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Liquid-phase hydrogenation of maleic anhydride over Pd–Sn/SiO_2

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Abstract

Pd and Pd–Sn supported on SiO_2 and active carbon were prepared and tested as catalysts in the hydrogenation of maleic anhydride. Particularly Pd–Sn/SiO_2 was active and selective in the hydrogenation of maleic anhydride to γ-butyrolactone, and showed a resistance to the deactivation. The results of XPS and CO adsorption evidenced that the catalytic performance of Pd–Sn/SiO_2 was related to the modification of electronic configuration of Pd due to the effective interaction between Pd and Sn.

Keywords: Pd; Pd–Sn; Active carbon; SiO_2; Hydrogenation; Maleic anhydride; γ-Butyrolactone; Deactivation

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1. Introduction

The hydrogenation of maleic anhydride to γ-butyrolactone is a reaction of relevant importance in the synthesis of various fine chemicals. γ-Butyrolactone is an excellent solvent and an important intermediate to synthesize *N*-methyl-pyrrolidone, vinyl-pyrrolidone, 2-pyrrolidone, 1,4-butanediol and tetrahydrofuran [1]. The reaction pathway of the hydrogenation of maleic anhydride to 1,4-butanediol and tetrahydrofuran is illustrated in Fig. 1.

Currently, there are two main processes for the production of γ-butyrolactone, the Reppe process (based on acetylene and formaldehyde condensation, Fig. 2) and the Davy McKee process (based on the hydrogenation of the diethyl or dimethyl maleates, Fig. 3). Both processes present some disadvantages. The Reppe process uses acetylene and formaldehyde as starting material, and severe reaction conditions (140–280 bar, 250–350 °C) [1,2]. Moreover, acetylene is a hazardous material and formaldehyde is a carcinogenic material. The Davy McKee process needs two different reactors, catalysts and reactions conditions [3,4]. The first reaction is an esterification in presence of ion exchange resin. The second one is a hydrogenation reaction in presence of copper–chromium catalyst. Chromium is poisonous so that a disposal problem is inevitable.

Compared with the other processes, hydrogenation of maleic anhydride is the most direct, environmentally benign and economic way to produce γ-butyrolactone [4].

A few studies have been made for developing a suitable catalytic system for the liquid-phase hydrogenation of maleic anhydride [5–9]. The transition metals like copper-, cobalt- or nickel-based catalysts as well

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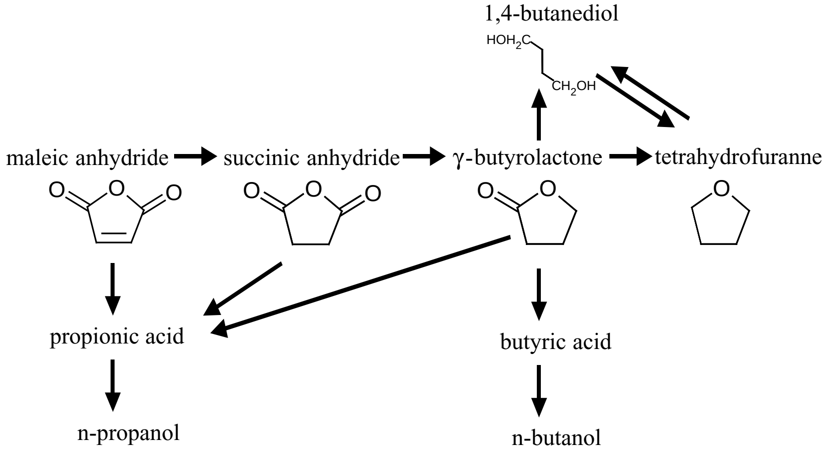

Fig. 1. Reaction scheme of the hydrogenation of maleic anhydride.

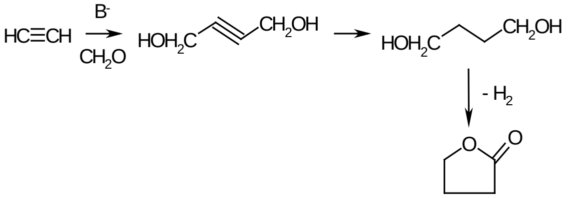

Fig. 2. Scheme of Reppe process for the hydrogenation of maleic anhydride.

as noble metal catalyst are used for direct hydrogenation of maleic anhydride.

In this paper, we report a study on the hydrogenation of maleic anhydride on palladium and palladium–tin supported catalysts. The aim of this work is to realize an investigation of the effects of the presence of tin on supported palladium catalysts. Moreover, the effects of the nature of the reactants and the supports, and the resistance of catalyst against the deactivation according to the catalyst reduction temperature have been investigated.

2. Experimental

2.1. Preparation of catalysts

The monometallic palladium catalysts were prepared by impregnation of the support with an aqueous solution of palladium chloride. Active carbon (Darko, 100 mesh) and silica (Grace Davison, 100 mesh) have been used as support. Before the preparation, the pore volume of the supports was calculated by manual impregnation of dry support with water. The pore volumes for active carbon and silica are, respectively, 0.78 and 1.82 ml. In order to modify the chemical properties

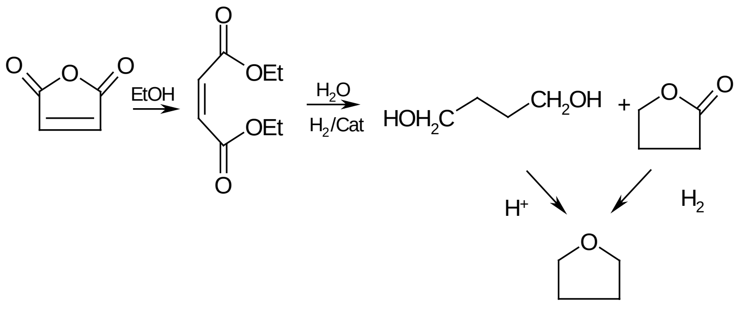

Fig. 3. Scheme of Davy McKee process for the hydrogenation of maleic anhydride.

Table 1
BET measurement

Support	Specific area (m^2/g)	Total pore volume (cm^3/g)	Percentage of micropore[a]	Percentage of macro and mesopores[a]
SiO_2	227	1.75	12	88
C	993	0.77	91	9
$C_{treated}$	967	0.81	93	7

[a] Calculated by *t*-plot method.

of the support, a part of active carbon were agitated during 3 h in the concentrated nitric acid at 60 °C. The surface area, the pore volume and the pore size are not affected by a mild activation of the support (Table 1). Then the active carbon treated was washed until the pH of the washing water was six. After drying, this sample was impregnated with an aqueous solution of $Pd(NO_3)_2$.

Bimetallic samples of palladium–tin were prepared by co-impregnation of supports with acidified (with HCl 5%) aqueous solutions of $PdCl_2$ and $SnCl_2$ precursors. All the catalysts were prepared in order to have a loading of 1% palladium and 0.5% of tin. All samples, after drying for 3 h at 120 °C under N_2, were reduced under H_2 at 200 or 350 °C.

2.2. XPS measurement

X-ray photoelectron spectra were obtained with a Surface Science Instruments SSX-100 model 206 spectrometer with a monochromatized Al Kα source, operating at 10 kV and 12 mA. Samples were compressed in a small cup under a $5\,kg/cm^2$ pressure for 30 s and supported on a holding carousel. The residual pressure inside the analysis chamber was below 6.66×10^{-12} bar. The binding energies of Pd 3d, Sn 3d were referenced to the C 1s band at 284.8 eV.

2.3. CO adsorption

Pd dispersion was determined from the amount of chemisorbed CO measured by pulse method. The experiments were carried out using a Micromeritics instrument. The sample was set in the quartz U-tube and reduced with H_2 stream (35 ml/min). After the pretreatment at 90 °C for 2 h, CO pulses were repeated until the adsorption was saturated at room temperature. The dispersion of Pd was calculated based on $CO/Pd = 1$.

2.4. 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 pressurized up to 20 bar with hydrogen and heated to 240 °C. When the temperature was reached, the pressure was raised to 50 bar with hydrogen. The reaction mixture was stirred at 1000 rpm for 4 h. The sampling was carried out with the 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 m × 0.53 mm i.d.) coated with a 1.2 μm film of polyethyleneglycol ester (AT-1000). The flow rate of helium carrier gas was 80.4 ml/min (2 psig head pressure), at the injector and detector temperatures were 100 and 250 °C, respectively. Column temperature was programmed at 80 (5 min) to 230 °C (15 min) with a heating rate of 10 °C/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

Three Pd catalysts with different support, Pd/SiO_2, Pd/C and $Pd/C_{treated}$, were reduced at 200 °C and tested during the hydrogenation of maleic anhydride at a temperature of 240 °C and a pressure of 50 bar. For all catalysts, 100% conversion of maleic anhydride was achieved before temperature reached at 240 °C.

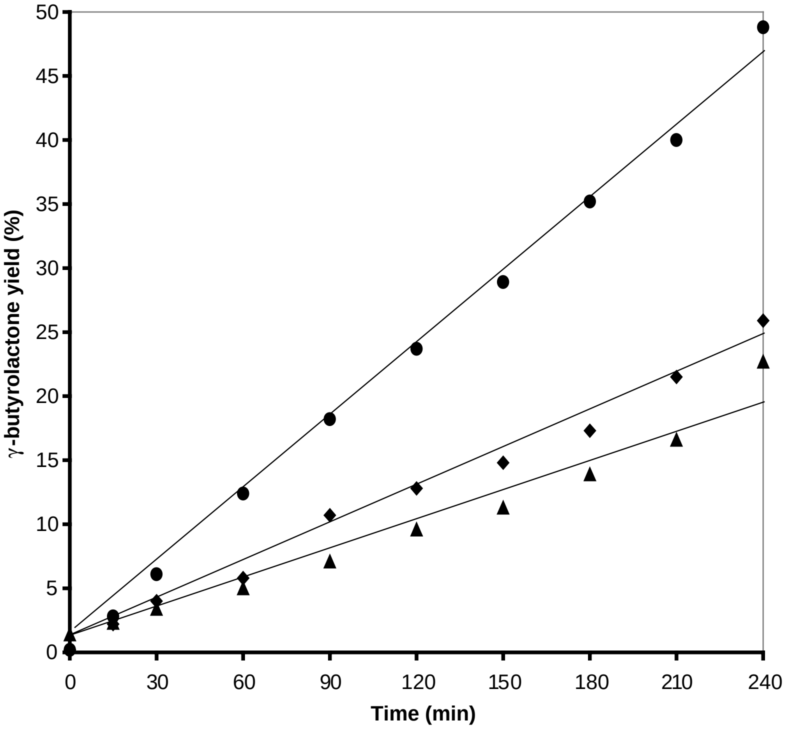

Fig. 4. Yield in γ-butyrolactone in maleic anhydride hydrogenation according to the reaction time: Pd/SiO_2 (●), Pd/C (▲) and Pd/$C_{treated}$ (◆) catalysts reduced at 200 °C ($T = 240$ °C, $P = 50$ bar).

No significant amounts of over-hydrogenated products like tetrahydrofuran and 1,4-butanediol were detected under the reaction conditions. The major products consisted of succinic anhydride and γ-butyrolactone. Since γ-butyrolactone forms via the hydrogenation of succinic anhydride [4], 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 on the yield of γ-butyrolactone.

Fig. 4 illustrates the obtained results using three catalysts. The most active catalyst for the hydrogenation of maleic anhydride was found to be Pd/SiO_2. Pd/$C_{treated}$ showed a slightly higher activity than Pd/C. But, the yield of γ-butyrolactone of Pd/$C_{treated}$ is only half compared with Pd/SiO_2.

In order to modify the activity of catalysts, Sn was added to Pd/SiO_2 and Pd/C. The reactions were carried out at 240 °C and 50 bar for 2 h over Pd–Sn/C and Pd–Sn/SiO_2 catalysts reduced 200 °C, using maleic anhydride as a starting material. A comparison of the yield in γ-butyrolactone is presented in Table 2.

Pd–Sn/C showed almost same activity with Pd/C. It means that there is no promotional effect of Sn. The γ-butyrolactone yield of Pd–Sn/SiO_2 is increased to 33.2%, which is higher by 40% than that of Pd/SiO_2.

Table 3 presents a comparison of the yield in γ-butyrolactone for Pd–Sn/SiO_2 catalysts reduced at 200 and 350 °C. The yield of γ-butyrolactone over Pd–Sn/SiO_2 reduced at 350 °C is higher by 60% than at 200 °C.

Table 2
Effect of Tin on the yield of γ-butyrolactone over the catalyst reduced at 200 °C using maleic anhydride as a starting material, after 2 h of reaction time ($T = 240$ °C, $P = 50$ bar)

Catalyst	γ-Butyrolactone yield (%)
Pd/C	9.6
Pd–Sn/C	11.8
Pd/SiO_2	23.7
Pd–Sn/SiO_2	33.2

Table 3
Effect of reduction temperature on the yield of γ-butyrolactone on Pd–Sn/SiO_2 catalysts ($T = 240\,^{\circ}C$, $P = 50$ bar, $t = 2$ h) and electronic property measured by XPS

	Reduction temperature (°C)	
	200	350
Yield of γ-butyrolactone (%)	33.2	53.5
Sample binding energy (eV)		
Pd $3d_{5/2}$	334.9	334.9
Sn(0) $3d_{5/2}$	483.2	483.9
Sn(II, IV) $3d_{5/2}$	486.3	486.4
Atomic ratio		
Sn(0)/(Sn(0) + Sn(II, IV) 3d	0.16	0.57

Table 4 compares the yield of γ-butyrolactone obtained for maleic and succinic anhydride as a starting material. For all cases reduced at 200 °C, the yield of γ-butyrolactone is higher when the starting reactant is succinic anhydride. But, the Pd–Sn/SiO_2 reduced at 350 °C shows no difference in the yield of γ-butyrolactone according to the different feed.

Table 4
Effect of feed on the yield of γ-butyrolactone over the catalysts ($T = 240\,^{\circ}C$, $P = 50$ bar, $t = 2$ h)

	Reduction temperature (°C)	Feed[a]	Yield of γ-butyrolactone (%)
Pd/C	200	M	9.6
		S	20.6
Pd–Sn/C	200	M	11.8
		S	24.3
Pd/SiO_2	200	M	23.7
		S	51.0
Pd–Sn/SiO_2	200	M	33.2
		S	57.4
	350	M	53.5
		S	53.2

[a] M: maleic anhydride, S: succinic anhydride.

Fig. 5 shows the activity change of catalysts versus the number of reactions performed using Pd/SiO_2 and Pd–Sn/SiO_2 reduced at 350 °C. In the case of Pd–Sn/SiO_2, the decreasing rate of the yield of

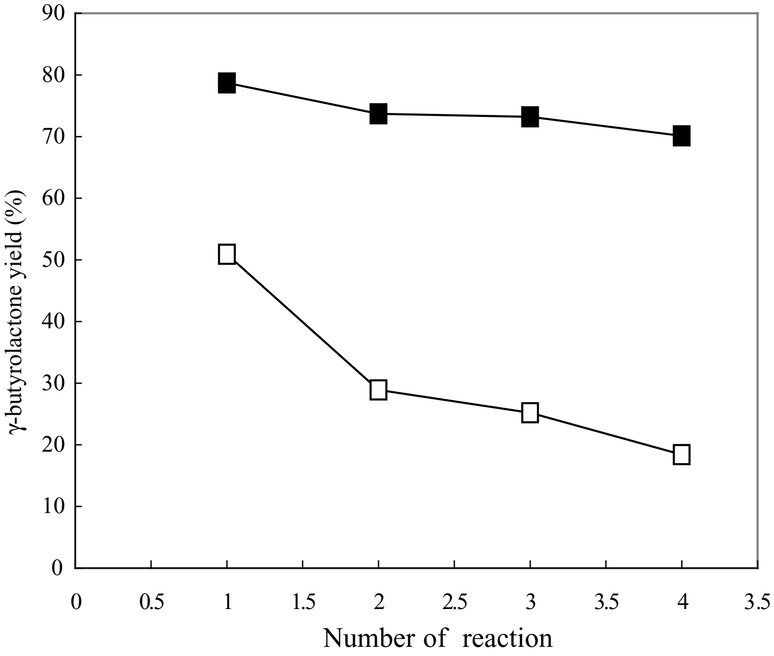

Fig. 5. Comparison of the catalyst deactivation rate according to the number of reactions: Pd/SiO_2 (□) and Pd–Sn/SiO_2 (■) catalysts reduced at 350 °C (reaction time = 4 h, $T = 240\,^{\circ}C$, $P = 50$ bar, feed = maleic anhydride).

γ-butyrolactone according to the number of reaction is smaller than that of Pd/SiO_2.

4. Discussions

The performance of Pd was dependant on the kind of supports and Sn addition, as shown in above results. Generally, the influence of supports and co-metal on the Pd performance can be explained by electronic and geometric effect [10,11].

Since the used supports showed no strong interaction with supported materials, the textural properties of the supports (Table 1) and Pd dispersion are considered in the interpretation of the catalytic activity. Pd dispersions were measured by CO adsorption measurements. The results are shown in Table 5. Despite that Pd/SiO_2 showed two times higher activity than Pd/C, the dispersions of Pd on SiO_2 and C are similar. This suggests that the dispersion of palladium is less important to the production of γ-butyrolactone by the maleic anhydride hydrogenation. Considering the different pore-size distribution in the textural properties, the accessibility of the substrate to the active phase (palladium) of the catalyst is likely to play an important role in the hydrogenation of maleic anhydride.

In order to explain the effect of Sn on the performance of Pd catalysts, both of the geometric effects and electronic effects should be considered. With respect of the C=O hydrogenation, several researchers have already discussed in the frame of electronic aspects. Firstly it was proposed that noble metal–Sn alloy showed both zero and oxidized states in the reduced catalysts and the enhancement of the activity to hydrogenate the carbonyl group can be correlated with the modification of its electronic properties towards the improved adsorption of C=O bond [12–17]. Coq and Figueras [10] 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. [18] reported that the electronic configuration of Pd d-band could be due to the band overlap with a second metal.

Table 5
Pd dispersion measured by CO adsorption method

Catalyst	Reduction temperature (°C)	Dispersion (%)
Sn/SiO_2	200	0
Pd/C	200	11.3
Pd/SiO_2	200	10.1
Pd–Sn/C	200	7.4
Pd–Sn/SiO_2	200	6.3
Pd–Sn/SiO_2	350	4.5

As mentioned above, the evidences of electronic modification and the arrangement between Pd and Sn become important to explain the outstanding properties of Pd–Sn/SiO_2 in the hydrogenation of maleic anhydride.

To elucidate the modification of electronic properties of Pd in Pd–Sn/SiO_2, XPS measurements were carried out according to the different reduction temperature. In XPS measurements (Table 3), the binding energy of Sn and the atomic ratio of $Sn^0/(Sn^0 + Sn^{2+} + Sn^{4+})$ in Pd–Sn/SiO_2 are increased, as reduced at 350 °C. The upward shift of binding energy of Sn presents an electron deficiency of Sn due to an electron transfer from Sn to Pd. The increase in the metallic Sn concentration indicates the possibility of the increase in the Pd_2Sn and/or Pd_3Sn phases [19].

On the other hands, as shown in Table 5, 10.1% of Pd dispersion value in Pd/SiO_2 is decreased to 6.3% after added Tin and reduced at 200 °C. Pd dispersion of Pd–Sn/SiO_2 is further decreased to 4.5%, when the reduction is increased to 350 °C. The decrease of Pd dispersion can be explained by that tin would be as adatom "decorating" the palladium surface.

From the results of XPS and CO adsorption, it can be suggested that the effective interaction between Pd and Sn takes place in the case of Pd–Sn/SiO_2 catalysts and the formation of Pd–Sn due to the migration of Sn to Pd surface, which is operative as higher temperature. As a result, it is concluded that the promotional effect between Pd and Sn supported on SiO_2 could be explained by the electron donating effect from Sn to Pd in Pd–Sn alloy.

In terms of reactant such as maleic anhydride or succinic anhydride, The γ-butyrolactone yield for the Pd–Sn/SiO_2 reduced at 350 °C, is the same regardless of the feed. 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 [20]. 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. Thus, no difference in the activity between maleic anhydride and succinic anhydride over the Pd–Sn/SiO_2 reduced at 350 °C means that the adsorption energy of C=C bond of maleic anhydride over Pd is relatively weak when Sn added. Based on XPS results, the modification of C=C adsorption effect on Pd–Sn/SiO_2 according to the reduction temperature can also be explained by the change of electronic configuration of Pd d-band.

Since 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 [1,21], 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 palladium–tin phase.

5. Conclusions

One of the efforts to develop new catalyst for the direct liquid-phase hydrogenation of maleic anhydride to γ-butyrolactone is introduced, in order to overcome the several disadvantages of the present process such as Reppe process and Davy Mckee process.

Among the catalysts tested, Pd–Sn/SiO_2 shows a remarkable activity and a resistance to the deactivation regardless of reactants. The promotional effect of tin on Pd–Sn/SiO_2 catalyst can be explained by the change of electronic configuration of Pd due to the interaction with Sn. The effective interaction between Pd and Sn in the hydrogenation of maleic anhydride to γ-butyrolactone is enhanced when the reduction temperature is performed at higher temperature.

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