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Influence of metal particle size on the hydrogenation of maleic anhydride over Pd/C catalysts in $scCO_2$

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ABSTRACT

Hydrogenation of maleic anhydride (MAH) with Pd/C catalysts in supercritical carbon dioxide ($scCO_2$) was investigated. The selectivity for γ-butyrolactone (GBL) reached 97.3% in $scCO_2$ at 100% conversion of MAH, which was notably higher than that of 77.4% obtained in organic solvent of ethylene glycol dimethyl ether (EGDME). The particle size of Pd exhibited large influence on the reaction rate and selectivity of GBL. Higher selectivity of GBL was obtained with Pd/C catalyst of smaller Pd particle size, and the rate of GBL selectivity increase as a function of CO_2 pressure was found to be significantly correlated with Pd particle size.

1. Introduction

Supercritical carbon dioxide ($scCO_2$) is an environmentally desirable replacement of conventional organic solvents for sustainable chemical synthesis in a wide range of processes [1–5]. Hydrogenation has been presented as a typical case of advantageous use of $scCO_2$ as solvent in chemical reactions. Additional attractive features of $scCO_2$ as solvent for hydrogenation include higher hydrogenation rates and selectivity compared to conventional organic solvents [6–17]. Hydrogenation in $scCO_2$ has recently been reviewed by Baiker and co-workers [6]. The positive effects of $scCO_2$ were attributed to (1) enhancement of dissolved H_2 concentration due to the miscibility of H_2 in $scCO_2$, (2) decrease of mass transfer resistance for the lower viscosity and higher diffusivity of $scCO_2$, (3) possible modification of substrate reactivity through molecular interactions between CO_2 and substrates and (4) possible change of catalyst specific activity via modification of metal nanoparticles. The first two merits have been discussed extensively in catalytic hydrogenations like asymmetric hydrogenation [7,8], hydroformylation [9,10] and selective hydrogenation of aromatic nitro compounds [11], unsaturated aldehydes/ketones [12] and arene [13] in $scCO_2$. In our previous work, some progresses were made in understanding the molecular interactions through in situ FTIR in unsaturated aldehydes and nitrocompounds hydrogenations [14,15]. It was found that the effects of CO_2 pressure were different for the hydrogenation of benzaldehyde and cinnamaldehyde. High pressure FTIR results revealed that the molecular interaction between CO_2 and cinnamaldehyde is stronger than that between CO_2 and benzaldehyde. However, the effect of $scCO_2$ on the catalytic activity of metal catalyst is poorly understood. In literature, the absorption spectrum of small gold particles measured in $scCO_2$ depends significantly on pressure, suggesting there is a direct interaction between gold particles and $scCO_2$ medium [18]. It was also suggested that the interaction between the transition metal particles themselves may depend on the metal particle size, thus affecting the activity of the metal catalyst in $scCO_2$. In our previous work, the effects of Pt particle size on the hydrogenations of cinnamaldehyde and nitrobenzene in $scCO_2$ was investigated [16,17]. The Pt particle size presented larger effect on nitrobenzene hydrogenation than cinnamaldehyde hydrogenation.

In our latest work, the hydrogenations of maleic anhydride (MAH) and succinic anhydride (SAH) have been performed successfully with $RuCl_2(TPP)_3$ homogeneous catalyst in $scCO_2$. The total conversion and selectivity to γ-butyrolactone (GBL) in $scCO_2$ are higher than those obtained in organic solvent of ethylene glycol dimethyl ether (EGDME). A high selectivity of 99% was obtained for SAH hydrogenation in 14 MPa CO_2 under the optimum conditions [19]. Pillai et al. [20,21] reported that the hydrogenation of MAH over Pd/Al_2O_3 could be performed in $scCO_2$ and the selectivity to GBL was higher than that in organic solvents. It was found that all the MAH could be dissolved in the $scCO_2$ phase at 200 °C at pressures of 2.1 MPa H_2 and 12 MPa CO_2, resulting in 80% selectivity to GBL at complete conversion of MAH. However,

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catalyst deactivation was observed, possibly due to the agglomeration of Pd particles during hydrogenation. Herein, we focused our research on the catalytic activity of Pd nanoparticles in $scCO_2$. Specifically, we investigated the influence of particle size at different CO_2 pressures on the activity of Pd/C catalysts in $scCO_2$ and organic solvent. It is noteworthy that a high yield of GBL above 97% was obtained at 100% conversion of MAH in $scCO_2$.

2. Experimental

2.1. Catalyst preparation and characterization

2.1.1. Preparation of Pd nanoparticles of different sizes

Pd/C (Pd 5 and 10%) sample (Wako) was reduced in flowing H_2 under different temperatures to prepare Pd/C catalysts of different Pd particle sizes. The catalysts prepared were examined by X-ray diffraction (XRD) on a RINT2000 vertical goniometer diffractometer with Cu Kα radiation at 40 kV and 200 mA. The average crystallite sizes of supported Pd were determined from XRD line broadening using the Scherrer equation. The catalysts were also examined with a transmission electron microscope (TEM, JEM-2000EX).

2.1.2. Preparation of carbon supported Pd catalysts

Carbon supported Pd catalyst (5% Pd/C) was prepared in EG as follows: H_2PdCl_4 was generated from 0.05 g of $PdCl_2$ (0.282 mmol) and 0.5 ml of concentrated HCl. It was then dissolved in 20 ml of EG mixed with 0.3 M NaOH. The mixture was stirred for 2 h at room temperature. Then 0.57 g carbon (Vulcan XC-72, Cabot) was added. The mixture was ultrasonically suspended in 20 ml EG for 2 h and stirred at room temperature for 72 h. The pH value was adjusted to 12. The mixture was then refluxed at 100 °C for 3 h, cooled to room temperature and stirred for 24 h. Pd colloids deposited on the carbon support were filtered and extensively washed with water and dried in vacuum at 80 °C overnight.

2.2. Hydrogenation procedure

The hydrogenation of MAH was carried out in a 50 ml stainless steel batch reactor. Catalyst and MAH were loaded into the reactor. The reactor was then sealed and flushed three times with 2 MPa CO_2. After the reactor was heated up to the reaction temperature of 200 °C, first H_2 and then CO_2 were introduced into the reactor to the desired pressure using a high-pressure liquid pump. The reaction mixture was stirred continuously with a Teflon-coated magnetic stir bar. Upon completion of the reaction, the reactor was cooled to room temperature and depressurized with a back-pressure regulator. The liquid mixture was diluted with acetone. In the case of the hydrogenations in EGDME, the reaction procedures are the same as the reactions operated in $scCO_2$, except for addition of EGDME initially to the reactor replacing the step of introduction of dense CO_2.

2.3. Analysis of products

The products of hydrogenation were analyzed by gas chromatography (GC-Shimadzu-14C, FID, Capillary column, Rtx-Wax 30 m × 0.53 mm × 0.25 μm) and gas chromatography–mass spectrometry (GC–MS, Agilent 5890). The following temperature program was used: 50 °C for beginning, 10 °C/min to 230 °C. Some of the products were identified with GC–MS. The conversion rate was calculated by dividing moles of MAH consumed over initial moles of MAH supplied. The selectivity was calculated by dividing moles of a product over total moles of MAH consumed.

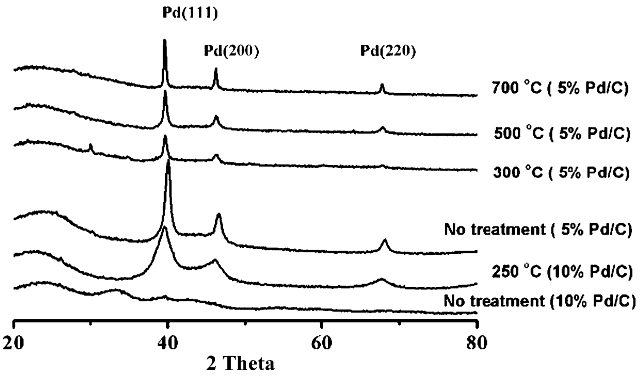


Fig. 1. The XRD patterns of Pd/C catalysts of different sizes.

3. Results and discussion

3.1. Catalyst characterization

The Pd/C (Pd content of 5 and 10%, Wako) catalysts were pretreated under flowing H_2 at different temperatures to obtain catalysts of different Pd particle sizes. 5% Pd/C catalyst of smaller Pd particle size was prepared in EG with in situ reduction. All the catalysts were characterized with XRD and TEM.

Fig. 1 shows the Pd diffraction patterns of Pd/C catalysts pretreated under different conditions. It was found that all the catalysts except the 10% Pd/C catalyst without any treatment presented diffraction peaks of Pd (1 1 1) at 39.7°, Pd (2 0 0) at 46.2°, and Pd (2 2 0) at 67.8°. The average Pd particle sizes were calculated from XRD line broadening using Scherrer equation, which are listed in Table 1. Pd particles grew larger and agglomerated with increasing pretreatment temperatures [16]. For 5% Pd/C catalysts, the Pd particle size is 17.7 nm on the sample without treatment, but increased to 21.9, 27.9, and 37.8 nm on the samples treated at 300, 500, and 700 °C, respectively. For 10% Pd/C catalysts, the Pd particle size was increased to 13.5 nm when it was pretreated at 250 °C for 3 h, as compared to the Pd size of 10.5 nm without any treatment. These results are in agreement with TEM images (Fig. 2). To obtain much smaller sized Pd particles, a 5% Pd/C catalyst was prepared as described in Section 2. The results of XRD and TEM characterization of this catalyst are shown in Fig. 3. It shows that the Pd/C catalyst has well dispersed Pd particles on the support, and the average Pd particle size is around 5.5 nm from the calculation through Scherrer equation and TEM estimation.

3.2. MAH hydrogenation in $scCO_2$ and EGDME

The hydrogenation of MAH is a complex process where different reactions occur in a series of consecutive steps and several products are produced as described in literature [19] (Scheme 1). Firstly, SAH is produced as an intermediate through the hydrogenation of C=C in MAH; then C=O of SAH is

Table 1
Pd particle size dependence on the reduction conditions.

Catalysts Pd/C Sample	Reduction conditions		
	Temp. (°C)	Time (h)	Particle size (nm)
10 wt.%	–	–	10.5
10 wt.%	250	3	13.5
5 wt.%	–	–	17.7
5 wt.%	300	3	21.9
5 wt.%	500	3	27.9
5 wt.%	700	4	37.8

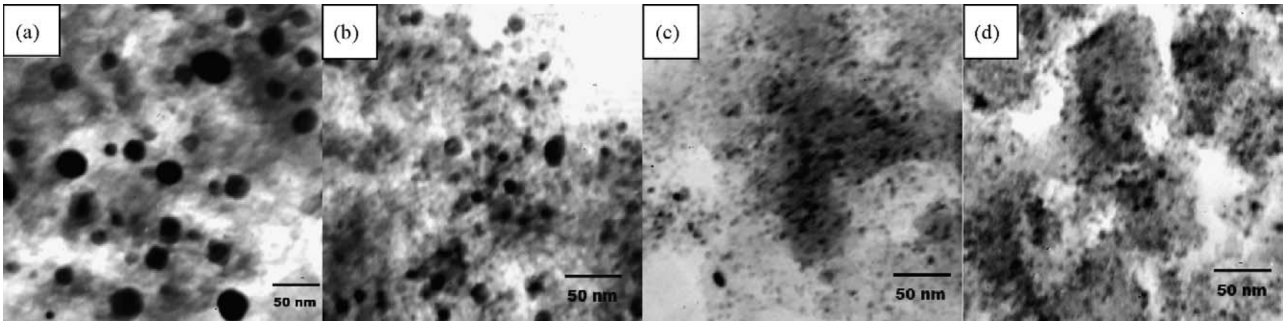
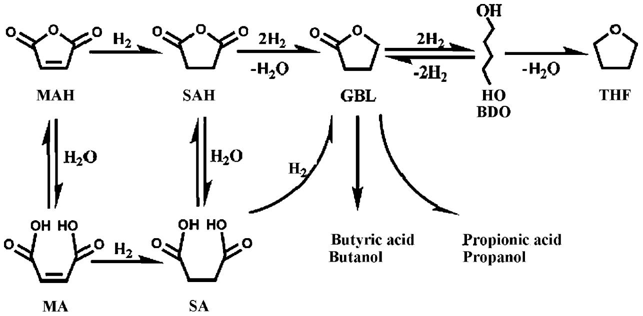


Fig. 2. TEM images of 5% and 10% Pd/C catalysts pretreated at different temperatures with H_2. (a) 5% Pd/C 700 °C, (b) 5% Pd/C no treatment, (c) 10% Pd/C 250 °C and (d) 10% Pd/C no treatment.

hydrogenated to give GBL and/or tetrahydrofuran (THF); and 1,4-butanediol is postulated to be formed directly from THF, GBL or SAH. Additionally, maleic acid, succinic acid, butyric acid and propionic acid could be formed from products hydrolysis and esterification between alcohols and acids. While, in the present work THF, 1,4-butanediol were not detected, but succinic acid was found in organic solvent and some cases in $scCO_2$.

Hydrogenation reactions were conducted in a 50 ml autoclave at temperature of 200 °C with 2.5 mmol MAH and 4 MPa H_2. For the reactions in $scCO_2$, the hydrogenation was performed in a CO_2 partial pressure of 14 MPa with a total pressure of 18 MPa. The reaction mixture is a gas–solid system where all the reactants including MAH and H_2 were dissolved in CO_2 phase. As shown in Table 2, the total conversion of MAH reached 100% for all the reactions conducted for 2 h. The selectivity of products differed with different Pd particle sizes. The selectivity of GBL increased, while the selectivity of SAH decreased, with decrease in Pd particle size in $scCO_2$. For reactions in EGDME, similar trends in conversion and selectivity changes were observed. However, the selectivities of GBL in EGDME are lower than those corresponding ones in $scCO_2$. In the case of 10% Pd/C catalyst, the selectivity of GBL was 92.8% in $scCO_2$, but it was only 70.4% in EGDME. These may be explained by the difference in reaction rates even though the total conversion of MAH reached 100% in all cases. As illustrated in Scheme 1, the reactant MAH is firstly reduced to SAH, and then SAH is hydrogenated to GBL. The first step is much faster with 100% conversion of MAH. The second step from SAH to GBL is slower, and it is much slower in EGDME than in $scCO_2$. Thus, the selectivity of GBL is larger in $scCO_2$. This can also be seen from the results in Fig. 4. The reaction was very fast under the reaction conditions used, MAH was converted completely and the conversions reached 100% within 20 min. With extension of reaction time, however, the selectivity of GBL increased and the increase is faster in $scCO_2$ than in EGDME, irrespective of the size of the Pd particles. Pillai et al. [20,21] reported that the hydrogenation of MAH over Pd/Al_2O_3 could be performed in $scCO_2$ and the selectivity of GBL was enhanced compared to those in organic solvents. However, catalyst deactivation was observed during the hydrogenation. They suggested that the selectivity of GBL decreased due to Pd particles agglomeration during the recycling runs. This is in agreement with the present results of higher selectivity of GBL presented on Pd/C catalyst of smaller Pd particle size. In our previous works, the structure sensitivity of nitrobenzene hydrogenation over supported Pt catalysts has been investigated in $scCO_2$ and in ethanol. The hydrogenation is structure sensitive in $scCO_2$ but less so in ethanol [16]. The structure sensitivity of the reactions may depend on several reaction variables [22,23]. For present reaction, the selectivity of GBL increased with decrease of Pd particle size in



Scheme 1. Reaction pathway of hydrogenation of MAH.

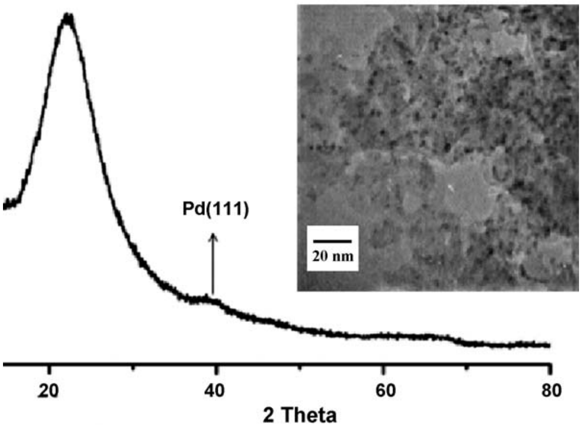


Fig. 3. XRD pattern and TEM image of 5% Pd/C catalyst prepared in EG.

Table 2
Maleic anhydride hydrogenation with Pd/C catalysts in $scCO_2$ and EGDME.

Pd particle size (nm)	Conversion (%)	Product selectivity (%)		
		GBL	SAH	Others
In $scCO_2$				
10.5	100	92.8	4.2	3.0
13.5	100	84.8	10.9	4.2
17.7	100	75.1	24.9	0.0
21.9	100	56.3	40.2	3.6
37.8	100	38.4	61.6	0.0
In EGDME				
10.5	100	70.4	23.8	5.8
13.5	100	68.1	19.1	12.8
17.7	100	62.9	25.3	11.8
21.9	100	52.1	36.3	11.7
37.8	100	18.7	73.5	7.8

Reaction conditions: MAH 2.5 mmol, temperature 200 °C, CO_2 pressure 14 MPa, H_2 4 MPa, 10% Pd/C 10 mg, 5% Pd/C 20 mg, time 2 h.

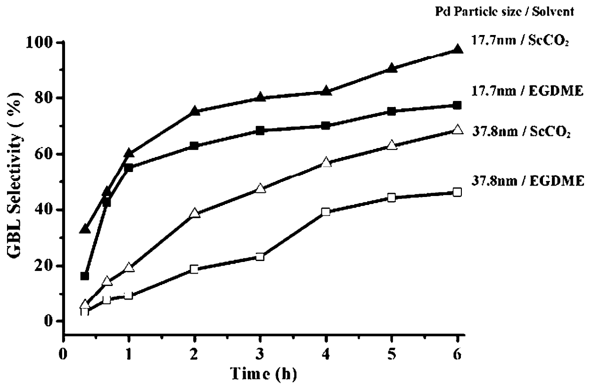


Fig. 4. GBL selectivity dependence of reaction times for hydrogenation of MAH in $scCO_2$ and EGDME. Reaction conditions: MAH 2.5 mmol, H_2 4 MPa, temperature 200 °C, catalyst 5% Pd/C 0.02 g. The conversions of MAH with all the catalysts are 100% after reaction for 20 min.

$scCO_2$. However, a different structure sensitivity profile was observed in EDGME. At particle sizes above 17.7 nm, the selectivity of GBL increased linearly with decreases in Pd particle size. The change was less dramatic at Pd particle sizes below 13.5 nm.

3.3. Influence of CO_2 pressure

It was shown that the absorption spectrum of small gold particles measured in $scCO_2$ depends significantly on pressure, indicating a direct interaction between gold particles and $scCO_2$ medium and which depended on the metal particle size [18], thus potentially affecting the activity of the metal catalyst in $scCO_2$. Herein, the influence of CO_2 pressure on the activity of Pd/C catalysts of different Pd particles size was investigated.

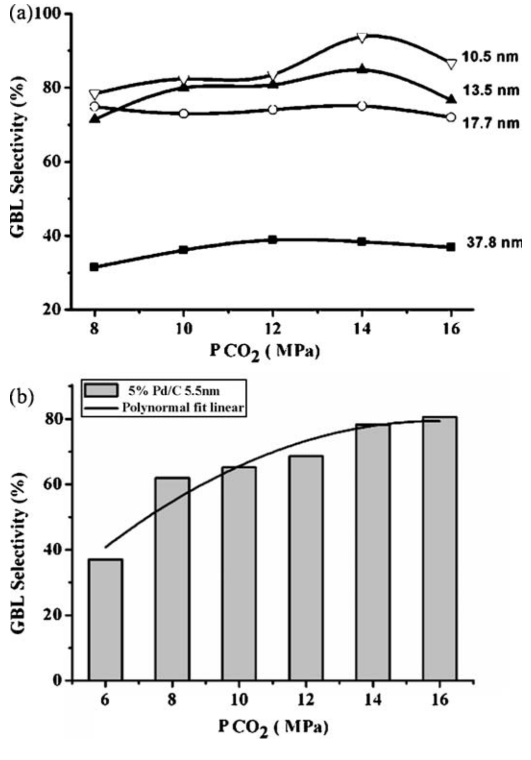


Fig. 5. Influence of CO_2 pressure on hydrogenation of MAH over Pd/C catalysts. Reaction conditions: MAH 2.5 mmol, H_2 4 MPa, temperature 200 °C, time 2 h, catalyst 5% Pd/C 0.02 g, 10% Pd/C 0.01 g. The total conversions are 100% in all the reactions in $scCO_2$. (a) 5 and 10% Pd/C reduced under different temperatures and (b) 5% Pd/C prepared in EG.

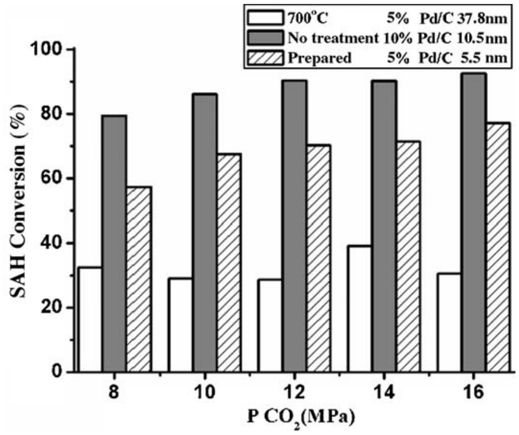


Fig. 6. Influence of CO_2 pressure on hydrogenation of SAH with different Pd nanoparticles in $scCO_2$. Reaction conditions: SAH 2.5 mmol, H_2 4 MPa, temperature 200 °C, time 2 h, catalyst 5% Pd/C 0.02 g, 10% Pd/C 0.01 g.

Fig. 5 shows the effect of CO_2 pressure on the selectivity of GBL with the Pd/C catalysts of different Pd particle sizes. Under these hydrogenation conditions, the conversion of MAH reached 100% in all cases. At large Pd particle sizes of 17.7 and 37.8 nm, the selectivity of GBL was independent of CO_2 pressure. However, at small Pd particle sizes of 10.5 and 13.5 nm, the selectivity of GBL was sensitive to CO_2 pressure and presented a maximum value at 14 MPa. Moreover, a Pd/C catalyst with Pd particles about 5.5 nm has been prepared. The GBL selectivity of this catalyst under different pressures of CO_2 was shown in Fig. 5(b). The selectivity of GBL increased significantly with increasing CO_2 pressure, from 37 to 81% as CO_2 pressure was enhanced from 6 to 16 MPa. These data suggested that the influence of CO_2 pressure was more significant on the activity of smaller Pd particles. Specifically, the interaction between catalyst and CO_2 molecule is stronger for catalysts with smaller Pd particles than larger Pd particles.

To further investigate the effect of the CO_2 pressure on the reaction rate, the hydrogenation of SAH, the second step of the MAH hydrogenation, was examined with Pd/C catalysts as shown in Fig. 6. Under reaction conditions, the selectivity to GBL was 100% with all the Pd/C catalysts, the conversion of SAH increased with increasing the pressure of CO_2 from 8 to 16 MPa over the catalysts with smaller Pd particles of 10.5 and 5.5 nm, and the conversion was larger over the former one, which may due to the different properties of catalysts from the source supports and preparation procedure. But the conversion did not change so much with increasing CO_2 pressure, over the catalyst with Pd particles of 37.8 nm. These are in agreement to the MAH hydrogenations discussed above. It is worth to noting that 100% selectivity to GBL was obtained in the SAH hydrogenation. But in the hydrogenation of MAH, some other by-products were produced from MAH.

4. Conclusions

The Pd/C catalysts with different Pd particle sizes were prepared in this work, and the influence of the Pd particle was investigated for MAH hydrogenation in $scCO_2$ and EDGME. The conversions of MAH reached 100% in all the cases. The selectivity of GBL in $scCO_2$ reached 97.4%, which was notably larger than the 77.4% reached in EGDME. The selectivity of GBL increased with decreasing Pd particle size in both $scCO_2$ and EGDME, but the rate of increase was larger in the former. With the catalysts of smaller Pd particle sizes, the selectivity of GBL increased with increasing CO_2 pressure. For the catalysts with larger Pd particle sizes, however, the selectivity of GBL was irrespective to CO_2 pressure. These results suggested that the influence of CO_2 pressure on the catalytic activity of Pd/C catalyst of smaller Pd particles was more significant, namely a possible interaction of CO_2 with smaller Pd particle existed and it is stronger compared to that with the larger Pd particles.

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