



Liquid-phase hydrogenation of maleic anhydride over Pd/SiO₂: effect of tin on catalytic activity and deactivation

Seong Moon Jung*, Eric Godard, Sang Yun Jung, Kwang-Cheon Park, Jung Uk Choi

*Process Technology Research and Development, LG Chem. Ltd. Research Park, P.O. Box 61,
Yu Seong, Science Town, Daejeon 305-380, South Korea*

Received 29 August 2002; received in revised form 29 August 2002; accepted 6 December 2002

Abstract

The promotional effects of Sn on Pd/SiO₂ have been investigated by the comparison of Pd/SiO₂ and Pd-Sn/SiO₂ activity in the hydrogenation of maleic anhydride and succinic anhydride to γ -butyrolactone, and XPS measurement. When reduced at 200 °C, both catalysts showed a strong dependence on the reactants, and the addition of tin led to an increase of γ -butyrolactone yield. When reduction temperature was increased to 350 °C, however, the influence of the reactants in the activity disappeared in the case of Pd-Sn/SiO₂. The disappearance of the feed effect may be suggested to be due to a decrease of the adsorption strength of maleic anhydride on active sites induced the formation of bimetallic Pd–Sn sites. A decrease of the deactivation rate found on Pd-Sn/SiO₂ can also be explained by the decreased rate of polymerization due to the diminution of the adsorption strength of maleic anhydride on Pd–Sn sites. As a result, it is proposed that Pd-Sn/SiO₂ catalyst can be an effective one-step catalyst for hydrogenation of maleic anhydride to γ -butyrolactone.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pd-Sn/SiO₂; Hydrogenation; Maleic anhydride; γ -Butyrolactone; Deactivation

1. Introduction

Hydrogenation of maleic anhydride to γ -butyrolactone has been highly interesting in the industrial view, since the γ -butyrolactone is an excellent solvent as well as an important intermediate to synthesize *N*-methyl pyrrolidone, vinylpyrrolidone, 2-pyrrolidone and others [1].

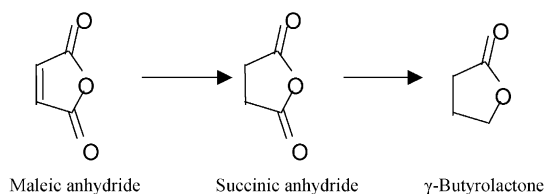
As shown in Scheme 1, the hydrogenation of maleic anhydride to γ -butyrolactone follows two-step reactions. Firstly, C=C bond in maleic anhydride is reduced and converted to succinic anhydride. And

then, γ -butyrolactone is formed via the subsequent oxidative-hydrogenation of C=O bond in succinic anhydride. Palladium is known as an effective hydrogenation catalyst. But, there is little interest in Pd for maleic anhydride hydrogenation to γ -butyrolactone [2], because Pd shows a low activity for the hydrogenation of carbonyl group, which has been explained by a too weak adsorption of carbonyls [3,4]. In addition, maleic anhydride readily undergoes decomposition and polymerization reaction under reaction conditions [5]. High molecule weight pitch-like product formed by polymerization leads to a fast deactivation of Pd. To improve the performance of Pd in maleic anhydride hydrogenation, the catalytic properties of Pd, like adsorption strength of C=C and C=O, should be modified. Until now, many bimetallic palladium catalysts

* Corresponding author. Tel.: +82-42-866-2892;

fax: +82-42-862-1319.

E-mail address: jungsm@lgchem.co.kr (S.M. Jung).



Scheme 1. The path of maleic anhydride hydrogenation to γ -butyrolactone.

have been reported [4–7]. Recently, Coq and Figueras have reviewed the positive effects of a second component in Pd-based heterogeneous catalysts [8] and Mahmoud et al. have studied the alterations of the catalytic properties of Pd by Sn, Ir and Cu additives [9].

Based on the physical and chemical effect of second metals [8], our group has studied the addition of a second metal like Ni, Mo, Cu to Pd, in order to develop Pd based catalysts applicable in the maleic anhydride hydrogenation. In this paper, we report an outstanding catalytic performance on the hydrogenation of maleic and succinic anhydrides observed by the addition of tin to palladium supported on SiO_2 .

2. Experimental

2.1. Preparation of catalysts

The monometallic palladium catalyst (1 wt.%) were prepared by impregnation of the support with an aqueous solution of palladium chloride. Silica ($300 \text{ m}^2/\text{g}$) has been used as support. Bimetallic compositions of palladium (1 wt.%) to tin (0.5 wt.%) were prepared by co-impregnation of supports with acidified (with HCl 5%) aqueous solutions of PdCl_2 and SnCl_2 precursors. Both the samples, after drying for 3 h at 120°C under N_2 , were reduced under H_2 at 200°C and 350°C , respectively.

X-ray photoelectron spectra were obtained with a Surface Science Instruments SSX-100 model 206 spectrometer with a monochromatised Al $\text{K}\alpha$ source, operating at 10 kV and 12 mA. Samples were compressed in a small cup under a $5 \text{ kg}/\text{cm}^2$ pressure for 30 seconds and supported on a holding carousel. The residual pressure inside the analysis chamber was below 5×10^{-9} Torr. The binding energies of Pd 3d, Sn 3d were referenced to the C 1s band at 284.8 eV.

2.2. Activity measurements

The hydrogenation of maleic anhydride and succinic anhydride was performed in a 300 ml high pressure stirred reactor (Autoclave Engineers). In a typical hydrogenation experiment, 142.5 g of dioxane, 7.5 g of substrate, 1 g of tetradecane and 1.5 g of catalyst were charged in the autoclave. The tetradecane was used as an internal standard for the analysis. The reactor was purged with nitrogen to remove the air, then it was pressurized up to 300 psi and heated to 240°C . When the temperature was reached, the pressure was raised at 750 psi. The reaction mixture was stirred at 1000 rpm for 4 h. The sampling was carried out with an interval of 1 h.

Samples of the reaction products were analyzed by using a Hewlett-Packard 6890 gas chromatograph equipped with a capillary column ($30 \text{ m} \times 0.53 \text{ mm}$ i.d.) coated with a $1.2 \mu\text{m}$ film of polyethyleneglycol ester (AT-1000). The flow rate of helium carrier gas was $80.4 \text{ ml}/\text{min}$ (2 psig head pressure), at the injector and detector temperatures of 100 and 250°C , respectively. Column temperature was programmed at 80°C (5 min) to 230°C (15 min) with a heating rate of $10^\circ\text{C}/\text{min}$. The products compositions were dioxane, tetradecane, γ -butyrolactone, maleic anhydride, succinic anhydride and succinic acid with retention time of 2.80, 7.81, 10.91, 11.79, 15.14 and 24.95 min, respectively.

3. Results and discussion

The catalytic liquid-phase hydrogenation was carried out at 240°C and 750 psi over Pd/ SiO_2 and Pd-Sn/ SiO_2 catalysts reduced at 200°C , using maleic anhydride and succinic anhydride as a starting material, respectively. For both the catalysts, 100% conversion of maleic anhydride was achieved before temperature reached at 240°C . No significant amounts of over-hydrogenated products like tetrahydrofuran and 1,4-butanediol were detected under the reaction condition. The major products consisted of succinic anhydride and γ -butyrolactone. Since γ -butyrolactone forms via the hydrogenation of succinic anhydride [2], it is understood that the yield to γ -butyrolactone can indicate the activity of catalyst. Accordingly, all comparisons in catalytic activity have been done based

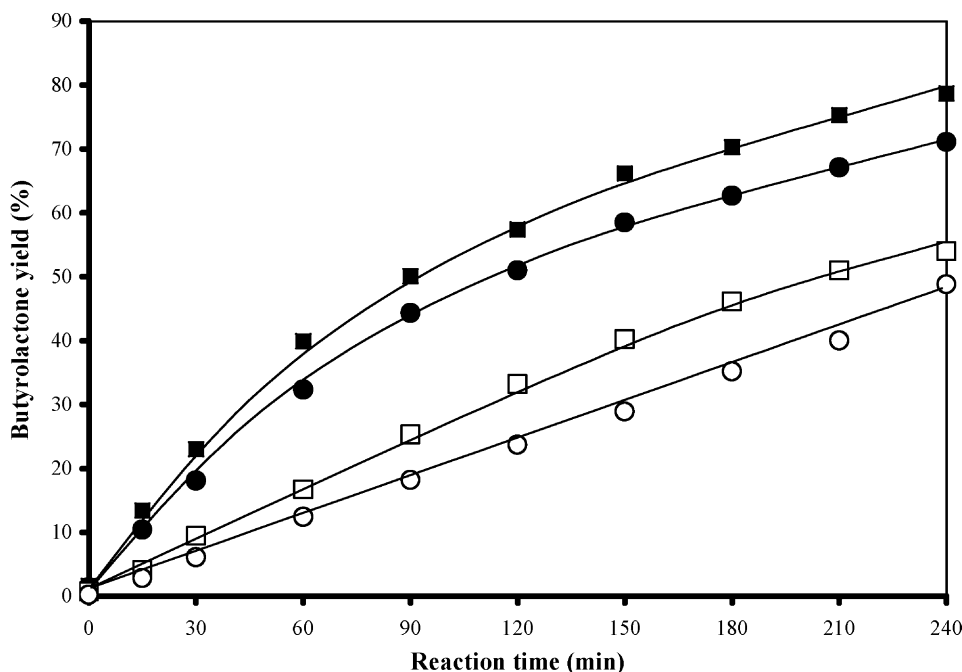


Fig. 1. Effect of feed on the yield of γ -butyrolactone over the catalyst reduced at 200 °C according to the reaction time ($T = 240$ °C, $P = 50$ bar): (○) maleic anhydride-Pd/SiO₂; (□) maleic anhydride-Pd-Sn/SiO₂; (●) succinic anhydride-Pd/SiO₂; (■) succinic anhydride-Pd-Sn/SiO₂.

on the yield of γ -butyrolactone. As shown in Fig. 1, Pd-Sn/SiO₂ catalyst showed a little more active than pure palladium supported SiO₂ in both the starting materials. This enhancement of the activity in Pd-Sn/SiO₂ can be explained by the modification of its electronic and geometric properties towards the improved adsorption of C=O bond [8]. Mahamoud et al. attributed the effect of Pd-Sn to the possible presence of Sn⁴⁺ species on the catalyst surface causing an activation of C=O bond [9]. In other words, a mixed site between Pd and SnO₂ participates in the catalytic transformation effectively without any electronic interaction. It was also proposed that noble metal-Sn alloy shows both zero and oxidized states in the reduced catalysts [10–13]. Accordingly, the electron donating effect from Sn to Pd in Pd-Sn alloy can lead to a decrease of the C=C bond adsorption strength and an increase of C=O bond activation. However, any single interpretation is not enough to be confirmed in this stage.

On the other hand, Fig. 1 also showed that the yield of γ -butyrolactone is increased by about 30%, in the case where the feed was succinic anhydride instead of

maleic anhydride. These results present strong dependence of reactivity on the starting material. Yamada et al. reported that, in cinnamaldehyde hydrogenation over Pd/C catalyst, the preferential adsorption of C=C bond of cinnamaldehyde inhibited the hydrogenation rate of hydrocinnamaldehyde to hydroxycinnamyl alcohol [3]. Considering the effect of C=C strong adsorption on Pd active site, the difference in activity according to the different reactants can be explained by the effect of the C=C bond in maleic anhydride inhibiting the C=O bond being hydrogenated. Moreover, it was known that the strong adsorption induces the polymerization of maleic anhydride [5,13]. Thus, it is imagined that the deactivation rate may be increased when maleic anhydride is used as a starting material.

Fig. 2 presents the comparison of γ -butyrolactone yield obtained over Pd-Sn/SiO₂ reduced at 200 °C and 350 °C, respectively. The yield of γ -butyrolactone over Pd-Sn/SiO₂ reduced at 350 °C after 4 h is higher by 25% than at 200 °C, whereas Pd/SiO₂ does not show any difference (not shown). This result indicates that the effective arrangement or interaction between

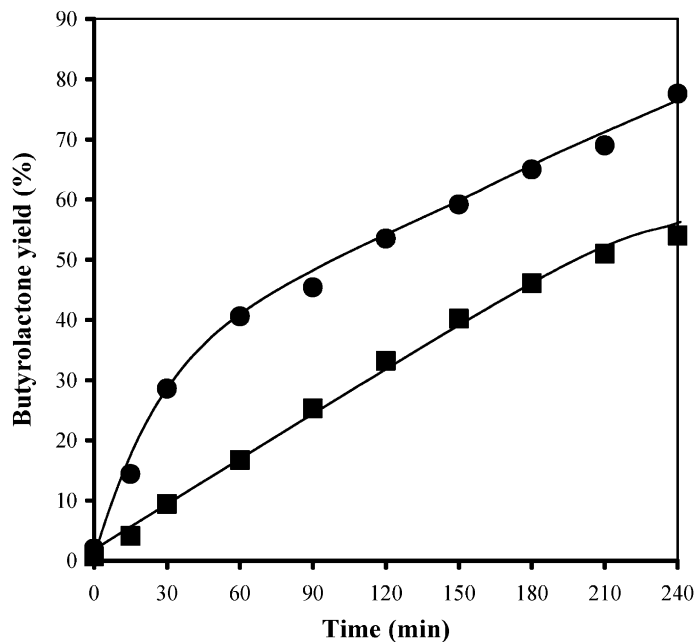


Fig. 2. Effect of reduction temperature on the yield of γ -butyrolactone on Pd-Sn/SiO₂ catalysts ($T = 240^\circ\text{C}$, $P = 50$ bar, feed = maleic anhydride): (■) 200°C; (●) 350°C.

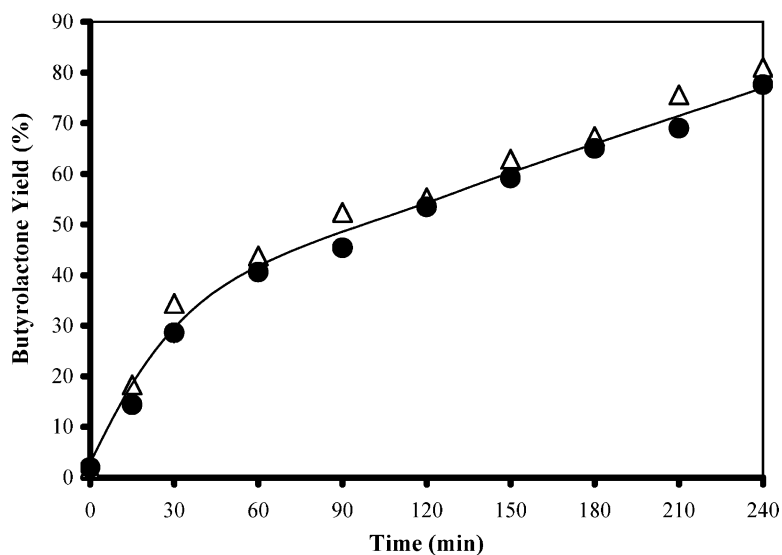


Fig. 3. Effect of feed on the yield of γ -butyrolactone over the catalyst reduced at 350°C ($T = 240^\circ\text{C}$, $P = 50$ bar): (●) maleic anhydride-Pd-Sn/SiO₂; and (△) succinic anhydride-Pd-Sn/SiO₂.

Table 1
XPS analysis

Sample	Reduction temperature (°C)	Binding energy (eV)			Atomic ratio
		Pd 3d _{5/2}	Sn(0)3d _{5/2}	Sn(II, IV)3d _{5/2}	Sn(0)/(Sn(0) + Sn(II, IV)3d)
Pd-Sn/SiO ₂	200	334.9	483.2	486.3	0.16
Pd-Sn/SiO ₂	350	334.9	483.9	486.4	0.57

Pd and Sn in the hydrogenation of maleic anhydride to γ -butyrolactone is increased with temperature increase. Thus, with Pd-Sn/SiO₂ reduced at 350 °C, the effect of the feed was investigated again.

Fig. 3 shows the result of the γ -butyrolactone yields obtained over Pd-Sn/SiO₂ reduced at 350 °C when the reactant was maleic anhydride or succinic anhydride. The γ -butyrolactone yield is exactly the same regardless of the feed.

No activity difference between maleic anhydride and succinic anhydride means that the adsorption energy of C=C bond of maleic anhydride over Pd is relatively weak when Sn is added. Therefore, the adsorption of C=C bond does not affect on the reaction rate of C=O reduction. Considering the Pd₂Sn and/or Pd₃Sn phases detected by Sales et al. [14], it may be suggested that the increase of activity in Pd-Sn/SiO₂ reduced at 350 °C is attributed to the electron donating effect of Sn.

In recent review [8], it was reported that the heat of adsorption of reactant and products could be governed by the degree of electron transfer between metal and reactant, which is modified by the formation of the alloys. Fuggle et al. reported that the electronic configuration of Pd d-band could be due to the band overlap with a second metal mainly [15]. In order to identify the electronic modification due to the formation of bimetallic Pd–Sn, XPS measurements were performed on the samples reduced at 200 °C and 350 °C, respectively. The binding energy of Sn in Pd-Sn/SiO₂ reduced at 350 °C and the atomic ratio of Sn⁰/(Sn⁰ + Sn⁺² + Sn⁺⁴) is increased, as shown in Table 1. The increase in the metallic Sn concentration indicates the possibility of the increase in the Pd₂Sn and/or Pd₃Sn phases. The upward shift of binding energy of Sn presents an electron deficiency of Sn due to an electron transfer from Sn to Pd. Accordingly, it can be explained that the modification of C=C adsorption effect

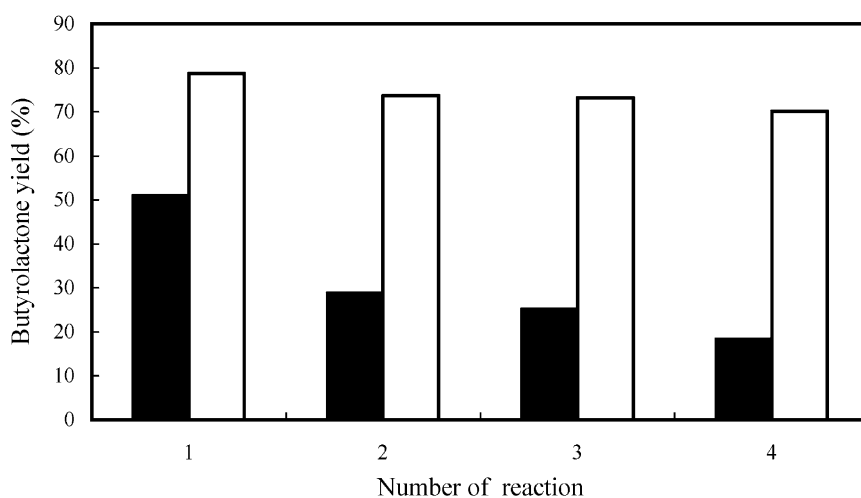


Fig. 4. The activity change of catalysts versus the number of reactions: Pd/SiO₂ (■) and Pd-Sn/SiO₂ (□) catalysts reduced at 350 °C (reaction time = 3 h, $T = 240$ °C, $P = 50$ bar, feed = maleic anhydride).

on Pd-Sn/SiO₂ according to the reduction temperature is due to the formation of Pd–Sn alloy, making the change of electronic configuration of Pd d-band. Besides, it can be imagined that the decreased adsorption strength of maleic anhydride can induce the decrease of the rate of coke formation due to the polymerization of maleic anhydride. Actually, it was recently mentioned that the coke formation was main reason of deactivation in Pd-based catalyst [16].

If the above explanation is correct, Pd-Sn/SiO₂ should show the resistance to the deactivation, which is originally caused by the strong adsorption of maleic anhydride.

To verify the expected promotion effect, four successive experiments were performed using of Pd/SiO₂ and Pd-Sn/SiO₂ reduced at 350 °C. Fig. 4 shows the activity change of catalysts versus the number of reactions. The results indicate unquestionably that the presence of tin decreases a deactivation rate of the palladium-based catalyst on the hydrogenation of maleic anhydride. As mentioned above, a process of deactivation or poisoning in the hydrogenation of maleic anhydride in the presence of noble metal catalysts is caused by the formation of maleic anhydride oligomers or polymers that would cover the active surface, due to their strong adsorption property of maleic anhydride. Therefore, a decrease in the deactivation rate confirms that the effect of tin is mainly related to the modification of electronic configuration of Pd d-band through the formation of Pd–Sn phase. The modified Pd electronic environment provides the effective active site for the hydrogenation of maleic anhydride to γ -butyrolactone.

4. Conclusions

One of the major problem related to the performance of Pd catalysis in the hydrogenation is the loss of catalytic activity during the reaction, i.e. deactivation. Specially, due to the coke formation from maleic anhydride, the two step liquid-phase hydrogenation process should be designed for maleic anhydride hydrogenation to γ -butyrolactone.

As shown in the results, the addition of tin to Pd/SiO₂ gives an opportunity to overcome the severe problem of deactivation in the application of Pd catalyst to the hydrogenation of maleic anhydride. Thus, the Pd-Sn/SiO₂ catalyst can be used for the direct one-step process for the hydrogenation of maleic anhydride to γ -butyrolactone.

Acknowledgements

Eric Godard would like to thank the LG Company for the financial support to realize his post-doctoral position.

References

- [1] R. Lancia, A. Vaccari, C. Fumagalli, E. Armbruster, US 5698713, 16 December 1997.
- [2] U. Hermann, G. Emig, Ind. Eng. Chem. Res. 36 (1997) 2885.
- [3] H. Yamada, H. Urano, S. Goto, Chem. Eng. Sci. 54 (1999) 5231.
- [4] V. Ponec, Appl. Catal. Part A: Gen. 149 (1997) 27.
- [5] F.J. Broecker, G. Duembgen, H. Glietenberg, E. Miesen, M. Schwarzmann, US 4192807, 11 March 1980.
- [6] M. Fernandez-Garcia, J.A. Anderson, G.L. Haller, J. Phys. Chem. 100 (1996) 16247.
- [7] M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas, A. Porras, F.J. Urbano, J. Catal. 172 (1997) 46.
- [8] B. Coq, F. Figueras, J. Mol. Catal. Part A: Chem. 173 (2001) 117.
- [9] S. Mahmoud, A. Hammoudeh, S. Gharaibeh, J. Melsheimer, J. Mol. Catal. Part A: Chem. 178 (2002) 161.
- [10] F. Coloma, A. Sepulveda-Escribano, J.L.G. Fierro, F. Rodriguez-Reinoso, Appl. Catal. Part A: Gen. 148 (1996) 63.
- [11] J. Llorca, N. Homs, J.L.G. Fierro, J. Sales, P.R. de la Piscina, J. Catal. 166 (1997) 44.
- [12] S. Recchia, C. Dossi, N. Poli, A. Fusi, L. Sordelli, R. Psaro, J. Catal. 184 (1999) 1.
- [13] S.M. Loktev, V.D. Dyshlis, A.Y. Rozovskii, Kinet. Katal. 20 (1979) 692.
- [14] E.A. Sales, G. Bugli, A. Ensuque, M. de Jesus Mendes, F.B. Verduras, Phys. Chem. Chem. Phys. 1 (1999) 491.
- [15] J.C. Fuggle, F.U. Hillebrecht, R. Zeller, Z. Zolnierrek, P.A. Bennett, C.H. Freiburg, Phys. Rev. B 27 (1983) 2145.
- [16] P. Albers, J. Pietsch, S.F. Parker, J. Mol. Catal. Part A: Chem. 173 (2001) 275.