

# Carbon-supported palladium-ruthenium catalyst for hydropurification of terephthalic acid

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## Abstract

The ruthenium-incorporated catalyst, (0.3% Pd–0.2% Ru)/CCM (carbon carbonaceous composite material) catalyst, has been studied as a candidate to replace an existing 0.5% Pd/C catalyst for hydropurification of crude terephthalic acid; it gives an excellent performance and is a promising catalyst. It has been confirmed that the (0.3% Pd–0.2% Ru)/CCM catalyst has higher stability in actual commercial condition and aging in lab condition compared with a commercial catalyst. The increased stability may be explained as the effect of ruthenium to prevent the sintering of supported metal particles. The (0.3% Pd–0.2% Ru)/CCM catalyst shows equal or less amount of side reaction of benzene ring hydrogenation. The dust from carbon support can also be decreased from the (0.3% Pd–0.2% Ru)/CCM catalyst due to the increased strength of the CCM. The (0.3% Pd–0.2% Ru)/CCM catalyst may be very competitive to the existing catalyst due to the inexpensive ruthenium and the expected long life of the catalyst. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydropurification; Ruthenium; Palladium; Carbon; Terephthalic acid; Carbon composite

## 1. Introduction

Terephthalic acid (TPA) is one of the most important chemicals, with an annual production capacity of more than 24,000,000 tonne in the year 2000 [1]. Crude TPA (CTA), usually produced by the liquid phase oxidation of *p*-xylene, contains impurities such as 4-carboxybenzaldehyde (4-CBA, 2000–6000 ppm) and several colored polyaromatic impurities that should be removed to obtain purified TPA (PTA). PTA is usually produced by the hydropurification

of CTA over granular Pd/C in a trickle bed reactor [2].

After the Pd/C catalyst was invented [3], there have been numerous efforts to improve or replace the Pd/C catalyst because the lifetime of the catalyst is relatively short, 6–18 months [2], the carbon support can contaminate the PTA, and palladium is very expensive. Some metals including Pt, Rh, Ni, Ru, Os and Ir supported on C, with and without Pd, have been tried as candidates for a hydropurification catalyst [4–8]. Support such as titanium dioxide has been tried to replace the carbon in order to eliminate the contamination of PTA from carbon dust [9]. However, the efforts to improve the Pd/C catalyst have not been so successful.

Recently, it was reported that ruthenium could disperse the palladium supported on carbon [10] and that

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the higher sintering resistance of the Pd-Ru catalyst could be explained by the increased surface heterogeneity [11]. Ruthenium was also reported to increase the dispersion of palladium on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for the combustion of methane [12]. The Ru/C, Rh/C or Pt/C catalyst, combined with Pd/C catalyst, were also claimed to reduce the 4-CBA very much in the hydropurification of CTA [4,5].

If part of palladium can be replaced with ruthenium, the catalyst will be very cost effective because ruthenium is very cheap compared with palladium [13]. Moreover, the contamination of PTA with the dust of active carbon made from coconut charcoal will be decreased greatly if a strong carbon such as a CCM including Sibunit [14] is used instead.

The Pd-Ru supported on CCM has been studied as a stable catalyst for CTA hydropurification. The results including the activity and stability of catalyst and a side reaction of benzene ring hydrogenation will be discussed in this report.

## 2. Experimental

### 2.1. Preparation of catalysts

Carbon-supported palladium and palladium-ruthenium catalysts were prepared by simultaneous spraying solutions of Na<sub>2</sub>CO<sub>3</sub> and metal complexes (H<sub>2</sub>PdCl<sub>4</sub> and/or Ru(OH)Cl<sub>3</sub> or RuCl<sub>3</sub>) on the carbon granules called Sibunit [14], a kind of CCM, drying in a vacuum oven followed by gas-phase reduction with hydrogen at 250 °C [15]. A commercial 0.5% Pd/C catalyst for CTA hydropurification was also used for this study.

### 2.2. Characterization of catalysts

To check the particle size of palladium or ruthenium, the amount of CO chemisorption was determined with a home-made pulse flow system at 25 °C. The samples were reduced in flowing hydrogen for 20 min at 100 °C just before CO chemisorption. The stoichiometry of CO/Pd = 1 and CO/Ru = 1 was used to calculate the metal size. The texture characteristics of the supports were determined with nitrogen adsorption at liquid nitrogen temperature.

### 2.3. Hydropurification and aging of catalysts

Hydropurification of CTA was conducted in a batch mode in a stirred (800 rpm) autoclave with 0.28 g of catalyst for 5–50 min. Twenty-five grams of CTA, which contains 3% of 4-CBA, and 250 g of water were charged as a substrate and solvent, respectively. Hydrogen (200 psi at STP; about 14 times of stoichiometry of hydrogenation) was used as a reductant and the reaction temperature was 250 °C.

To compare the residual activities, the catalysts were used for 41 days in a commercial reactor at 285 °C. The samples of catalysts were also aged in a stirred autoclave at 250 °C for 44 h by contacting the four catalysts (0.28 g each) with excess hydrogen (i.e., consumed hydrogen was replaced with fresh hydrogen via a check valve) and water of 250 g in the presence of 25 g of PTA and/or 4-CBA.

After the aging of catalysts in commercial or lab condition, the residual activity of each catalyst was measured with the hydropurification (for 30 min if time is not specified) mentioned above.

### 2.4. Analysis

After the reactor was cooled to room temperature, the resulting product was subjected to a solid-liquid separation such as filtration. The recovered solid product was washed, dried and analyzed with HPLC to determine the content of TPA and 4-CBA. The column and detector were C-18 (RP) and UV-DAD (254, 290 nm), respectively, and the eluent was 1% acetic acid/acetonitrile (20/80–40/60%). Before analysis with HPLC, 0.5 g of solid was dissolved in 100 ml of 1% NH<sub>4</sub>OH. Liquid component separated from solid product was also analyzed by HPLC to determine the concentration of TPA and 4-CBA.

The kinetic constant was calculated from the first-order plot of 4-CBA concentration with reaction time. The degree of purification (DOP) was defined as  $C_i/C_f$ , where  $C_i$  and  $C_f$  were initial and final concentrations of 4-CBA in TPA.

The color level of PTA is generally measured directly either by measuring the optical density of PTA solutions (the absorbance of light at 340 nm in its basic solution) or the  $b^*$ -value of the solid acid itself [16]. In our case, alkali transmittance (AT) of TPA was analyzed using a Hewlett Packard 8452A diode array

spectrophotometer with quartz cells of 10 mm thickness at 340 nm, with 2 M KOH solution as reference. Before the measurement, 7.5 g of TPA was dissolved in 50 ml of 2N KOH water solution and insoluble species were removed by centrifuging at 3000 rpm for 30 min.

The relative amount of carbon dust was determined by measuring the UV transmittance of water containing carbon dust. A water slurry containing 10 g of water and 2 g of catalyst was shaken for 5 min, and the intact catalyst was removed from the slurry containing dust. The UV transmittance of water containing carbon dust was measured at 340 nm, and water was used as reference material.

The relative ratio of non-aromatics/aromatics of mother liquor from a hydropurification reaction was determined with  $^1\text{H}$  NMR. The mother liquor was freeze-dried and dissolved in  $\text{D}_2\text{O}$  before the NMR measurement.

### 3. Results and discussion

#### 3.1. Fresh activity and lab aging of catalyst

The fresh activities of commercial 0.5% Pd/C and of developed (0.3% Pd–0.2% Ru)/CCM catalysts,

derived from the first-order kinetics, have the values of 0.206 and 0.126/min, respectively (refer to Fig. 1). The decreased activity of (0.3% Pd–0.2% Ru)/CCM catalysts as compared with 0.5% Pd/C cannot be explained directly by the replacement of palladium with ruthenium, due to the differences of supports such as pore structure, granule shape and size. On the other hand, it is shown that the substitution of part of palladium with ruthenium in Pd/CCM catalysts, other things being equal, reduces the fresh activity of these (Pd–Ru)/CCM catalysts. The rate constants of fresh 0.5% Pd/CCM, (0.2% Pd–0.3% Ru)/CCM and 0.5% Ru/CCM catalysts were 0.140, 0.098 and 0.025/min, respectively [17]. Therefore, it was supposed that the decreased activity of (0.3% Pd–0.2% Ru)/CCM as compared with 0.5% Pd/C was mainly due to the contribution of ruthenium. However, the contribution of CCM cannot be excluded because the fresh activities of 0.5% Pd/C and 0.5% Pd/CCM are 0.206 and 0.140/min, respectively.

However, one of the important characteristics of a catalyst is the steady state activity in actual conditions of operation. Therefore, the catalyst was aged with contacting hydrogen and 4-CBA and/or PTA in water for 44 h to check the steady state activity of a catalyst. The steady state activity of catalysts after the aging (hereafter called “aged activity”) was determined by the hydropurification of CTA, containing 3% 4-CBA,

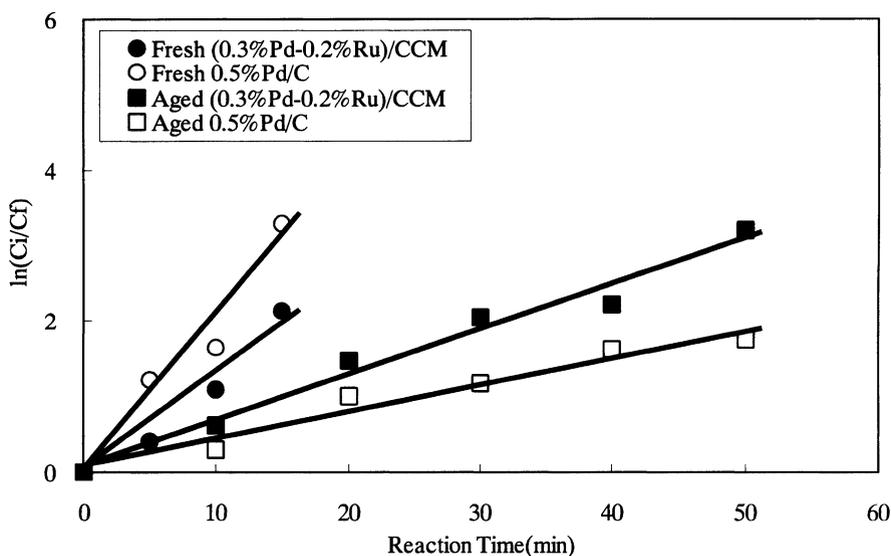


Fig. 1. Activity patterns of fresh catalysts and catalysts aged for 41 days in a commercial reactor.  $C_i$  and  $C_f$  are initial and final concentrations of 4-CBA in TPA.

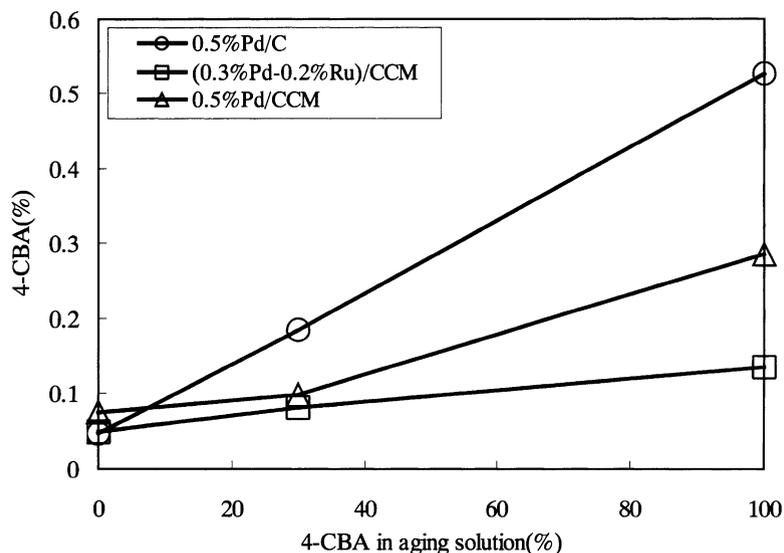


Fig. 2. Effects of aging solution (4-CBA vs. PTA) on the aged activity of the catalysts. The ordinate represents the concentration of 4-CBA of purified TPA that originally contains 3% of 4-CBA.

during 10–50 min (usually 30 min). Fig. 2 and Table 1 show that the aged activities of mono- and bimetallic catalysts are decreased with concentration of 4-CBA in aging solution. The aging through contacting with PTA, without the reducible formyl group, is not sufficient to differentiate the relative activity of each catalyst, even though the activities decrease a bit from fresh activities with aging (Table 1).

It is known that the activity of Pd/C catalysts in CTA hydro purification depends on palladium

particle sizes; the activity is decreased with the sintering of the supported metal [2]. High temperatures and operation in reaction medium result in sintering of the catalysts ([11] and Table 1). Since the aging of the catalyst is carried out most effectively in presence of 4-CBA (Fig. 2, Table 1), it is possible to assume that redox transformations of metallic species with hydrogen (reductant) and a substrate (oxidizer), promote the aging or sintering of catalyst.

Table 1

Quality such as 4-CBA and alkaline transmittance of purified terephthalic acid with catalysts aged in different conditions<sup>a</sup>

Catalyst	Item	4-CBA (100%)	4-CBA (30%) + PTA (70%)	PTA (100%)	Without aging
0.5% Pd/C	4-CBA (%) <sup>b</sup>	0.527	0.184	0.048	0.015
	AT340 (%) <sup>c</sup>	33.1	55.5	71.5	83.4
	Metal size (nm)	29.4	–	–	4.5
0.5% Pd/CCM	4-CBA (%) <sup>b</sup>	0.286	0.099	0.075	0.020
	AT340 (%) <sup>c</sup>	44.2	64.4	74	82.1
	Metal size (nm)	21.5	–	–	5.0
(0.3% Pd–0.2% Ru)/CCM	4-CBA (%) <sup>b</sup>	0.135	0.081	0.050	0.022
	AT340 (%) <sup>c</sup>	51.8	64.7	71.1	80.1
	Metal size (nm)	14.8	–	–	5.2

<sup>a</sup> The metal particles size before hydro purification, determined by CO chemisorption, of the aged catalysts is also shown.

<sup>b</sup> Residual 4-CBA (initial concentration: 3%) in terephthalic acid purified with aged catalysts.

<sup>c</sup> Alkaline transmittance at 340 nm of terephthalic acid purified with aged catalyst and dissolved in aqueous KOH.

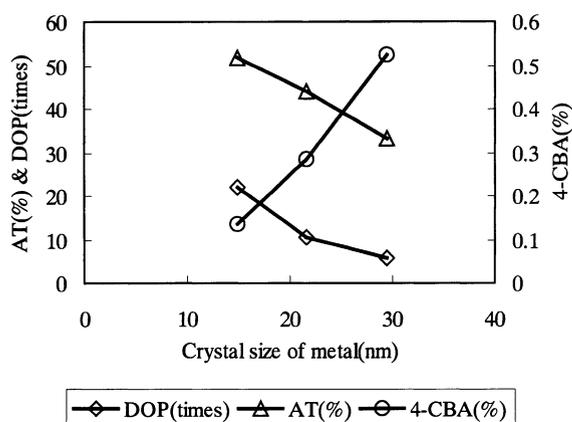


Fig. 3. Effects of crystal size of metal on the hydropurification (alkali transmittance at 340 nm, degree of purification and 4-CBA concentration) of CTA. All catalysts were aged for 44 h with 4-CBA.

From Fig. 3, one can also understand that the activity of a catalyst depends inversely on the size of metal or on the degree of sintering. The reason why the aged catalysts have decreased activity values can be explained mainly by the particle size of metals of catalyst, because the metal sizes of fresh catalysts are about 5 nm (Table 1). It is also confirmed that the bimetallic catalyst is more resistant, in a commercial condition, to sintering compared with Pd/C catalyst [11].

The blocking of pores with bulky organic materials during hydropurification may decrease the activity of catalyst. However, the parameters of pore structure of the supports for fresh and aged catalysts, presented in Table 2, do not allow us to estimate this effect on the aged activity.

One important characteristic of the bimetallic catalyst is that the (0.3% Pd–0.2% Ru)/CCM catalyst after the aging with 4-CBA or 4-CBA/PTA has higher aged activity, even though the activity of the fresh catalyst is lower than that of a commercial catalyst (Figs. 1–3). XRD, SAD, RDF and HREM techniques were used by us [11] to study the role of the Ru additives in the stabilization of carbon-supported palladium catalysts at high temperatures in hydrogen atmosphere and under the operation in reaction medium in process of terephthalic acid hydropurification. It was shown that the partial replacement of palladium with ruthenium in the Pd/C catalysts results in the increase of sintering stability (see also Table 1) via increased surface heterogeneity rather than via chemical interaction between palladium and ruthenium [11]. A decrease in the dispersity of bimetallic catalysts at high temperatures occurs mainly due to the sintering of palladium metal particles; the ruthenium particles in these conditions maintain high dispersity and exist as an individual phase [11]. The detailed inhibition effect of ruthenium on sintering of metal is explained by us elsewhere [11].

### 3.2. Residual activity after a commercial run

The (0.3% Pd–0.2% Ru)/CCM catalyst mixed well with a commercial catalyst was put into (four different positions) and used in a commercial reactor at 285 °C for 41 days. Data in Table 3 confirms that the (0.3% Pd–0.2% Ru)/CCM catalyst spent in a commercial condition shows better performance than a spent commercial catalyst in all positions in viewpoint of removal of 4-CBA and coloring materials. From Fig. 1, it can be understood that the (0.3% Pd–0.2% Ru)/CCM

Table 2  
Effect of treatment conditions on texture characteristics of the catalyst supports

Treatment condition	BET surface area (m <sup>2</sup> /g)		Total pore volume (cc/g)		Average pore diameter (Å)	
	(0.3% Pd–0.2% Ru)/CCM	0.5% Pd/C	(0.3% Pd–0.2% Ru)/CCM	0.5% Pd/C	(0.3% Pd–0.2% Ru)/CCM	0.5% Pd/C
Fresh	323	1214	0.49	0.51	60.7	16.8
Lab aging with 4-CBA <sup>a</sup>	306	938	0.57	0.38	75.2	16.3
Aging in a commercial plant <sup>b</sup>	277	1177	0.39	0.52	56.0	17.5

<sup>a</sup> For 44 h.

<sup>b</sup> For 41 days.

Table 3

Dependence of the residual activity for removal of 4-CBA and coloring impurities on the catalyst type and its position in a commercial reactor

Position	Catalyst	Degree of purification (times)	AT340 (%)
1	0.5% Pd/C	5.52	33.8
	(0.3% Pd–0.2% Ru)/CCM	6.57	36.4
2	0.5% Pd/C	3.68	25.2
	(0.3% Pd–0.2% Ru)/CCM	10.01	43.0
3	0.5% Pd/C	3.27	25.7
	(0.3% Pd–0.2% Ru)/CCM	5.60	32.5
4	0.5% Pd/C	3.59	24.3
	(0.3% Pd–0.2% Ru)/CCM	8.50	35.3
Average	0.5% Pd/C	4.02	27.3
	(0.3% Pd–0.2% Ru)/CCM	7.67	36.8

catalyst shows much higher residual activity, by 60%, than that of a commercial catalyst, in agreement with the lab aging results.

In summary, the (0.3% Pd–0.2% Ru)/CCM catalyst shows much higher residual activity than a commercial catalyst after not only lab aging but also actual commercial run.

### 3.3. Ring hydrogenation

The CTA hydropurification over a catalyst can be accompanied by hydrogenation of unsaturated bonds (refer to Fig. 4). These side reactions should be minimised to avoid the TPA loss. As the ruthenium exhibits activity in such processes, for example, in

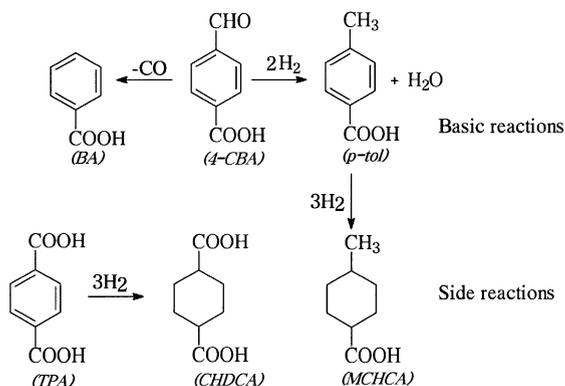


Fig. 4. Scheme of reactions in the hydropurification of CTA.

hydrogenation of benzene to cyclohexane [18], it is of interest to check the amount of side reaction of ring hydrogenation over (0.3% Pd–0.2% Ru)/CCM catalyst compared with that over a commercial 0.5% Pd/C.

However, the amount of this ring hydrogenation is quite difficult to measure because the degree of this reaction is very low and there are several kinds of species with cyclohexyl ring (substituents of this ring can be methyl and carboxyl etc.) (Fig. 4). The portion of this reaction can be checked by the relative amount of non-aromatics in mother liquor after a hydropurification reaction with NMR, because of the difference in the chemical shifts of protons for two groups of compounds (benzene versus cyclohexyl ring) (Fig. 5). The protons of aromatic compounds (*p*-toluic acid, 4-CBA, BA, etc.) induce signals at 6–9 ppm, whereas, chemical shifts of protons on saturated rings (CHDCA, MCHCA, etc.) are at 0.5–3 ppm. It should be noted that the sharp signal with maximum at 2.4 ppm is assigned to protons of CH<sub>3</sub>- group of *p*-toluic acid.

From Fig. 6, it can be understood that the amount of side reaction of ring hydrogenation over (0.3% Pd–0.2% Ru)/CCM catalyst is equal to or lower than over a commercial catalyst. It also can be deduced that the ring hydrogenation depends on the conversion of 4-CBA, as can be anticipated easily, rather than on the type of catalyst. The (0.3% Pd–0.2% Ru)/CCM catalyst seems not to decrease the yield of PTA due to the ring hydrogenation.

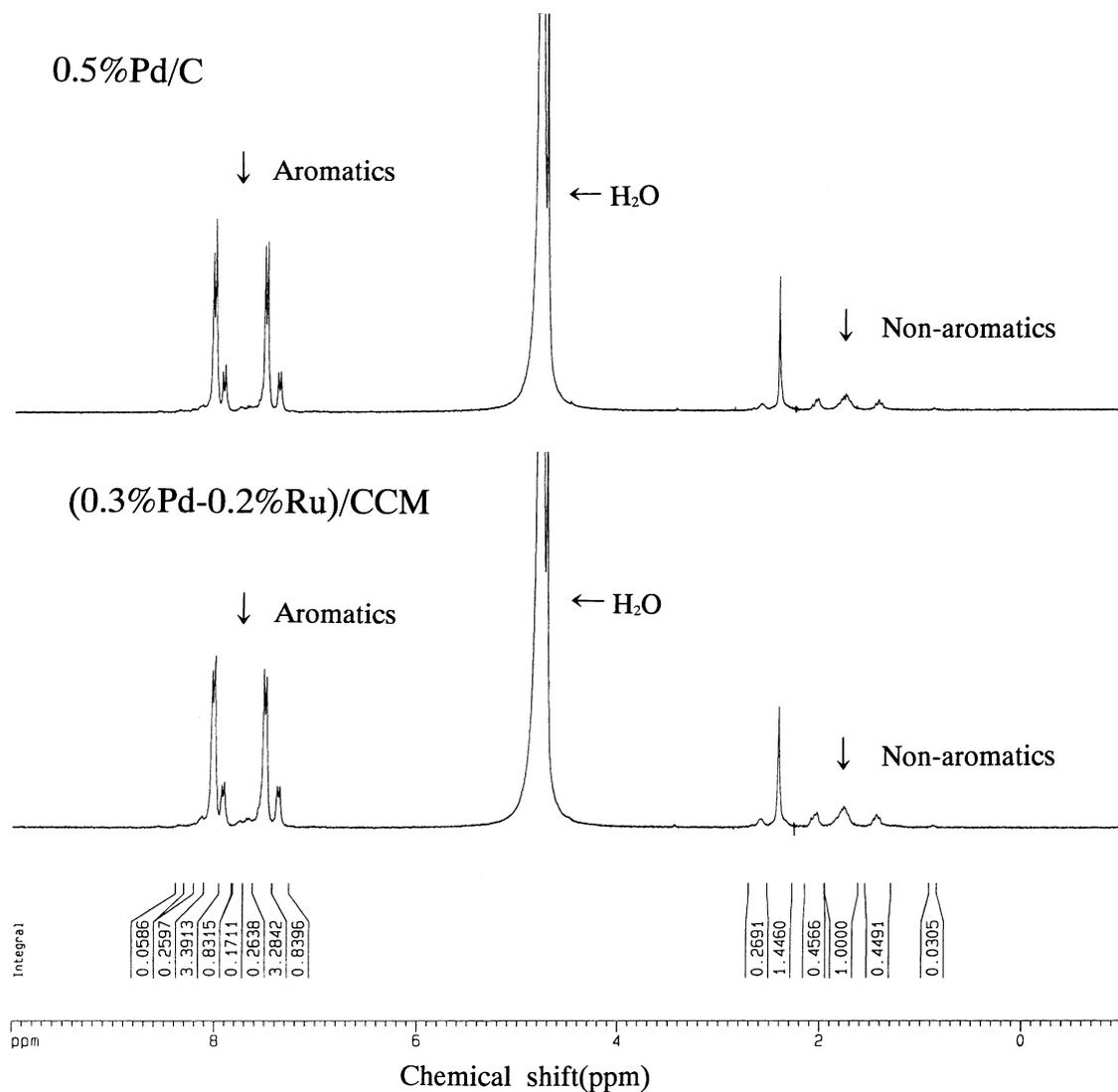


Fig. 5. Typical NMR spectra of mother liquor after the hydropurification of CTA to PTA. The mother liquor was dried and dissolved in D<sub>2</sub>O before the measurement. The upper and lower spectra correspond to the mother liquor from the commercial and (0.3% Pd–0.2% Ru)/CCM catalysts, respectively.

### 3.4. Dust formation from carbon support

The dust from carbon support may contaminate and deteriorate the PTA produced from hydropurification. It was confirmed that the (0.3% Pd–0.2% Ru)/CCM catalyst shows much lower attrition loss (0.08 wt.%) than usual 0.5% Pd/C (1.45 wt.%) [19].

The dust formation after the actual run for 41 days is compared with the UV transmittance at 340 nm of mother liquor after separating the intact catalyst from the shaken solution containing the catalyst. From Table 4, it can be clearly known that the (0.3% Pd–0.2% Ru)/CCM catalyst shows better performance in preventing the dust formation than a commercial catalyst, in agreement with the attrition loss of each catalyst.

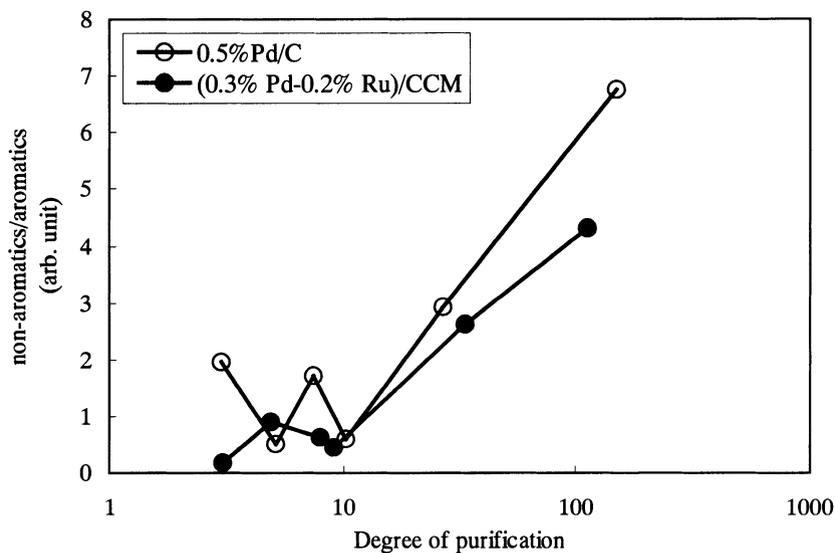


Fig. 6. Dependence of the ratio of non-aromatics/aromatics of mother liquor on the type of catalyst and degree of purification. The hydro-purification reaction was accomplished with aged catalysts in lab condition. The degree of purification depended on the aging conditions.

Table 4

Dependence of the amount of formation of carbon dust, determined by the UV transmittance of mother liquor, on the type of catalyst and position in a commercial reactor

Position	Catalyst	UV transmittance at 340nm (%)
1	0.5% Pd/C	83.1
	(0.3% Pd–0.2% Ru)/CCM	95.4
2	0.5% Pd/C	85.3
	(0.3% Pd–0.2% Ru)/CCM	96.7
3	0.5% Pd C	90.5
	(0.3% Pd–0.2% Ru)/CCM	97.1
Average	0.5% Pd/C	86.3
	(0.3% Pd–0.2% Ru)/CCM	96.4

#### 4. Conclusions

The (0.3% Pd–0.2% Ru)/CCM catalyst shows higher stability than an existing catalyst in the condition of a commercial reactor and lab aging, even though it has lower fresh activity. The increased aged activity of bimetallic catalyst may be explained as the effect of ruthenium to prevent the sintering of supported metal particles. This catalyst shows equal or less amount of side reaction of ring hydrogenation.

The (0.3% Pd–0.2% Ru)/CCM catalyst can be a promising candidate to replace the existing 0.5% Pd/C catalyst.

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