catalysts modified by Sn and Zn additions were employed. As we reported previously [14], these additives are effective for improving the selectivity for dehydrogenation and stability of Pt/Al_2O_3 in isobutane DH, which is similar to propane DH.

Figure 2 shows the catalytic activity of non-modified and modified Pt/Al_2O_3 catalysts in normal propane DH. Although the initial activity was high, the unmodified Pt/Al_2O_3 catalyst was rapidly deactivated, probably due to coke formation, and the formation of cracking products (CH_4 and C_2H_4). This resulted in a low selectivity for C_3H_6. By contrast, catalysts modified with Sn and/or Zn afforded more stable activities. In addition, the selectivity to propylene was increased, while the selectivities to C_2H_4 and CH_4 were decreased. These results are in good agreement with other reports on the additive effects of Zn and Sn in propane DH [18, 19, 29-32] and isobutane DH [14, 15, 20, 33-35], although we employed catalysts with high Pt loading (5 wt%) compared to the catalysts used in these previous studies.

Catalytic activity after reaction for 5 hours can be mostly regenerated by the subsequent reduction in hydrogen flow at 500 ºC for 1 h probably due to the removal of deposited coke. During this reduction, only CH_4 was observed as the hydrogenated product of deposited coke.

Optimization of Sn loading

Optimization of Sn loading of Pt-Sn/Al_2O_3 and Pt-Sn/Zn-Al-O was done by changing the amount of Sn loading from 2 wt% to 20 wt%. Figure 3 shows the influence of Sn loading on catalytic performance of Pt/Al_2O_3 (Fig. 3(a)) and Pt/Zn-Al-O (Fig. 3(b)). As the amount of Sn loading increased, higher propane conversions were obtained. However, propane conversion started to decrease when the amount of Sn loading exceeded 10 wt%. On the other hand, it seems like the stability of catalysts simply improved as the amount of Sn loading increased.

Figure 4 shows the influence of Sn content on CO uptake of Pt-Sn/Al_2O_3 and Pt-Sn/Zn-Al-O. It is clearly shown that CO uptake decreases monotonically as the amount of Sn loading increases. This suggests that the initial catalytic activity also decreases monotonically, and the higher conversions obtained by Sn addition can be attributed to the suppression of catalyst deactivation by coke formation during the initial stage of the reaction.

These experiments showed that there exists optimal amount of Sn addition of about 7.5 wt% (Sn/Pt ~ 2.5) for long-term activity for the reaction conditions investigated. A considerably larger proportion of Sn loading compared to Pt was needed for optimization of Pt catalysts, and it was nearly equal for both Pt/Al_2O_3 and Pt/Zn-Al-O.

Influence of contact time

Figure 5 shows the influence of the contact time (W/F) on conversion and selectivity that was brought about by changing the amount of Pt-Sn/Al_2O_3 catalyst used. The dashed line indicates the calculated equilibrium conversion for these reaction conditions. It can be seen that the theoretical equilibrium conversion could be achieved for at least 5 hours when the weight of the catalyst was over 0.3 g (W/F = 4.07 g-cat·h/mol). More importantly, no noticeable difference in propylene selectivity was observed with longer contact time. This result indicates that the equilibrium conversion for normal DH can be achieved with almost complete selectivity for C_3H_6 (~ 99.8%) using Pt-Sn catalysts. This confirms that normal dehydrogenation can be utilized as the first part of the proposed multi-stage process.

In the thermodynamic calculations (section 4.3), it was assumed that the equilibrium conversion for normal DH could be achieved with 100% selectivity for C_3H_6 in the first reactor (prior to the SHC and DH reactions in the second reactor). The results obtained here demonstrate that this assumption is indeed correct.

4.3 Thermodynamic simulation of equilibrium conversions

Figure 6 indicates the equilibrium conversions for conventional DH and for DH combined with combustion of half or all of the hydrogen formed through DH in the first reactor. It can be seen that the equilibrium conversions with hydrogen combustion are higher than that of conventional DH alone. At 500ºC, with combustion of half of the hydrogen, the equilibrium conversion is 1.3 times higher than that of normal DH. With combustion of all hydrogen, the equilibrium conversion is 1.6 times higher.

This shift in equilibrium conversion can also be attributed to the dilution by N_2 contained in air because the number of molecules increases as a result of dehydrogenation. However, when O_2 is introduced instead of air, equilibrium conversion at 500ºC is 1.5 times higher than that of normal DH with combustion of all of the hydrogen. This is largely equivalent to the equilibrium shift when air was used as oxidant (1.6 times higher). Therefore, the change in equilibrium due to the dilution by addition of N_2 is not important, compared to that of hydrogen combustion. The calculated equilibrium conversions were used for evaluation of experimental results of propane DH combined with SHC (Section 4.4).

4.4 Propane Dehydrogenation Combined with Hydrogen combustion

In this section, propane DH combined with SHC was studied with a setup simulating a reaction carried out in the second reactor following normal DH in the first reactor. The feed gas mixture was the equilibrium composition for conventional dehydrogenation at 500ºC. Particular emphasis was placed on the achievement of conversions higher than the equilibrium conversion for normal DH due to selective hydrogen combustion. The experiment was conducted isothermally as far as possible by diluting the catalyst with quartz sand.

Comparison of various catalysts

Fig. 7 shows the results when the stoichiometric amount of oxygen for hydrogen combustion (O_2:H_2 = 1:2) was provided in the form of air.

As shown in Fig. 7(a), oxygen conversion was about 95% over all catalysts tested. No significant difference was observed among all the catalysts tested. This trend was consistent with previous reports by Late et al. [11] and Berretta et al. [36]. This minor incomplete conversion was probably due to some of the reactant gas by-passing the catalyst bed, or limitation of oxygen conversion by diffusion. A blank test carried out prior to the catalytic test showed an oxygen conversion of only about 5%. This indicates that the consumption of oxygen was due almost completely to catalytic reaction.

Figure 7(b) shows O-selectivity for H_2O. The other oxygen-containing compounds are CO and CO_2 (CO_x), derived from combustion of C_3H_8 and C_3H_6. As shown in Fig. 7(b), the Pt-Sn catalysts showed excellent properties for producing H_2O and only small amounts of CO_x were produced. This result is in good agreement with that reported by Late et al., although they conducted the reaction using different gas compositions [11]. As they reported, it was possible to combust hydrogen selectively in the presence of C_3H_8 and C_3H_6 over Pt-Sn bimetallic catalysts. The reason why hydrocarbon combustion was prevented is discussed later (see section 5). From Fig. 7(a) and (b), it can be seen that most of the O_2 and H_2 in the feed was consumed and turned into H_2O over Pt-Sn catalysts.

Fig 7(c) shows the assumed conversion of C_3H_8. This is indicated as the total value for the hypothetical two-stage reaction, based on the assumption that propane conversion was 28% (equilibrium conversion for normal DH at 500 °C) and C_3H_6 selectivity was 100% in the first reactor. Over modified catalysts, it was possible to obtain conversions higher than the equilibrium conversion for normal dehydrogenation; the highest conversion was achieved over Pt-Sn/Zn-Al-O. By comparison, conversions only slightly higher than the equilibrium conversion were obtained in the beginning of reaction over Pt/Al_2O_3, Pt/Zn-Al-O, and also Pt-Sn/SiO_2, which was used by Late et al. [11]. This indicates that the support material of the Pt-Sn catalyst also has an important role in achieving high conversions in this reaction and demonstrated that Zn addition to Pt-Sn/Al_2O_3 was effective to achieve conversions higher than the equilibrium conversion for normal DH. However, some may argue that CO uptake (number of surface Pt atoms) of Pt-Sn/SiO_2 was too low to compare its activity with that of other catalysts. If it is possible to improve the number of surface Pt by modifying the preparation method, Pt-Sn/SiO_2 may be as good catalyst as Pt-Sn/Al_2O_3 and Pt-Sn/Zn-Al-O.

Another problem is the stability of catalysts. Deactivation of the catalysts was much more severe than in normal DH; Pt-Sn catalysts lost most of their ability to overcome the equilibrium of normal dehydrogenation after 1 hour of the reaction. This was probably due to rapid coke formation accelerated by high partial pressure of C_3H_6 and low partial pressure of H_2 as it was consumed through combustion. It has been suggested in the literature that coke is mainly derived from C_3H_6 [31, 32], and that deactivation due to coke formation is suppressed by H_2 [16, 30]. Also, as suggested by Waku et al., [12] deactivation may be accelerated via CO disproportionation.

Fig. 7(d) shows assumed C-selectivity for C_3H_6, calculated in the same way as the conversion for C_3H_8 (see the above paragraph). Selectivity for C_3H_6 over Pt/Al_2O_3 was relatively low due to the formation of CO_x by combustion of C_3H_8 and/or C_3H_6, and the formation of CH_4 and C_2H_4 through cracking. In contrast, catalysts modified by Zn and Sn showed much higher C_3H_6 selectivity due to the prevention of cracking and hydrocarbon combustion. As in normal dehydrogenation, cracking was prevented by the addition of Sn and Zn.

Influence of O_2/H_2 feed rate

In order to prevent the rapid deactivation mentioned above, the influence of experimental conditions on the reaction profile was also investigated. Figure 8 shows the influence of the O_2/H_2 feed ratio on the reaction in the presence of Pt-Sn/Zn-Al-O. When the feed ratio of O_2: H_2 was smaller than 1: 2 (1: 3 and 1: 4), the activity of the catalyst towards dehydrogenation was much more stable. This was probably due to the stabilizing effect of hydrogen, which was present in greater amounts after being only partially consumed via combustion with O_2. In conclusion, using Pt-Sn/Zn-Al-O it was possible to achieve selective combustion of hydrogen and to obtain stable conversions higher than that of equilibrium for conventional dehydrogenation when the O_2: H_2 feed ratio was smaller than 1: 2. In addition, as shown in Fig. 8(b), smaller O_2: H_2 ratios resulted in greater C_3H_6 selectivity. However, a smaller ratio of hydrogen combustion leads to a smaller degree of equilibrium shift (the calculated equilibrium conversions for each set of reaction conditions are shown in Fig. 8(a), assuming a 100% yield for hydrogen combustion).

Influence of contact time

Figure 9 illustrates the influence of contact time on the reaction (O_2:H_2 = 1:3). With an increase in catalyst weight, it was possible to obtain conversions that were largely equal to the calculated equilibrium conversion as shifted by hydrogen combustion. This confirms the relevance of the equilibrium calculations. However, regardless of the contact time, conversions exactly equal to the calculated equilibrium conversion could not be achieved. The achievement of conversions equal to the calculated equilibrium conversion was probably impeded by the incomplete combustion of hydrogen because the calculated equilibrium can be achieved only when both O_2 conversion and O-selectivity to H_2O are 100 %. Also, initial decreases in selectivity for C_3H_6 at catalyst weights of 0.10 g (W/F = 1.36 g-cat・h/mol) and 0.20 g (W/F = 2.71 g-cat・h/mol) were probably due to the smaller ratio of dilution of catalyst, which may have resulted in local temperature elevation by hydrogen combustion. As reported by Late et al., [11] a high reaction temperature accelerates combustion of C_3H_6 and C_3H_8 and leads to a decline in C-selectivity for C_3H_6.

In conclusion, it was possible to obtain conversions largely equal to the calculated equilibrium conversion as shifted by hydrogen consumption. Control of the reaction temperature is also important for maintaining high selectivity for C_3H_6.

5. Discussion

The main finding reported here is that Pt-Sn catalysts can promote selective combustion of hydrogen, resulting in the achievement of conversions higher than the equilibrium conversion for normal DH. In this regard, Pt-Sn/Zn-Al-O with the optimal loading of Sn (Sn/Pt ~ 2.5) was found to be the best catalyst among those studied. Importantly, Pt-Sn/Zn-Al-O was a far better catalyst in terms of achieving conversions higher than the equilibrium conversion for normal DH compared to Pt-Sn/SiO_2 employed by Late et al. [11]. Furthermore, the importance of reaction conditions, especially the O_2/H_2 feed ratio, was pointed out. We argue that these are new findings compared to related previous studies [10-12]. We have demonstrated the possibilities of this new propane DH system, although the research is still at a basic stage. More detailed studies are required to develop this reaction system for practical use.

For industrial application, an adiabatic operation is more practical compared to the isothermal process, which was simulated in this study [2]. Actually, application of SHC is much more effective in an adiabatic process as seen in the Lummus/UOP SMART SM™ process for DH of ethylbenzene. In this process, the heat generated via SHC is utilized especially for reheating of the reaction gas cooled down by the heat absorption due to DH. This enables to a significant reduction in the energy costs of this process.

According to our rough estimation (detail not shown), an adiabatic two-stage DH-SHC process might achieve propane conversions more than twice as high as that of normal adiabatic DH and compensate for about 80 % of the heat required for the whole DH reaction in the first and second reactors. This is due to both the shift in equilibrium and the elevation of the reaction gas temperature by SHC. This suggests the great superiority of the adiabatic process compared to isothermal process. Therefore, future studies should be done in adiabatic conditions.

Furthermore, from the academic point of view, it is of great interest to clarify the reaction mechanism of selective hydrogen combustion over Pt-Sn catalysts, which has not yet been elucidated.

Many efforts have been made to clarify the relationship between the structure of Pt-Sn catalysts and the effects of Sn addition on normal propane DH. It has been suggested that the catalytic properties of Pt-Sn catalysts can be explained by Pt-Sn alloy formation. In the Pt-Sn alloy, the Pt surface is diluted with Sn, and Pt ensembles are divided into separate atoms [20, 21, 32, 34, 37, 38]. This has been clarified from the fact that Pt-Sn alloy formation eliminates the adsorption sites which cause bridge and three fold types of adsorbed CO. This was confirmed from FT-IR measurement of adsorbed CO on Pt-Sn/Al_2O_3 (no data shown). It is generally accepted that this dilution leads to suppression of coke formation and cracking reactions, which require Pt ensemble sites to occur [20, 34, 39, 40]. This is called the ensemble effect.

Although the mechanisms involved in this ensemble effect are still controversial, recent adsorption studies suggest that changes in the adsorption mode of propylene assume an important role. It has been pointed out that the addition of Sn suppresses the formation of strongly adsorbed species, including di-σ species, η-allyl species, and propylidine [34, 41-46]. Furthermore, Zaera et al. suggested that coke formation and cracking proceed via formation of these strongly-adsorbed species on a monometallic Pt surface [41] and, according to Butnett et al., [42] this is also true for combustion of propylene. Considering these reports, the high selectivity of hydrogen combustion over Pt-Sn catalysts may be explained by the fact that combustion of hydrocarbons via formation of strongly-adsorbed species on the Pt surface is inhibited by the ensemble effect of Sn, while combustion of hydrogen can take place in the absence of Pt ensemble sites. From this point of view, it may be possible for other bimetallic Pt catalysts with surfaces diluted by non-catalytic metals to achieve selective hydrogen combustion.

In addition, the promotion mechanism by the Zn promotion mechanism may be similar to this ensemble effect. It is known that the SMSI effect modifies the adsorption properties of surface Pt, and this may result in the improvement in selectivity toward DH and SHC as well as stability of Pt catalysts [20, 21]. Based on these previous studies, the additive effect of Zn is most likely to be attributable to this SMSI effect.

5. Conclusions

Dehydrogenation of propane combined with selective hydrogen combustion was studied over supported Pt-Sn bimetallic catalysts. A catalytic test for normal dehydrogenation was also carried out as the first part of the proposed multi-stage process. A noble catalyst suitable for both of these two reactions has been developed in this study.

Among the catalysts studied, Pt-Sn/Zn-Al-O was found to be the best for both normal dehydrogenation and dehydrogenation combined with hydrogen combustion. Optimization of the amount of Sn loading was done and Sn/Pt ~ 2.5 was found to be the optimal ratio in the reaction conditions we employed.

In normal dehydrogenation, it was possible to achieve conversions equal to the calculated equilibrium conversion with almost complete selectivity for propylene. For dehydrogenation combined with hydrogen combustion, it was possible to achieve selective combustion of hydrogen with stable conversions higher than the equilibrium conversion for conventional dehydrogenation.

In conclusion, this study demonstrated that dehydrogenation combined with hydrogen combustion is a viable alternative to the conventional dehydrogenation process.

References

[1] E. A. Mamedov, V. Cortes Corberan, Appl. Catal. A 127 (1995) 1

[2] M. M. Bhasin, J. H. McCain, B. V. Vora, T. Imai, P. R. Pujado, Appl Catal. A 221 (2001) 397

[3] T. Imai, US Patent No. 4435607 (1984)

[4] C. P. Tagmolila, US Patent No. 5043500 (1991)

[5] R. K. Grasselli, D. L. Stern, J. G. Tsikoyiannis, Appl. Catal. A 189 (1999) 1

R. K. Grasselli, D. L. Stern, J. G. Tsikoyiannis, Appl. Catal. A 189 (1999) 9

[6] E. A. de Graaf, A. Andereini, E. J. M. Hensen, A. Bliek, Appl. Catal. A 262 (2004) 201

[7] L. M. Zande, E. A. de Graaf, G. Rothenberg, Adv. Synth. Catal, 344 (2002) 884

[8] L. Late, W. Thelin, E. A. Blekkan, Appl. Catal. A 262 (2004) 63

[9] C. H. Lin, K. C. Lee, B. Z. Wan, Appl Catal A 164 (1997) 59

[10] T. Imai, US Patent No. 4788371 (1988)

[11] L. Late, W. Thelin, E. A. Blekkan, Appl. Catal. A 262 (2004) 53

[12] T. Waku, J. A. Biscardi, E. Iglesia, J. Catal. 222 (2004) 481

[13] C. L. Yaws, Chemical properties handbook: physical, thermodynamic, environmental, transport, safety, and health related properties for organic and inorganic chemicals, McGraw-Hill, New York, 1999

[14] H. Miura, T. Itoh, React. Kinet. Catal. Lett. 66 (1999) 189

[15] M. Ohta, Y. Ikeda, A. Igarashi, Appl. Catal. A 266 (2004) 229

[16] F. Z. Bentahar, J. P. Candy, J. M. Basset, F. Le Peltier, B. Didillon, Catal. Today 66 (2001) 303

[17] M. H. Kim, J. R. Ebner, R. M. Friedman, M. A. Vannice, J. Catal. 204 (2001) 348

[18] S. B. Kogan, M. Herskowitz, Catal. Comm. 2 (2001) 179

[19] S. B. Kogan, H. Schramm, M. Herskowitz, Appl. Catal. A 208 (2001) 185

[20] F. Humblot, J. P. Candy, F. Le Peltier, B. Didillon, J. M. Basset, J. Catal. 179 (1998) 459

[21] F. B. Passos, D. A. G. Aranda, M. Schmal, J. Catal. 178 (1998) 478

[22] S. A. Bocanegra, A. Guerrero-Ruiz, S. R. de Miguel, O. A. Scelza, Appl. Catal. A 277 (2003) 11

[23]H. Satoh, H. Taguchi, H. Miura, J. Jpn. Petrol. Inst. 38 (1995) 34

[24] M. A. Valenzuera, P. Bosch, G. Aguilar-Rios, B. Zapana, C. Maldonado, I. Shifter, J. Mol. Catal. 84 (1993) 177

[25] F. Z. Bentahar, J. P. Candy, J. M. Basset, F. Le Peltier, B. Didillon, Catal. Today, 66 (2001) 303

[26] G. J. Siri, J. M. Ramallo-Lopez, M. L. Casella, J. L. G. Fierro, F. G. Requejo, O. A. Ferretti, Appl. Catal. A 278 (2005) 239

[27] A. Vazquez-Zavala, A. Ostoa-Montes, D. Acosta, A. Gomez-Cortes, Appl. Surf. Sci. 136 (1998) 62

[28] A. Goguet, D. Schweich, J. P. Candy, J. Catal, 220 (2003) 280

[29] S. R. de Miguel, E. L. Jablonski, A. A. Castro, O. A. Scelza, J. Chem. Technol. Biotechnol. 75 (2000) 596

[30] C. L. Padro, S. R. de Miguel, A. A. Castro, O. A. Scelza, Catalyst Deactivation 1997 p-191

[31] O. A. Barias, A. Holmam, E. A. Blekkan, J. Catal. 158 (1996) 1

[32] P. Meriaudeau, A. Thangaraj, J. F. Dutel, C. Naccache, J. Catal. 167 (1997) 180

[33] M. A. Valenzuela, P. Bosch G. Aguilar-Rios, B. Zapata, H. Armendariz, P. Salas, I. Shifter, React. Kinet. Catal. Lett. 48 (1992) 121

[34] R. D. Cortright, J. A. Dumesic, J. Catal. 148 (1994) 771

[35] G. Aguilar-Rios, M. Valenzuela, P. Salas, H. Armenderiz, P. Bosch, G. Del Toro, R. Silva, V. Bertin, S. Castillo, A. Ramirez-Solis, I. Schifter, Appl. Catal. A 127 (1995) 65

[36] A. Berretta, L. Piovesan, P. Forzatti, J. Catal., 184 (1994) 455

[37] Y. K. Park, F. H. Ribeiro, G. A. Somorjai, J. Catal. 178 (1998) 66

[38] J. Llorca, N. Homs, J. Leon, J. Sales, J. L. G. Fierro, P. Ramirez de la Piscina, Appl. Catal. A 189 (1999) 77

[41] P. Biloen, F. M. Dautzenberg, W. M. H. Satcher, J. Catal. 50 (1977) 77

[42] F. H. Ribeiro, A. L. Bonivardi, C. Kim, G. A. Somorjai, J. Catal. 112 (1994) 186

[43] F. Zaera, D. Chrysostomou, Surf. Sci. 457 (2000) 89

[44] D. J. Burnett, A. M. Gabelnick, A. L. Marsh, D. A. Fischer, J. L. Gland, Surf. Sci. 553 (2004) 1

[45] D. Stacchiola, L. Burkholder, W. T. Tysoe, Surf. Sci. 542 (2003) 129

[46] J. M. Hill, R. D. Cortright, J. A. Dumesic, Appl. Catal. A 168 (1998) 9

[47] R. D. Cortright, J. M. Hill, J. A. Dumesic, Catal. Today 55 (2000) 213

[48] Y-L Tsai, Surf. Sci. 385 (1997) 37

Captions

Fig. 1. Schematic of the two-phase DH process assumed for the thermodynamic simulation.

Fig. 2. Effect of Sn and Zn additions to catalyst in normal dehydrogenation of propane: (a) Propane conversion (b) Selectivity for propylene. Reaction conditions: T = 500ºC, W/F = 0.678 g-cat·h/mol (W = 0.05 g), C_3H_8:He = 1:2, total feed rate = 90 ml/min. ○Pt/Al_2O_3, △ Pt/Zn-Al-O, ●Pt-Sn/Al_2O_3, ▲Pt-Sn/Zn-Al-O.

Fig. 3. Influence of Sn content on catalytic performance : (a) Pt-Sn/Al_2O_3 , (b)Pt-Sn/Zn-Al-O: T = 500 ºC , W/F = 0.678 g-cat·h/mol (W = 0.05 g) , C_3H_8:He = 1:2, total feed rate = 90 ml/min. ○Sn 0wt% , □Sn 2wt% , △Sn 5wt% , ＊Sn 7.5wt% , ◇Sn 10wt% , ×Sn 20wt%.

Fig. 4. Influence of Sn content on CO uptake : □Pt-Sn/Al_2O_3 , ○Pt-Sn/Zn-Al-O

Fig. 5. Influence of catalyst weight in normal dehydrogenation over Pt-Sn/Al_2O_3: (a) Propane conversion (b) Selectivity for propylene. Reaction conditions: T = 500ºC, C_3H_8:He = 1:2, total feed rate = 90 ml/min. ○W = 0.05 g (W/F = 0.678 g-cat·h/mol), □W = 0.1 g (W/F = 1.36 g-cat·h/mol), △W = 0.3 g (W/F = 4.07 g-cat·h/mol), ◇W = 0.5 g (W/F = 6.78g-cat·h/mol). Dashed line: equilibrium conversion.

Fig. 6. Calculated equilibrium conversions for isothermal propane dehydrogenation combined with selective hydrogen combustion. ○equilibrium for normal dehydrogenation, △

equilibrium when half of hydrogen is combusted, □equilibrium when all hydrogen is combusted.

Fig. 7. Catalytic activity test for propane dehydrogenation combined with selective hydrogen combustion: (a) Oxygen conversion (b) O-selectivity for H_2O (c) propane conversion (d) C-selectivity for propylene. Reaction conditions: T = 500ºC, W = 0.05 g, C_3H_8:C_3H_6:H_2:Air:He = 0.72:0.28:0.28:0.70:1.02 (O_2:H_2 = 1:2), total feed rate = 90 ml/min. ○Pt/Al_2O_3, △ Pt/Zn-Al-O, ●Pt-Sn/Al_2O_3, ▲Pt-Sn/Zn-Al-O, ■ Pt-Sn/SiO_2. Solid line: equilibrium conversion for normal dehydrogenation; Dashed line: equilibrium conversion for complete hydrogen combustion.

Fig. 8. Influence of O_2/H_2 feed ratio in propane dehydrogenation combined with selective hydrogen combustion over Pt-Sn/Zn-Al-O: (a) Propane conversion (b) Selectivity for propylene. Reaction conditions: T = 500ºC, W = 0.05 g, C_3H_8:C_3H_6:H_2:Air:He = 0.72:0.28:0.28:0.35-0.70:1.02-1.37 (O_2:H_2 = 1:2 - 1:4), total feed rate = 90 ml/min. ○O_2:H_2 = 1:2, △O_2:H_2 = 1:3, □O_2:H_2 = 1:4. Solid line: equilibrium conversion for normal dehydrogenation; Dashed line: equilibrium conversion when all or part of the hydrogen was combusted.

Fig. 9. Influence of catalyst weight in propane dehydrogenation combined with selective hydrogen combustion over Pt-Sn/Zn-Al-O: (a) Propane conversion (b) Selectivity for propylene. Reaction conditions: T = 500ºC, W = 0.05 g, C_3H_8:C_3H_6:H_2:Air:He = 0.72:0.28:0.28:0.47:1.25 (O_2:H_2 = 1:4), total feed rate = 90 ml/min. ○W = 0.05 g (W/F = 0.678 g-cat·h/mol), △W = 0.10 g (W/F = 1.36 g-cat·h/mol), □W = 0.20 g (W/F = 2.71 g-cat·h/mol).

Solid line: equilibrium conversion for normal dehydrogenation; Dashed line: equilibrium conversion when two thirds of the hydrogen was combusted.

Table 1 Catalyst properties

Catalyst	Pt loading [wt%]	Sn loading [wt%]	Support composition	Surface area[a] [m^2]	CO uptake[b] [ml/g-cat]
Pt/Al_2O_3	5.0	0.0	-	194	144
Pt/Zn-Al-O	5.0	0.0	Zn/Al = 1/3	175	79
$Pt\text{-}Sn/Al_2O_3$	5.0	7.5	-	175	46
Pt-Sn/Zn-Al-O	5.0	7.5	Zn/Al = 1/3	162	28
$Pt\text{-}Sn/SiO_2$	5.0	7.5	-	382	6.4

[a] Determined by BET surface area measurement

[b] Determined by CO adsorption measurement

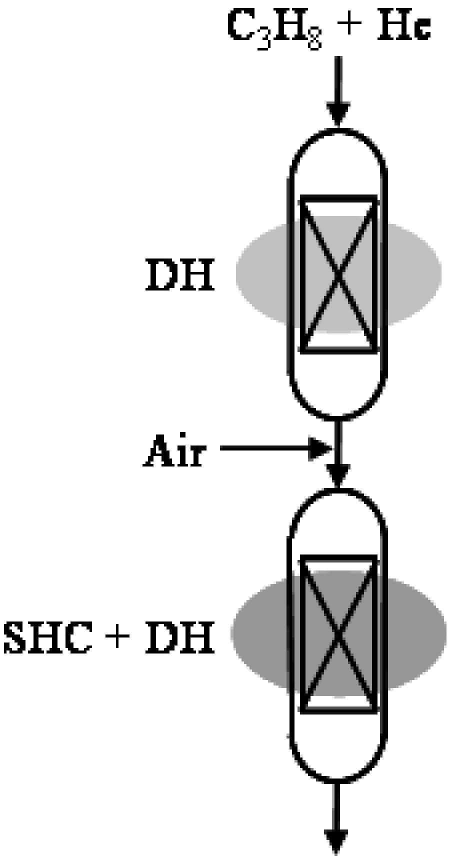

Fig. 1

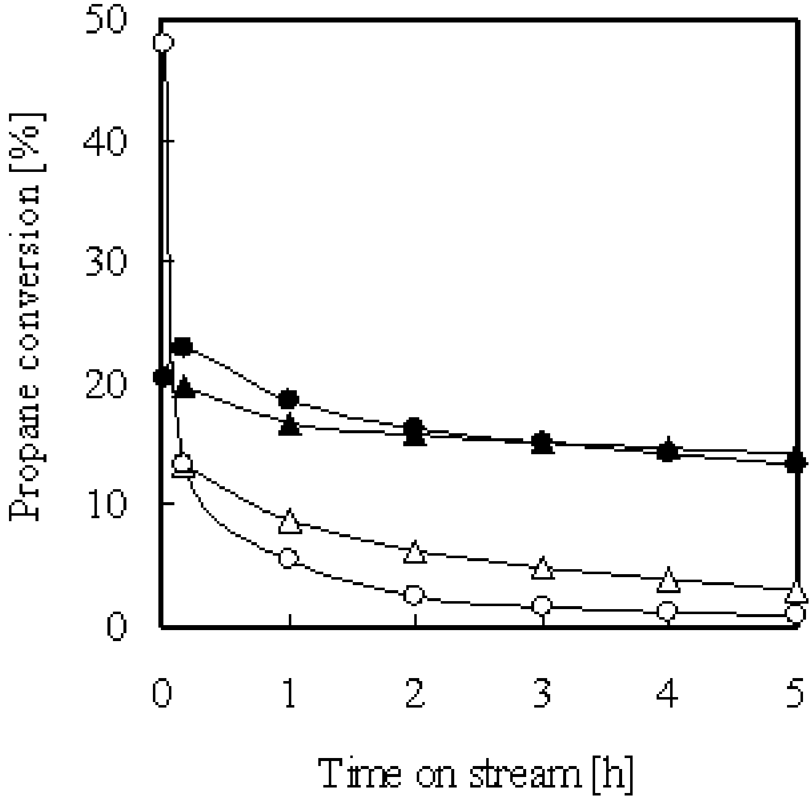

Fig. 2(a)

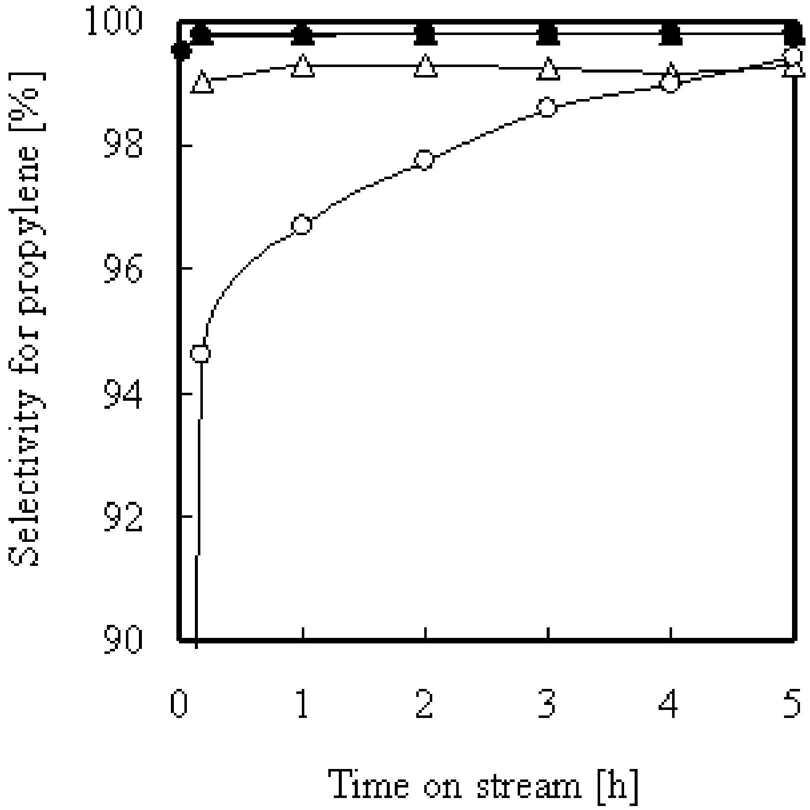
100
98
96
94
92
90
0
1
2
3
4
5
Selectivity for propylene [%]
Time on stream [h]

Fig. 2(b)

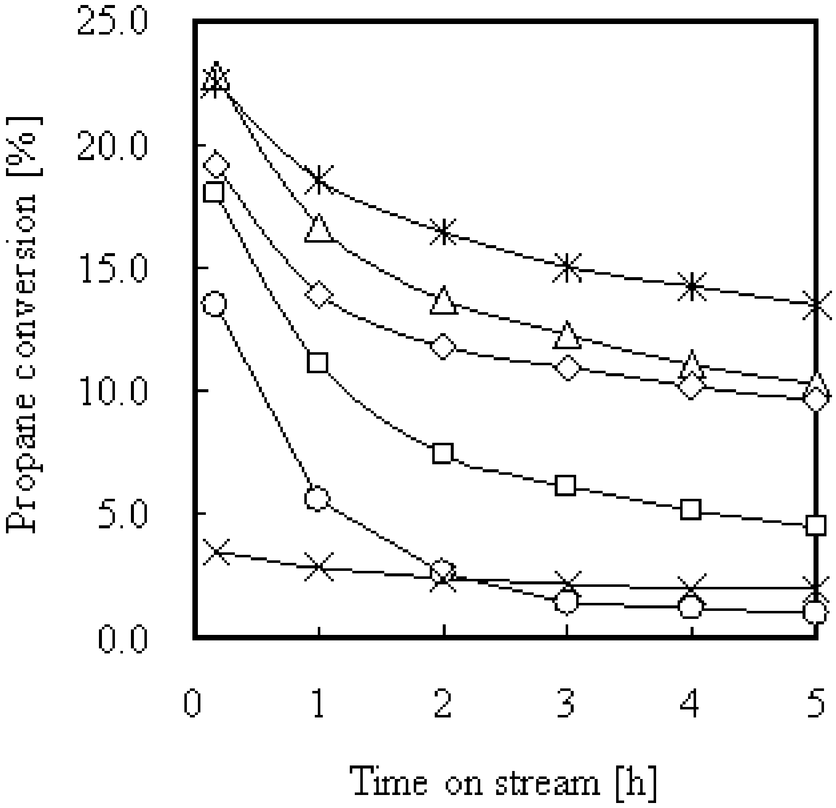
25.0
20.0
15.0
10.0
5.0
0.0
Propane conversion [%]
0
1
2
3
4
5
Time on stream [h]

Fig. 3(a)

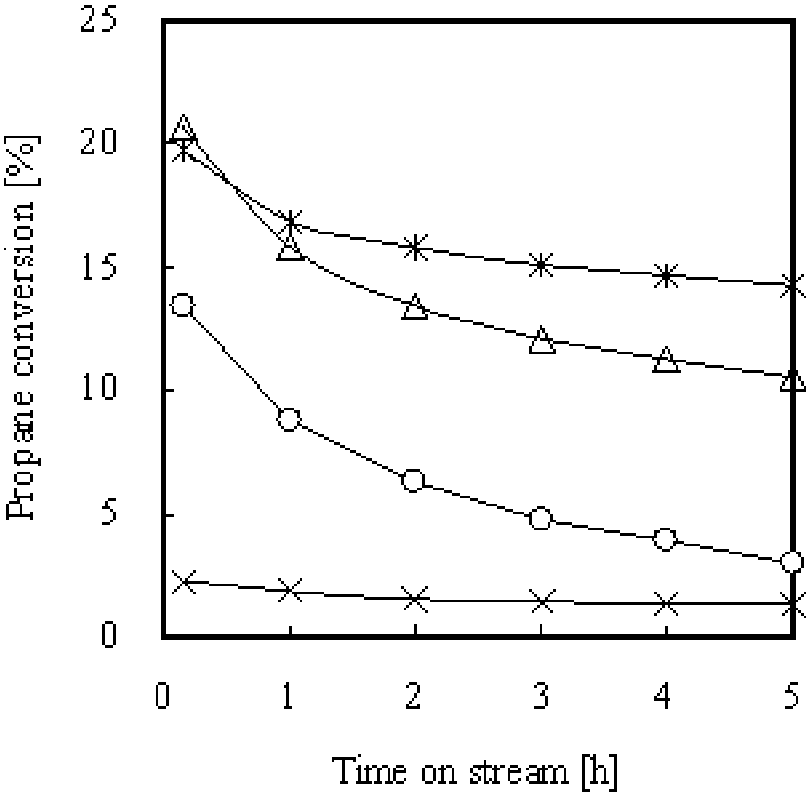

Fig. 3(b)

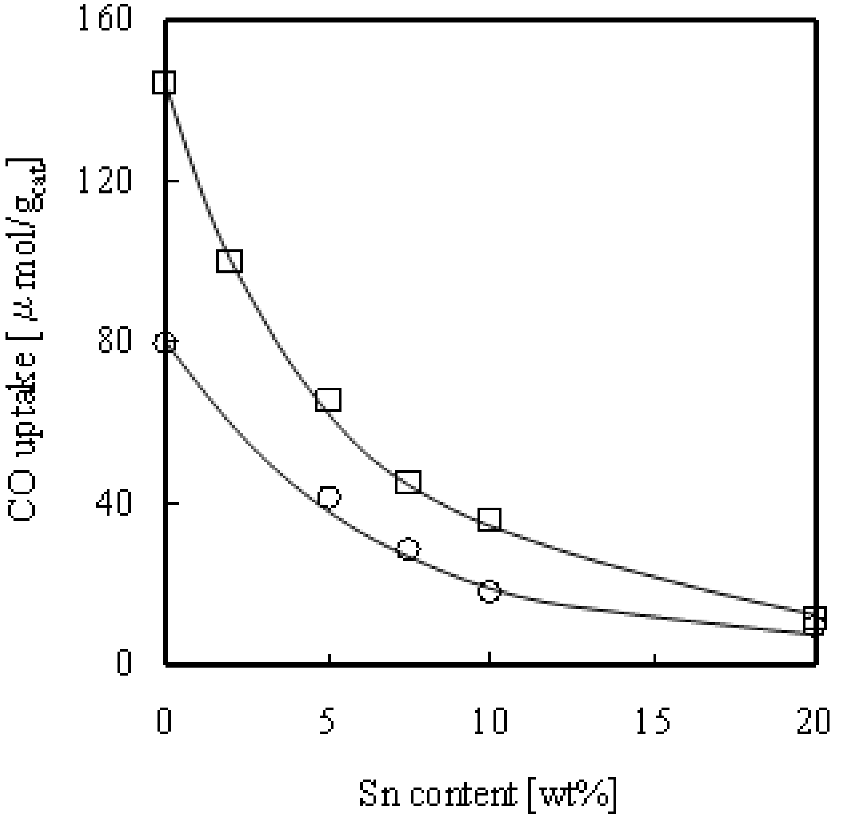

Fig. 4

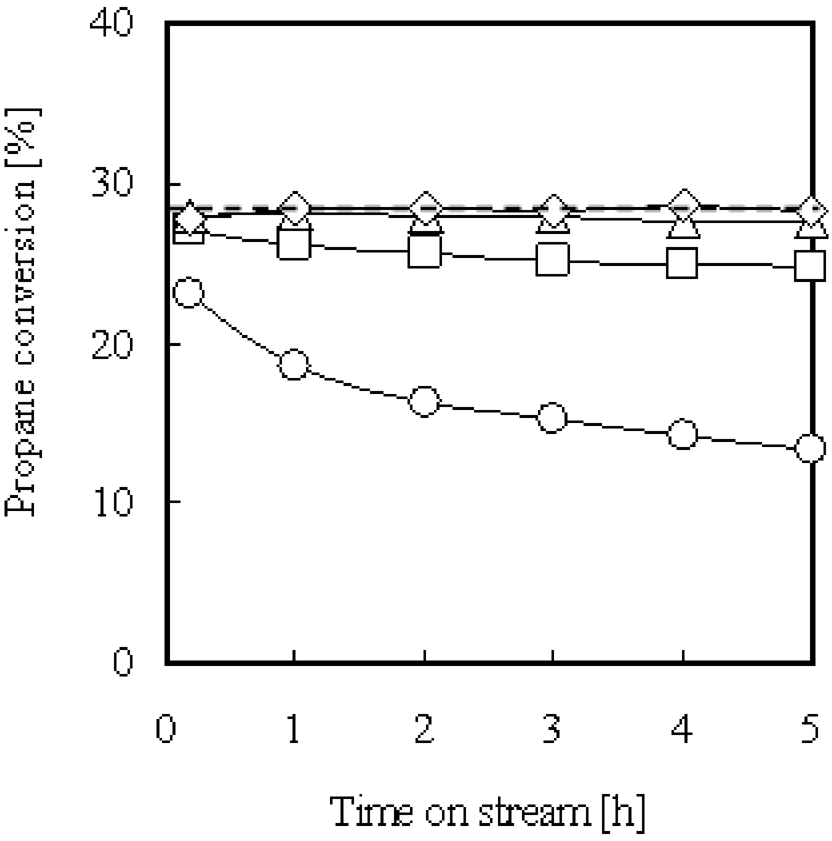

Fig. 5(a)

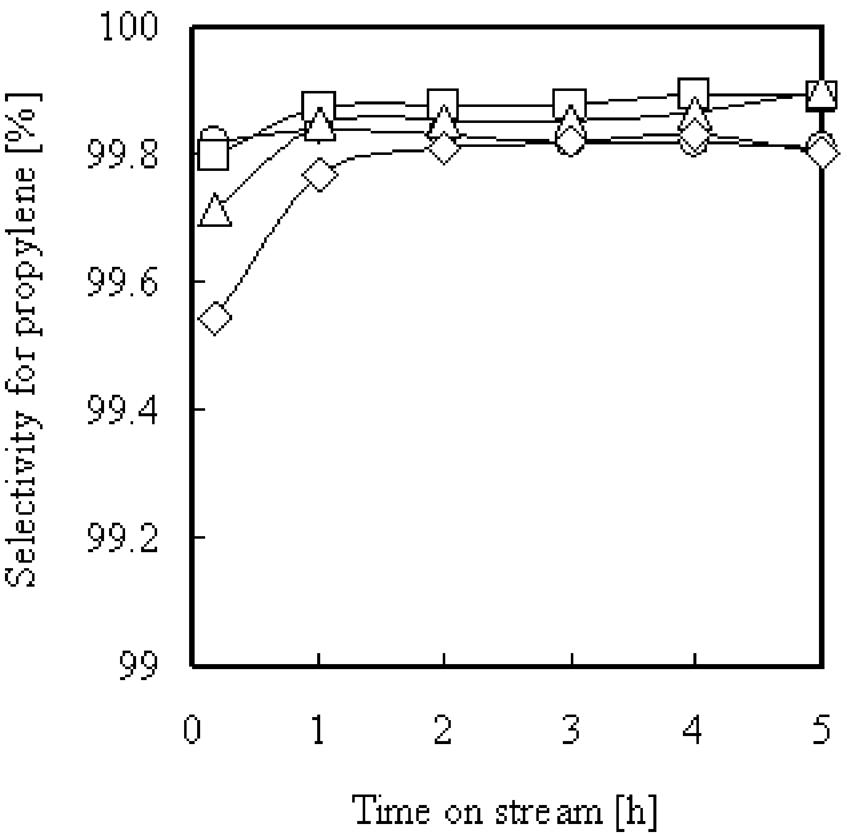
100
99.8
99.6
99.4
99.2
99
0
1
2
3
4
5
Selectivity for propylene [%]
Time on stream [h]

Fig. 5(b)

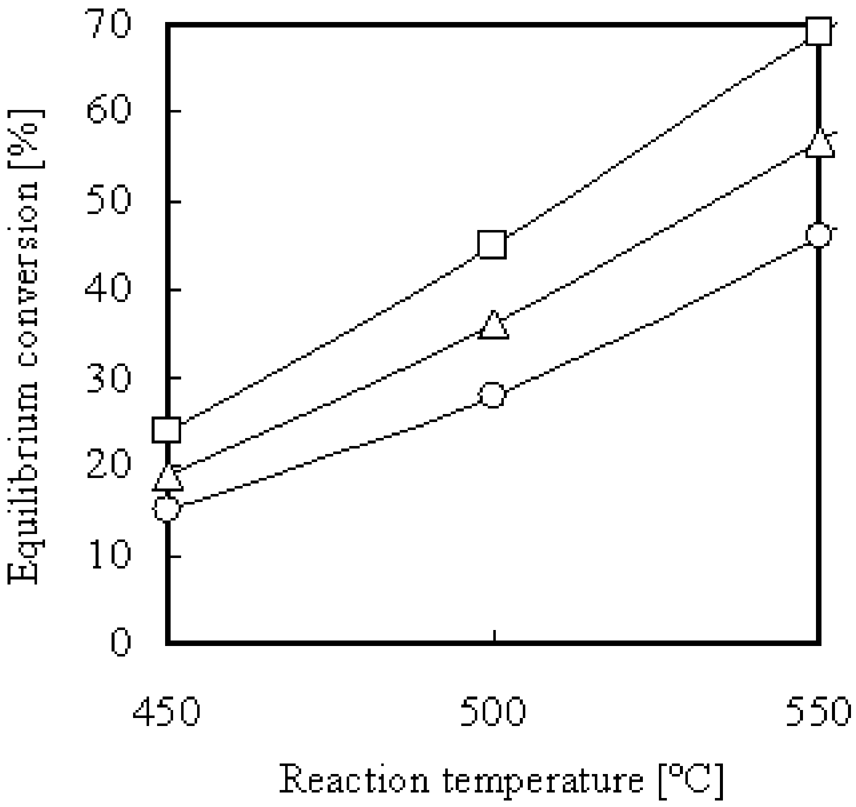
70
60
50
40
30
20
10
0
450
500
550
Equilibrium conversion [%]
Reaction temperature [°C]

Fig. 6

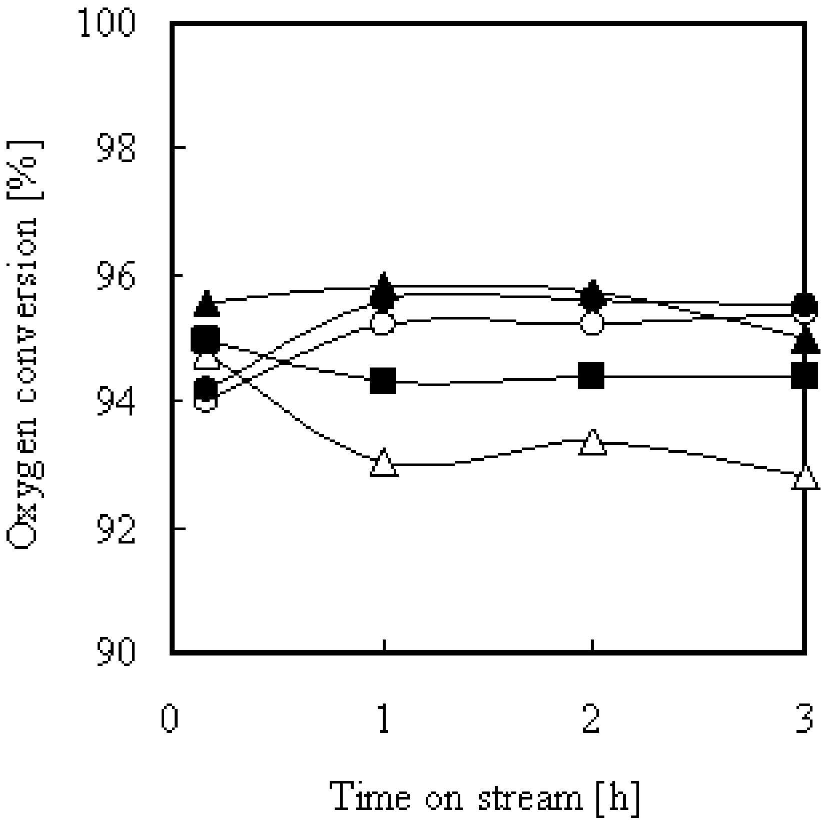

Fig. 7(a)

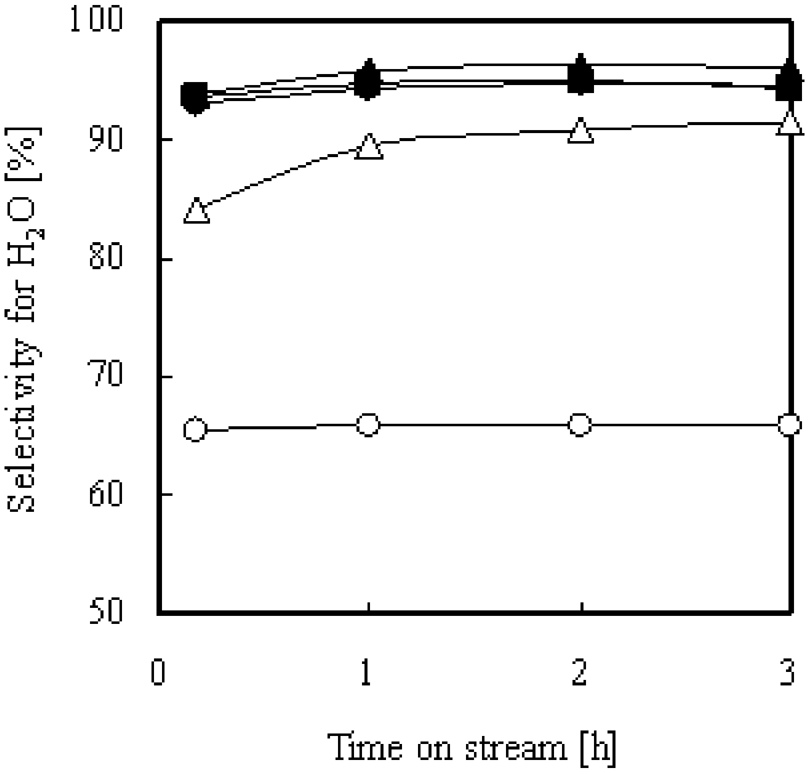

Fig. 7(b)

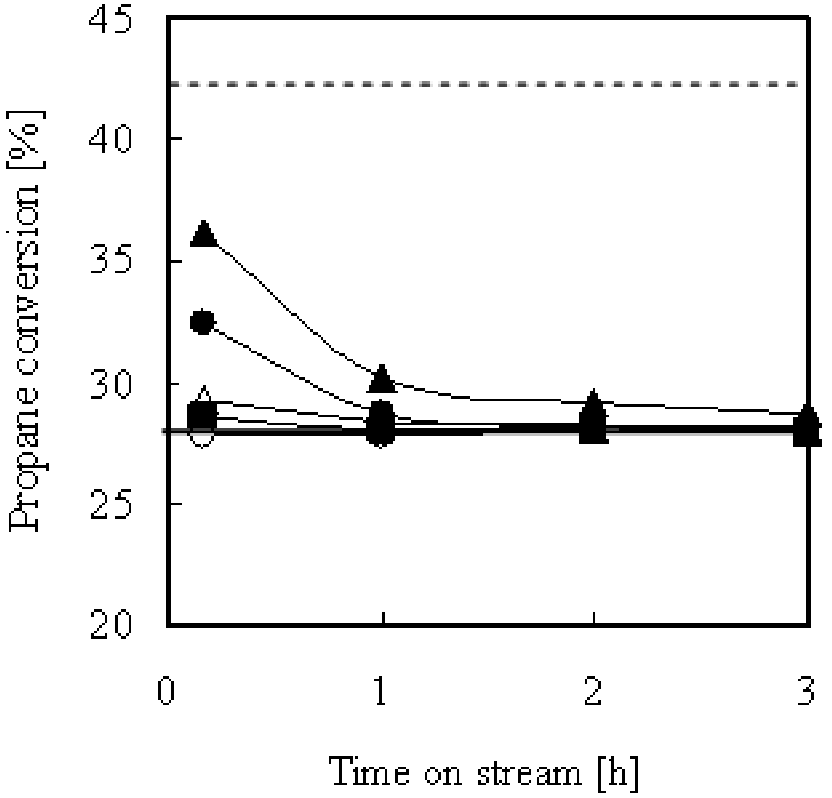

Fig. 7(c)

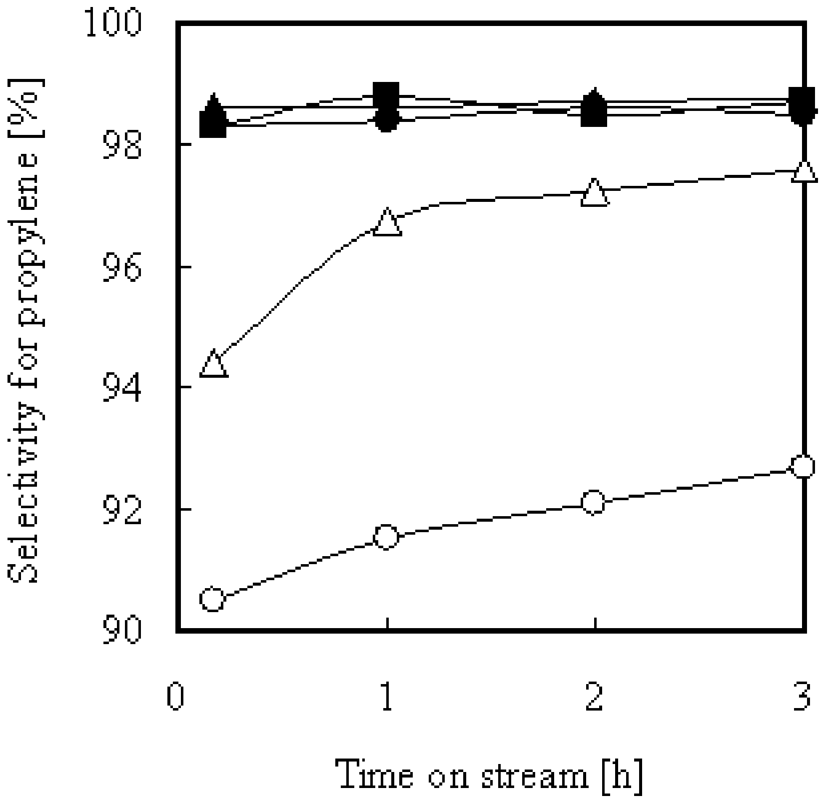
100
98
96
94
92
90
0
1
2
3
Selectivity for propylene [%]
Time on stream [h]

Fig. 7(d)

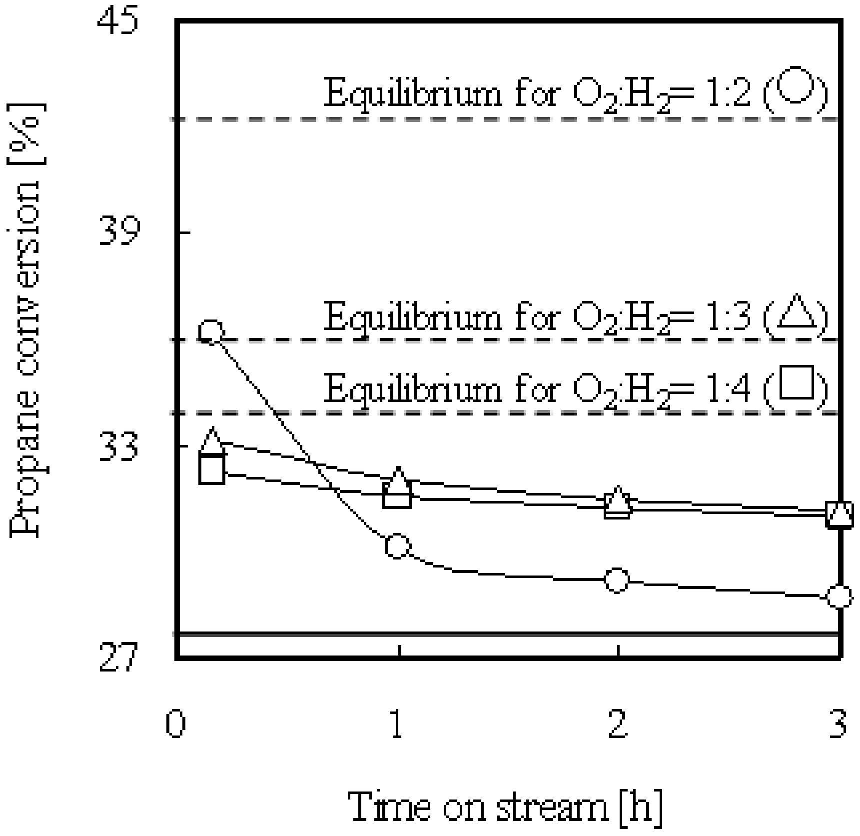
45
39
33
27
0
1
2
3
Propane conversion [%]
Time on stream [h]
Equilibrium for O2:H2= 1:2 (○)
Equilibrium for O2:H2= 1:3 (△)
Equilibrium for O2:H2= 1:4 (□)

Fig. 8 (a)

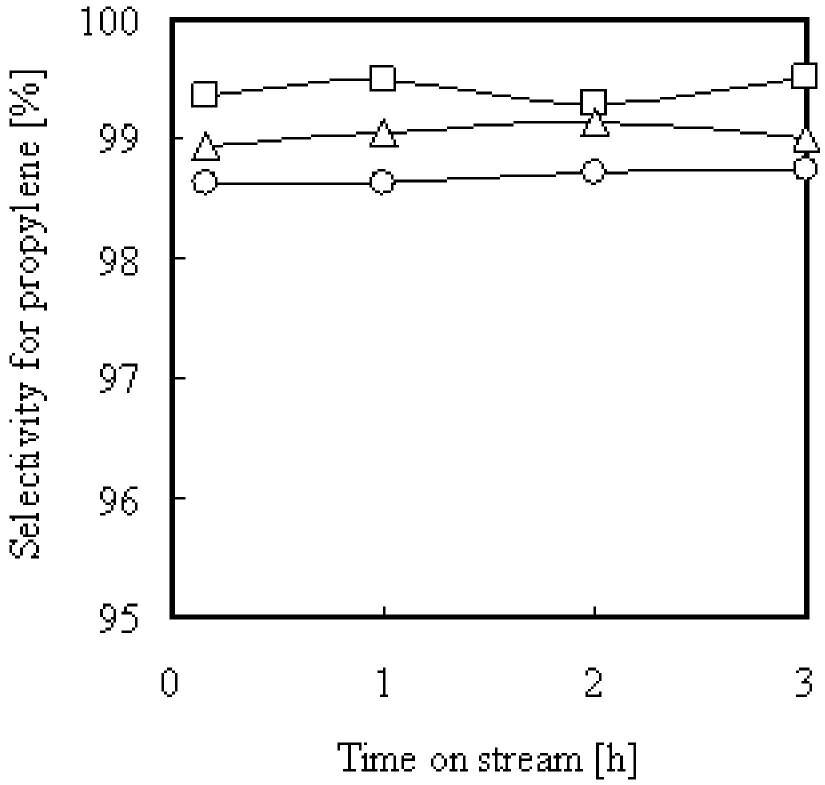
100
99
98
97
96
95
Selectivity for propylene [%]
0
1
2
3
Time on stream [h]

Fig. 8(b)

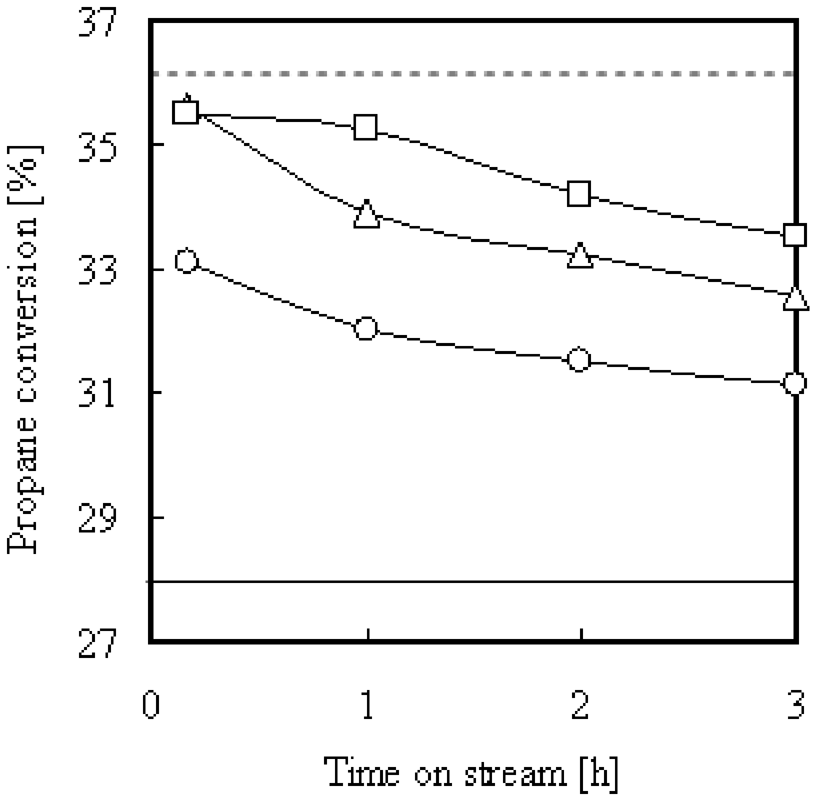

Fig. 9 (a)

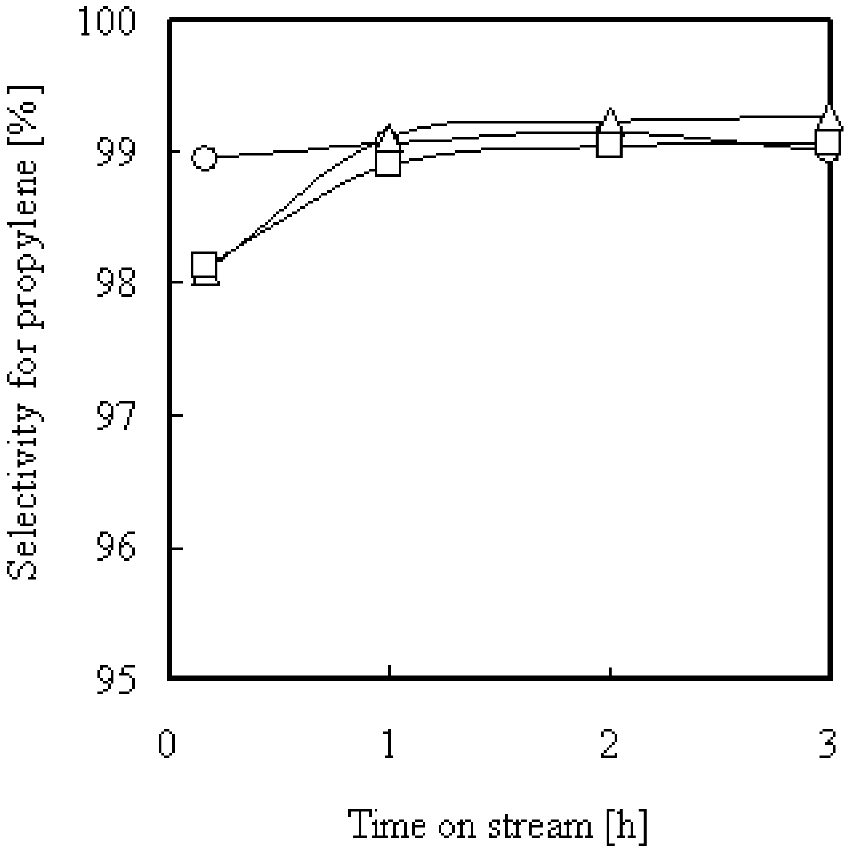
100
99
98
97
96
95
0
1
2
3
Selectivity for propylene [%]
Time on stream [h]

Fig. 9 (b)