Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 123 (2007) 151–157
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Formation of C4 species in the deactivation of a Pd/SiO_2 catalyst during the selective hydrogenation of acetylene

In Young Ahn, Ji Hoon Lee, Sang Seop Kum, Sang Heup Moon *

School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, San 56-1, Shillim-dong, Kwanak-ku, Seoul 151-744, Republic of Korea

Available online 12 March 2007

Abstract

The deactivation characteristics of Pd/SiO_2 in the selective hydrogenation of acetylene were correlated with changes in the amount of the C4 species produced. The amounts of butenes produced changed in parallel with the catalyst activity, indicating that the rate limiting step for butene production was the same as that for acetylene hydrogenation. On the other hand, the amount of 1,3-butadiene produced changed, showing a maximum with catalyst deactivation because 1,3-butadiene is an intermediate in the sequential reaction process which involves both the production and consumption of 1,3-butadiene. This was verified by a simultaneous TG/reaction experiment showing that 1,3-butadiene was a precursor of green oil. The catalyst showed a self-regenerative behavior in its activity and the amounts of C4 species produced during the early stage of deactivation because two opposite factors, which contributed to either the lowering or the promotion of activity, were involved in the process. A specific type of polymer species, produced during the initial period of deactivation, is proposed to be responsible for the promotion of catalyst activity.

Keywords: Acetylene hydrogenation; Pd catalyst; Deactivation; Green oil; 1,3-Butadiene; Butene

1. Introduction

Supported Pd catalysts are typically used in the selective hydrogenation of acetylene to remove acetylene from the ethylene stream from naphtha crackers [1–3]. In addition to hydrogenation, acetylene undergoes hydropolymerization, leading to the formation of not only various C4 compounds but higher hydrocarbons (green oil) on the catalyst surface. The influence of green oil on ethylene selectivity has been studied by several groups [4–7]. The amount of the oligomeric species deposited on the catalyst increases with decreasing H_2/acetylene ratio, resulting in decreased overall activity and ethylene selectivity [5]. In particular, surface coverage by hydrogen was found to be a crucial factor in catalyst deactivation by accumulated green oil [6,8]. Although the composition of green oil and the deactivation characteristics of catalysts have been investigated [5,9–11], the mechanism of deactivation during acetylene hydrogenation remains largely unknown.

Several authors have proposed a reaction mechanism that involves oligomer formation from dissociatively adsorbed acetylene [6,12–15]. Sarkany et al. [6] considered C4 formation to be an indication of green-oil production, but only the influence of total C4 species on catalyst deactivation was discussed. Recently, butadiene has been proposed to be a precursor candidate because it is volatile, easily polymerized, and is formed in appreciable amounts during acetylene hydrogenation [10,16]. In order to design improved catalysts that produce smaller amounts of green oil, it is necessary to understand the effects of the production of different C4 species during the deactivation process.

In this study, the deactivation mechanism was further investigated by introducing a novel method for verifying the precursor of green oil. In order to clarify the role of individual C4 species, a specially-designed apparatus combining a thermogravimetric instrument and gas chromatography (TG–GC) was used for *in situ* observation. *In situ* changes in catalyst properties, including deactivation rates, catalyst weight, and the amounts of C4 species produced, were monitored under different conditions of process parameters, including reaction temperature and H_2/acetylene ratio.

* Corresponding author.
E-mail address: shmoon@surf.snu.ac.kr (S.H. Moon).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.02.011

2. Experimental

2.1. Catalyst preparation

One weight percentage of Pd/SiO_2 catalyst was prepared using silica (D11-10 obtained from BASF, surface area = 145 m^2/g, pore volume = 0.42 ml/g, average pore diameter = 11.5 nm, particle size = 85–120 μm) as a support and $Pd(NH_3)_4(OH)_2$ as a Pd precursor by an ion exchange method reported in a previous study [17]. After drying overnight at 110 °C, the catalyst was calcined in air at 300 °C for 2 h, and then reduced in H_2 at 300 °C for 1 h prior to use. The Pd dispersion of catalyst, estimated by H/Pd ratio, is 0.45 after reduction at 300 °C [17].

2.2. Reaction tests and temperature programmed analysis (TGA)

For acetylene hydrogenation, 0.05 g samples of catalyst were tested under atmospheric condition in a quartz reactor. The reactant stream contained 4.1% acetylene in ethylene flowing at either 31 ml/min or 42 ml/min (space time: 4.19×10^{-3} min or 3.10×10^{-3} min), the H_2/acetylene ratio was 1 or 2, and the temperature was varied between 50 °C and 110 °C. The products were analyzed with an on-line GC (HP model 6890 series with FID) using a capillary column (HP-AL/S).

In situ experiments to monitor changes in the catalyst weight during reaction were conducted using a specially-designed apparatus combining a TG and GC. Catalyst weight was thermogravimetrically measured with a Magnetic Suspension Balance (Rubotherm) during the catalyst deactivation process. A 0.05 g sample of catalyst was loaded in a basket made of stainless-steel tubing (OD = 13 mm, ID = 10 mm, height = 9 mm) welded with a stainless-steel grid. The flow rate of the reactant stream was 31 ml/min, and the H_2/acetylene ratio and temperature were fixed at 1 °C and 70 °C, respectively. Contrary to the case of reaction tests conducted using a quartz reactor, a large fraction of the reactant stream bypassed the catalyst through the space between sample basket (OD = 13 mm) and the inner wall (ID = 24 mm) of TG instrument. The products were analyzed with an on-line GC and catalyst weights were simultaneously measured.

3. Results

3.1. Deactivation rates versus the H_2/acetylene ratio

Fig. 1 shows the deactivation of the catalyst during a reaction carried out at a fixed H_2/acetylene ratio of 1 and different temperatures (Pd/110 denotes Pd/SiO_2 used for the reaction at 110 °C). The absolute conversion increases with reaction temperature, as shown in Fig. 1(a). Catalyst activity, represented by the conversion normalized to the initial value, was monitored as a function of the total amount of converted acetylene, such that the deactivation characteristics could be compared based on the same load of the reaction. The catalyst was deactivated slowly during the initial period, but was

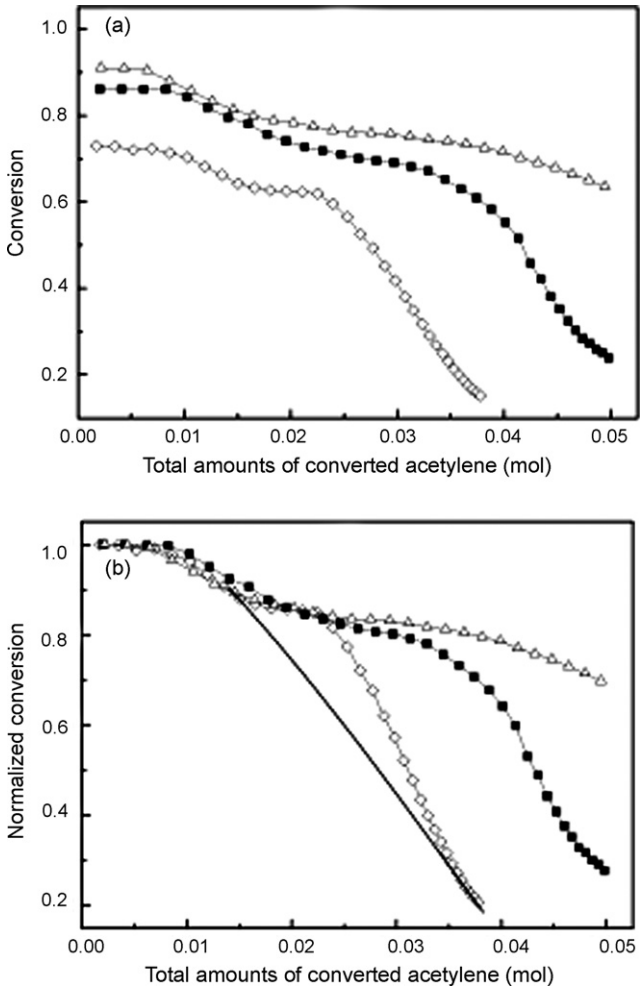

Fig. 1. Changes in the catalyst activity as a function of the total amounts of converted acetylene (H_2/acetylene = 1): Pd/110 (△); Pd/90 (■); Pd/70 (◇): (a) actual conversion; (b) normalized conversion.

deactivated at higher rates when the total amounts of converted acetylene were larger than *ca*. 0.025 mol. Catalyst deactivation in the later stage was accelerated when the reaction temperature was decreased from 110 °C to 70 °C [18].

Fig. 2 shows the mol fractions of different C4 species produced in a reaction at 70 °C. The amounts of butene species, including 1-butene, *trans*-2-butene, and *cis*-2-butene, decreased with the amounts of converted acetylene, in parallel with catalyst activity. On the other hand, the amounts of 1,3-butadiene started to increase when the amounts of converted acetylene were larger than 0.020 mol, but eventually decreased in the later stage after reaching a maximum at *ca*. 0.025 mol.

Fig. 3(a) shows simultaneous changes in the activity and weight of the catalyst during the reaction process, as measured using a combined TG/reactor unit. Due to the bypass of the reactant stream in the TG/reactor unit, the initial conversion, 50%, was lower than the 73% obtained in the reaction tests and displayed in Fig. 1(a) for Pd/70. The activity decreased together with an increase in catalyst weight, suggesting that the accumulation of green oil is a major contributor to the deactivation [5,6,9]. The gradients of the TG curve, which represent the rates of green-oil formation, were compared with

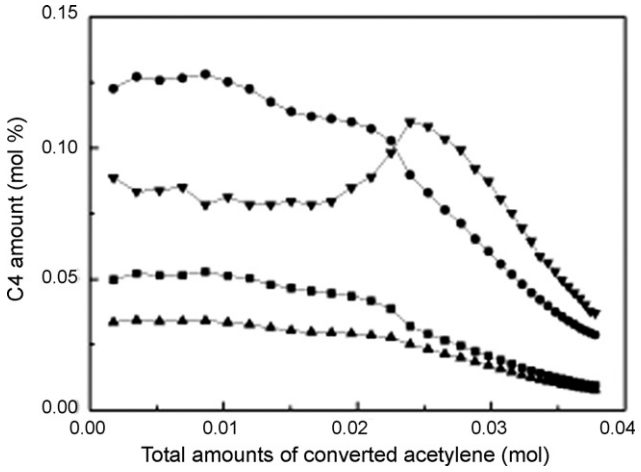

Fig. 2. Changes in the amount of C4 products as a function of the total amounts of converted acetylene (H_2/acetylene = 1, reaction temperature = 70 °C): 1-butene (●); *trans*-2-butene (■); *cis*-2-butene (▲); 1,3-butadiene (▼).

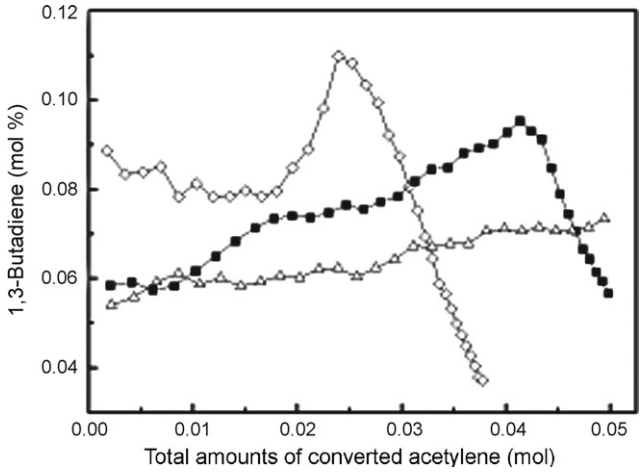

Fig. 4. Changes in the amount of produced 1,3-butadiene with the total amounts of converted acetylene (H_2/acetylene = 1): Pd/110 (△); Pd/90 (■); Pd/70 (◇).

the amounts of 1,3-butadiene produced in the reaction, as shown in Fig. 3(b). The results demonstrate a close similarity between the two parameters and, consequently, it can be concluded that 1,3-butadiene is a precursor of green oil, as has been proposed by other researchers [10,16].

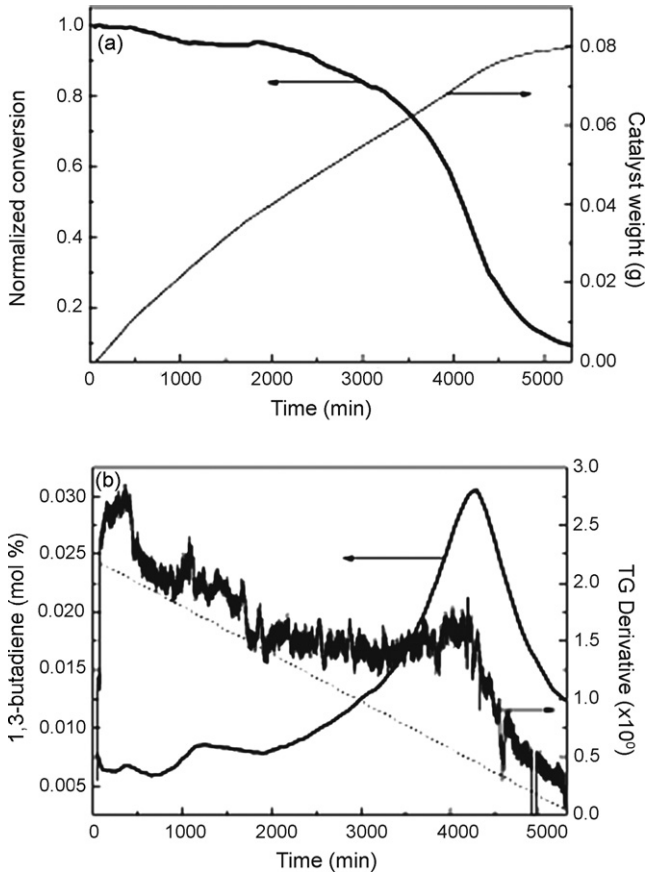

Fig. 3. Changes in the activity, catalyst weight, and the amount of produced 1,3-butadiene with process time, obtained by simultaneous TG/reaction experiments (H_2/acetylene = 1, reaction temperature = 70 °C): (a) the activity (normalized to initial conversion, 50%) and catalyst weight; (b) the amount of produced 1,3-butadiene and gradients in the TG curve.

The production of 1,3-butadiene was further investigated at different reaction temperatures. Fig. 4 shows that, when the reaction proceeds at lower temperatures, 1,3-butadiene is initially produced in larger amounts, reaching a maximum early in the reaction. It is noteworthy that the periods, i.e., the total amounts of converted acetylene, for the maximum butadiene production, shown in Fig. 4, nearly coincide with those for the rapid decrease in catalyst activity, shown in Fig. 1. In fact, this coincidence was demonstrated by a similarity between the gradients in the TG curve and the amounts of 1,3-butadiene produced (Fig. 3(b)).

Catalyst deactivation was retarded when the reaction was conducted at a high H_2/acetylene ratio of 2, obviously because green-oil formation was suppressed due to increased supply of hydrogen [5,6,8]. However, catalyst deactivation followed a characteristic pattern. Fig. 5 shows that the activity was recovered after the initial drop and reached a maximum before it was significantly decreased in the later stage. Such a self-regenerative behavior in activity was more distinct and the interim maximum activity was observed at earlier periods when the reaction proceeded at lower temperatures.

Fig. 6 shows the selectivity for ethylene formation and the amounts of C4 species, which were obtained at an H_2/acetylene ratio of 2. The ethylene selectivity increased after the total amounts of converted acetylene were larger than *ca*. 0.05 mol. According to Sarkany et al. [9,19], carbonaceous materials present on Pd sites reduce the hydrogen availability and enhance the steric hindrance on the catalyst surface, which results in the improvement of the ethylene selectivity. Even though carbonaceous deposits were assumed to be inactive for acetylene hydrogenation, they could modify the ethylene selectivity by diminishing the average ensemble size available for the reaction [20,21]. The amounts of C4 species also changed in a regenerative manner, although 1,3-butadiene followed an opposite trend to butenes. In fact, a close examination of Fig. 1, which was obtained at an H_2/acetylene ratio of 1, reveals that the same regenerative behavior is also present, although it is less remarkable than at an H_2/acetylene ratio of 2.

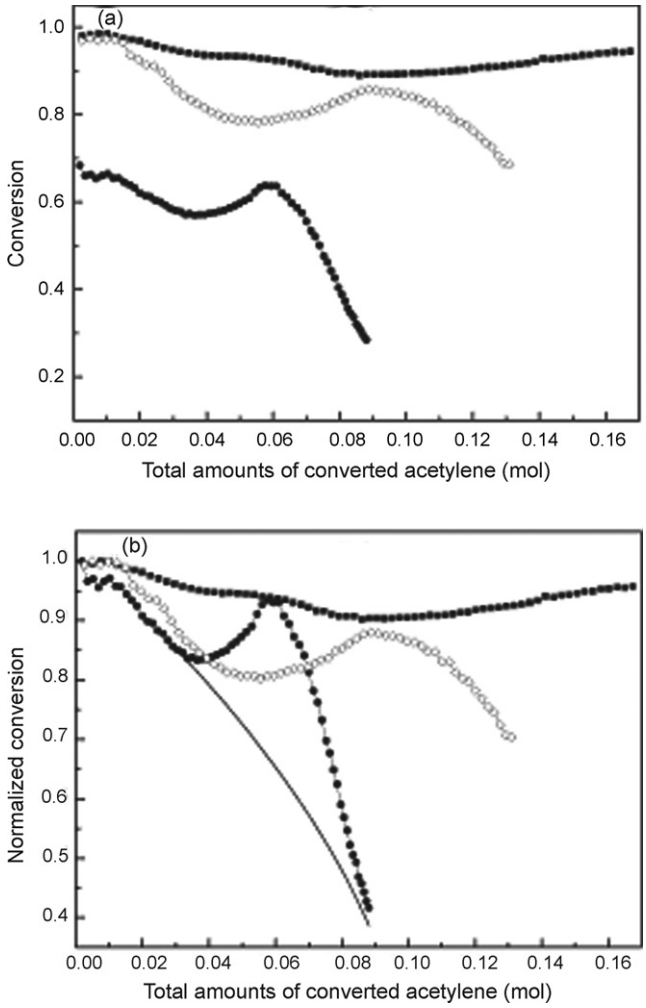

Fig. 5. Changes in the catalyst activity as a function of the total amounts of converted acetylene (H_2/acetylene = 2): Pd/90 (■); Pd/70 (◇); Pd/50 (●): (a) actual conversion; (b) normalized conversion.

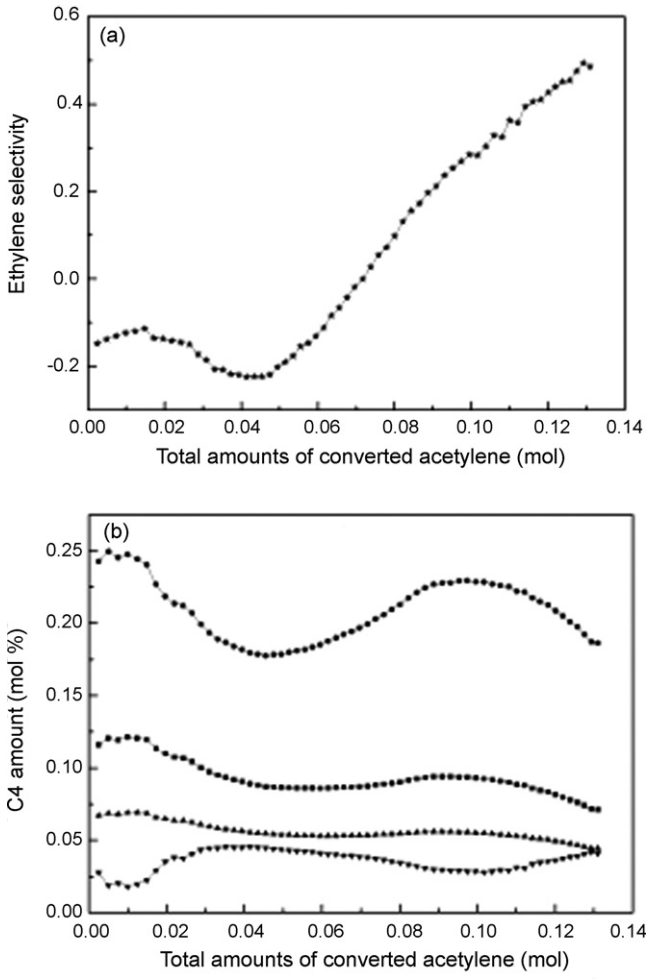

Fig. 6. Changes in the ethylene selectivity and amount of C4 products as a function of the total amounts of converted acetylene (H_2/acetylene = 2, reaction temperature = 70 °C): ethylene (★); 1-butene (●); *trans*-2-butene (■); *cis*-2-butene (▲); 1,3-butadiene (▼): (a) ethylene selectivity; (b) C4 production.

3.2. Changes in C4 production with the conversion

To further investigate the relationship between catalyst activity and C4 production, the amounts of C4 species produced at an H_2/acetylene ratio of 1 were plotted as a function of catalyst activity, denoted as ''conversion'' in Fig. 7. Because the catalyst was deactivated during the reaction, the high conversions in the figure correspond to the high activities of a relatively fresh catalyst while the low conversions to the low activities of a used catalyst.

The amounts of produced butenes were linearly dependent on the conversion and fell on the same correlation lines, independent of reaction temperature, suggesting that the rates of butadiene hydrogenation, leading to the production of butenes, were directly correlated with the activity of the catalyst. Contrary to the case of butenes, the amounts of 1,3-butadiene changed in a characteristic manner, as shown in Fig. 7(b). That is, the production of 1,3-butadiene was promoted by catalyst deactivation during the early stage of the reaction, but was eventually retarded along with the catalyst activity when the catalyst was deactivated to a significant extent.

Fig. 8 shows a plot of butene production obtained at an H_2/acetylene ratio of 2. The deactivation rates showed a self-regenerative pattern during the initial stage of catalyst deactivation, represented by regions I, II, and III. That is, the catalyst was initially deactivated, along with a decrease in butene production. However, after a certain period in the early stage, the catalyst was rejuvenated and the production of butenes was enhanced until the catalyst was again deactivated, showing a linear relationship between conversion and butene production. It is noteworthy, particularly in the case of 1-butene, that the correlation line after the rejuvenation step deviated significantly from the original one at the start of the reaction. The regenerative pattern was also observed for the production of 1,3-butadiene (data are not shown here), although, in this case, 1,3-butadiene production was retarded as the activity was recovered in the same regions.

Consequently, the above results can be summarized as follows. After use for a certain period in the early stage of the reaction, the catalyst is rejuvenated to the extent that the production of butenes is promoted and that of 1,3-butadiene is suppressed. The catalyst is eventually deactivated in the later

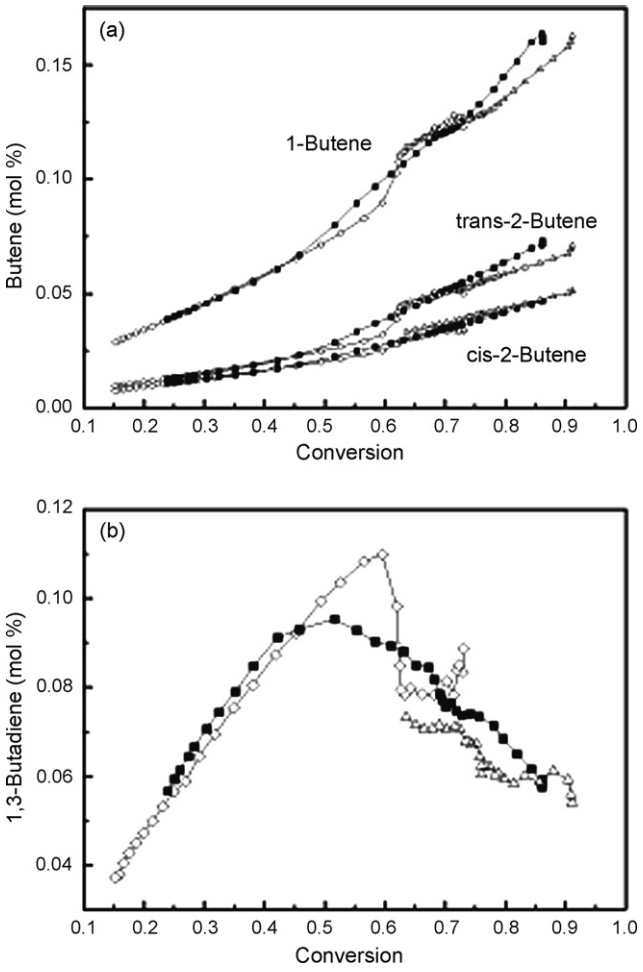

Fig. 7. Changes in the amount of produced C4 species with catalyst deactivation (H_2/acetylene = 1): Pd/110 (△); Pd/90 (■); Pd/70 (◇): (a) butene production; (b) 1,3-butadiene production.

stage, following the same general trend as observed for an H_2/acetylene ratio of 1.

4. Discussion

4.1. Maximum production of 1,3-butadiene

Fig. 9 shows the reaction steps involved in acetylene hydrogenation and catalyst deactivation during the process. Steps 1 and 2 are the major reactions involved in forming ethylene and ethane by the selective and full hydrogenation of acetylene, respectively [12,13]. Acetylene is also converted to 1,3-butadiene (Step 3), which is either hydrogenated to butenes (Step 4) or converted to green oil by insertion of C2 units (Step 5). 1,3-Butadiene was confirmed to be a precursor of green oil (Fig. 3). Accordingly, Steps 2 and 4 lower ethylene selectivity and Step 5 contributes to catalyst deactivation. The fractional amounts of green oil, consisting of polymers in the range of C_8 and C_{10} [9], can be removed from the catalyst surface by vaporization at high temperatures (Step 6).

The linear correlation between the amounts of butenes produced and acetylene conversion, observed in Figs. 7(a) and 8, indicates that the rate limiting step for the hydrogenation of

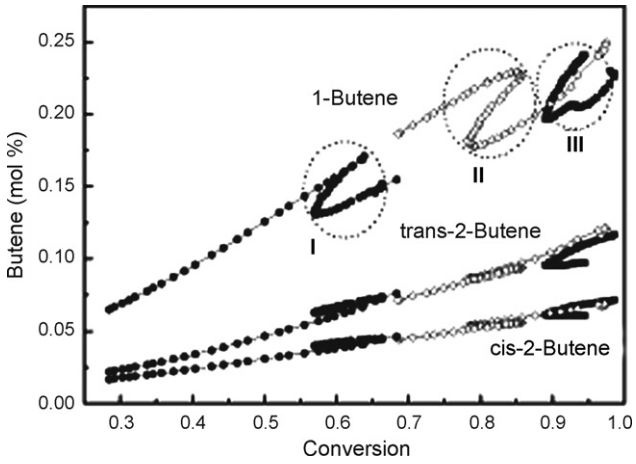

Fig. 8. Changes in the amount of butenes with catalyst deactivation (H_2/acetylene = 2): Pd/90 (■); Pd/70 (◇); Pd/50 (●).

1,3-butadiene to produce butenes (Step 4) is the same as that for the hydrogenation of acetylene (Step 1) [20]. Hydrogenation activity is decreased as the catalyst is deactivated due to the accumulation of green oil, which is accelerated when the reaction proceeds at low temperatures (Fig. 1).

Unlike the case of butenes, the amounts of 1,3-butadiene change showing a maximum with the conversion (Fig. 7(b)). As 1,3-butadiene is an intermediate in the consecutive reaction process comprising Steps 3, 4, and 5, the amounts of 1,3-butadiene produced should be determined by the relative rates of Step 3, which produces 1,3-butadiene, and Steps 4 and 5, which consume 1,3-butadiene. Between Steps 4 and 5, the former is a major rate-determining step for butadiene consumption because the latter, which is responsible for catalyst deactivation, proceeds at much lower rates, on a scale of several months, than the former, which proceeds on the scale of process time.

When the catalyst is deactivated, the rates for Steps 3 and 4 are decreased simultaneously, but the former step is retarded to a greater extent than the latter, such that 1,3-butadiene accumulates in the process. This trend is reasonable because Step 4 involves hydrogenation, which is directly affected by catalyst deactivation, while Step 3 involves the dimerization of acetylene, which is less sensitive to catalyst deactivation because the acetylenic species are adsorbed to the catalyst more strongly than hydrogen [22,23].

When the catalyst is covered with large amounts of green oil at the later stage of deactivation, the rates for both Steps 3 and 4 are significantly decreased and eventually the amounts 1,3-butadiene are decreased in parallel with catalyst activity,

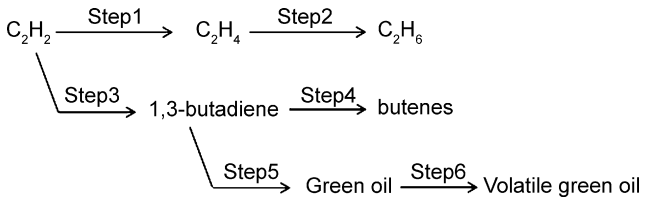

Fig. 9. Reaction steps involved in acetylene hydrogenation process.

similar to the case of butenes. The maximum amounts of 1,3-butadiene are observed at early reaction periods, i.e., at smaller total amounts of converted acetylene, when the reaction temperature is lowered (Fig. 4). This trend is consistent with the above explanation. That is, the accumulation of 1,3-butadiene is accelerated under the severe reaction conditions because the catalyst is significantly deactivated and, accordingly, Step 4 is retarded to a greater extent. This scenario also explains the opposite trends for the amounts of butenes and 1,3-butadiene (Fig. 6(b)), in that an increase in butene production is accompanied by a decrease in 1,3-butadiene production.

4.2. Regenerative behavior of the catalyst activity

The catalyst showed self-regenerative behavior in its activity and the amounts of C4 species produced during deactivation, which was distinct at an H_2/acetylene ratio of 2 (Figs. 5, 6(b), and 8) and less distinct at an H_2/acetylene ratio of 1 (Fig. 1). These results strongly suggest that two opposite factors are involved in the deactivation process. One is obviously the formation of green oil which accumulates on the catalyst eventually lowering its activity. The other factor promotes activity, at least during the initial period in the early stage of catalyst deactivation, although the mechanism of this aspect of the reaction is not completely understood. This factor will be discussed more extensively below. At the early stage of catalyst deactivation, the detrimental effect of green-oil accumulation is dominant such that the overall activity is decreased with the reaction period [5,6,9]. As the deactivation proceeds, the contribution of the promotional factor to the overall activity is gradually increased until the activity reaches a maximum and then decreased afterwards.

To elaborate on the above explanation, subsidiary lines were added to the deactivation curves of Figs. 1(b) and 5(b), although the lines carry no quantitative significance. The added lines represent catalyst deactivation due to green-oil accumulation, which is accelerated in the later stage of the reaction because the average molecular weight of the deposited polymers is increased [24–26]. The difference between the deactivation curve and the added line represents the promotional effect due to the other factor, which changes showing a maximum with the reaction period.

The regenerative behavior was also observed in the plot of the amounts of butenes versus the conversion (Fig. 8). The following two aspects are noteworthy in the results. One is that the catalyst was rejuvenated after use for a certain period, independent of the initial activity at the start of the reaction. The other is that the rejuvenated catalyst was deactivated again following a correlation line that deviated from the initial one such that larger amounts of butenes, particularly 1-butene, were produced, compared to those produced at the same conversion before the rejuvenation.

If the catalyst sites were rejuvenated simply by the removal of the accumulated green oil from the surface, then the amounts of butenes produced would be increased along the original correlation line. The deviation in the second correlation line from the initial one suggests that new hydrogenation sites were generated during the rejuvenation process. Accordingly, it is proposed in this study that a specific type of green oil, which is produced during the initial period of catalyst deactivation, is responsible for the additional hydrogenation activity.

In fact, a previous study revealed that carbonaceous deposits produced on Pd during acetylene hydrogenation acted as bridges promoting hydrogen spillover from the Pd to the support [27,28]. Another study proposed that a ‘‘reactive surface polymer’’ produced in acetylene hydrogenation could spillover from the support to the Pd sites to furnish hydrogen atoms for the hydrogenation steps [6]. A study made with Pt for hydrocarbon conversion processes reported that carbonaceous deposits produced on Pt were capable of holding 10 times as much hydrogen as the metal itself [29–31]. Such beneficial effects of carbonaceous deposits on the catalytic behavior of the metallic surface were reviewed by Webb [32].

Green oil and/or carbonaceous deposits, which are produced by the hydropolymerization of acetylene, have been found to consist of paraffins and olefins ranging from about C_8 and C_{24} with an H/C ratio of about 1.9 [4,8]. Fig. 8 indicates that the polymer species responsible for the additional hydrogenation activity started to be produced after the catalyst had been deactivated to a certain extent. The nature of the specific polymer species and the mechanism of hydrogen supply by them are subjects of future study.

5. Conclusion

The deactivation characteristics of Pd/SiO_2 in acetylene hydrogenation were studied by simultaneously monitoring changes in catalyst activity and the amounts of C4 species produced in the reaction. The following conclusions can be made, based on the results:

1. The rates of deactivation were accelerated when the reaction temperature and the H_2/acetylene were lowered. 1,3-Butadiene was confirmed to be a precursor of green oil, which was responsible for catalyst deactivation.
2. The amounts of butenes produced in the reaction varied in parallel with catalyst activity, suggesting that the rate limiting step for butene production was the same as that for acetylene hydrogenation.
3. The amounts of 1,3-butadiene, produced as an intermediate in the sequential reaction process for converting acetylene to either butenes or green oil, changed showing a maximum with catalyst deactivation. This result can be explained as follows. At an early stage of catalyst deactivation, the rates of butadiene hydrogenation were retarded to a greater extent than those for acetylene dimerization and, consequently, the amounts of 1,3-butadiene produced were increased with catalyst deactivation. At the late stage of the deactivation, both steps of the sequential process were significantly retarded and therefore the production of 1,3-butadiene was also retarded in parallel with catalyst activity.
4. The catalyst showed a self-regenerative behavior in its activity and the amounts of C4 species produced in the early stage of catalyst deactivation, which suggests that two

factors, contributing to the activity in opposite ways, were involved in the deactivation process. One was the accumulation of green oil on the catalyst surface, which lowered its activity. The other, proposed in this study, involves the production of a specific type of polymer, which has the capability to store and spillover hydrogen and consequently contribute to the promotion of activity.

Acknowledgements

This study was supported by BASF Aktiengesellschaft, Germany, the Brain Korea 21 project and the Korea Science and Engineering Foundation (KOSEF) through the National Research Laboratory Program of Ministry of Science and Technology (No. M10318000095-04J0000-02810), Korea.

References

[1] C.M. Pradier, M. Mazina, Y. Berthier, J. Oudar, J. Mol. Catal. 89 (1994) 211.
[2] A.H. Weiss, B.S. Gambhir, R.B. La Pierre, W.K. Bell, Ind. Eng. Chem. Proc. Des. Dev. 16 (1977) 352.
[3] H.R. Aduriz, P. Bodnariuk, M. Dennehy, C.E. Gigola, Appl. Catal. 58 (1990) 227.
[4] J.P. Boitiaux, J. Cosyns, M. Derrien, G. Leger, Hydrocarbon Process. 64 (1985) 51.
[5] G.C. Battiston, L. Dalloro, G.R. Tauszik, Appl. Catal. 2 (1982) 1.
[6] A. Sarkany, L. Guczi, A.H. Weiss, Appl. Catal. 10 (1984) 369.
[7] D.K. Lee, Korean J. Chem. Eng. 7 (1990) 233.
[8] M. Larsson, J. Jansson, S. Asplund, J. Catal. 178 (1998) 49.
[9] A. Sarkany, A.H. Weiss, T. Szilagyi, P. Sandor, L. Guczi, Appl. Catal. 12 (1984) 373.
[10] S. Asplund, J. Catal. 158 (1996) 267.
[11] P. Albers, K. Seibold, G. Prescher, H. Muller, Appl. Catal. A 176 (1999) 135.
[12] J. Margitfalvi, L. Guczi, A.H. Weiss, React. Kinet. Catal. Lett. 15 (1980) 4.
[13] J. Margitfalvi, L. Guczi, A.H. Weiss, J. Catal. 72 (1981) 185.
[14] A. Borodzinski, A. Cybulski, Appl. Catal. A 198 (2000) 41.
[15] A. Molnar, A. Sarkany, M. Varga, J. Mol. Catal. A 173 (2001) 185.
[16] M. Larsson, J. Jansson, S. Asplund, J. Catal. 162 (1996) 365.
[17] I.Y. Ahn, W.J. Kim, S.H. Moon, Appl. Catal. A 308 (2006) 75.
[18] J.T. Wehrli, D.J. Thomas, M.S. Wainwright, D.L. Trimm, N.W. Cant, Catalyst Deactivation, Studies in Surface Science and Catalysis, Elsevier Science BV, 1991，p. 203.
[19] A. Sarkany, A. Horvath, A. Beck, Appl. Catal. 229 (2002) 117.
[20] A. Borodzinski, Catal. Lett. 63 (1999) 35.
[21] J. Houzvicka, R. Pestman, V. Ponec, Catal. Lett. 30 (1995) 289.
[22] Y.H. Park, G.L. Price, Ind. Eng. Chem. Res. 31 (1992) 469.
[23] E.W. Shin, J.H. Kang, W.J. Kim, J.D. Park, S.H. Moon, Appl. Catal. A 223 (2002) 161.
[24] W.J. Kim, E.W. Shin, J.H. Kang, S.H. Moon, Appl. Catal. A 251 (2003) 305.
[25] S. Srihiranpullop, P. Praserthdam, Korean J. Chem. Eng. 20 (2003) 1017.
[26] S. Srihiranpullop, P. Praserthdam, T. Mongkhonsi, Korean J. Chem. Eng. 17 (2000) 548.
[27] A.H. Weiss, S. Leviness, V. Nair, L. Guczi, A. Sarkany, Z. Schay, in: Proceedings of the 8th International Congress on Catalysis, vol. 5, 1984, p. 591.
[28] S. Leviness, V. Nair, A.H. Weiss, Z. Schay, L. Guczi, J. Mol. Catal. 25 (1984) 131.
[29] S.J. Thomson, G. Webb, J. Chem. Soc., Chem. Commun. 13 (1976) 526.
[30] G.A. Somorjai, S.M. Davis, Chemtech (1983) 502.
[31] S.M. Davis, F. Zaera, G.A. Somorjai, J. Catal. 77 (1982) 439.
[32] G. Webb, Catal. Today 7 (1990) 139.