

## PdRu/Carbon Composite 촉매를 이용한 테레프탈산의 수소화 정제

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### Hydropurification of Crude Terephthalic Acid over PdRu/Carbon Composite Catalyst

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**요 약.** CTA(crude terephthalic acid)의 수소화 정제 반응이 고온의 회분식 반응기에서 PdRu/CCM(carbon-carbonaceous composite material) 촉매 상에서 수행되었다. 반응 시간에 따른  $\ln(4\text{-CBA}; 4\text{-carboxybenzaldehyde})$ 의 의존도가 선형성을 보임에서 수소화 정제는 1차 속도론을 따름을 알 수 있었다. 촉매량에 따른 반응 속도의 선형성에서 조사된 반응 조건은 정제 반응을 잘 대변할 수 있음을 알 수 있었다. 반응 전환율이 증가하면(4-CBA가 감소하면) 고체 및 액체의 *p*-toluic acid(*p*-tol)의 농도는 증가하였으나 벤조산(BA)의 농도는 크게 변하지 않았다. 4-CBA 농도가 대략 0.15% 이하일 때에는 PTA의 AT(alkali transmittance)는 4-CBA농도에 반비례하며 이는 4-CBA의 수소화에 따라 발색물질도 제거 됨을 보여 준다. 4-CBA농도가 약 0.2% 이상이면 AT는 일정하였는데 이는 4-CBA 자체는 발색 효과를 가지지 않음을 보여 준다. (0.3%Pd-0.2%Ru)/CCM 촉매는 0.5%Pd/C 상업 촉매에 비해 초기 활성은 낮으나, 상업 공장 반응기에서 사용한 후에는 오히려 큰 잔존 활성을 보였고 PdRu/CCM 촉매는 루테늄 함량이 약 0.2~0.35% 일 때 활성의 상승효과를 보였다. PdRu/CCM 촉매는 0.5%Pd/C 상업 촉매를 대체할 가능성이 높음을 알 수 있다.

**주제어:** 테레프탈산, 수소화 정제, 팔라듐, 루테늄, 탄소

**ABSTRACT.** The hydropurification reaction of CTA (crude terephthalic acid) was carried out with hydrogen over PdRu/CCM (carbon-carbonaceous composite material) catalyst in a batch reactor at high temperature. The first order kinetics of hydropurification is confirmed with the linear dependence of  $\ln(4\text{-CBA}; 4\text{-carboxybenzaldehyde})$  with reaction time. The reaction condition studied is thought to represent the hydropurification well because of the linear dependence of catalytic activity on the catalyst weight. The *p*-toluic acid (*p*-tol) in solid and liquid increases with the conversion of reaction or the decrease of 4-CBA. However, the benzoic acid (BA) concentration does not depend much on the conversion. The AT (alkali transmittance) does not depend on the 4-CBA when the concentration is higher than about 0.2% which shows the 4-CBA, in itself, does not cause the coloring effect. The AT of PTA depends inversely with the concentration of 4-CBA when the 4-CBA is less than about 0.15%. This may show the coloring materials are removed in parallel with the hydrogenation of 4-CBA. The (0.3%Pd-0.2%Ru)/CCM shows larger residual catalytic activity than a commercial catalyst, 0.5%Pd/C, after using in a commercial reactor even though the former has smaller fresh activity than the latter. The palladium and ruthenium in PdRu/CCM show the synergetic effect in activity when the ruthenium concentration is about

0.2~0.35 wt%. It may be supposed that the PdRu/CCM catalyst can be a promising candidate to replace the commercial Pd/C catalyst.

**Keywords:** terephthalic acid, hydropurification, palladium, ruthenium, carbon

## INTRODUCTION

Terephthalic acid (TPA) is one of the most important chemicals with the annual production capacity of more than 24,000,000 tons in the year 2000. The production capacity of Korea is the highest in the world with the capacity of 4,540,000 t/yr in the year 2000<sup>1</sup>. 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 for purified TPA (PTA). PTA is usually produced by the hydropurification of CTA over a granular Pd/C in a trickle bed reactor.<sup>2</sup>

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

Although the Pd/C catalyst for PTA is one of the most important petrochemical catalysts and fundamental understanding is inevitable to develop a competitive catalyst, scientific literature is almost completely lacking.<sup>2</sup> Only a few Chinese<sup>10-12</sup> and Italian researchers<sup>2, 13-15</sup> have published some papers dealing with mainly the deactivation of Pd/C catalyst. Recently some of results including the increased stability of a bimetal catalyst, (0.3%Pd-0.2%Ru)/CCM (carbon-carbonaceous composite material), have been reported by us.<sup>16-18</sup>

Moreover, it is quite hard to simulate the continu-

ous hydropurification of CTA in a laboratory reactor because of high reaction temperature of about 285 °C and very low solubility of TPA in water (For example, the solubility of TPA is less than 2 g at 200 °C in water.). In this paper the fundamental research in lab condition on PdRu/CCM including the effects of reaction parameters on hydropurification, dependence of product quality such as *p*-toluic acid, benzoic acid (BA) and color properties on the conversion of 4-CBA are reported. The catalytic activities of (0.3%Pd-0.2%Ru)/CCM and commercial 0.5%Pd/C are compared and the synergetic effect of palladium and ruthenium on the activity of PdRu/CCM is also reported.

## EXPERIMENTAL

**Preparation of catalysts.** Carbon-supported palladium-ruthenium catalysts, PdRu/CCM, were prepared by simultaneous spraying of 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,<sup>19</sup> a kind of CCM, drying in a vacuum oven followed by gas-phase reduction with hydrogen at 250 °C with an apparatus of Fig. 1. The flowing air was used as a

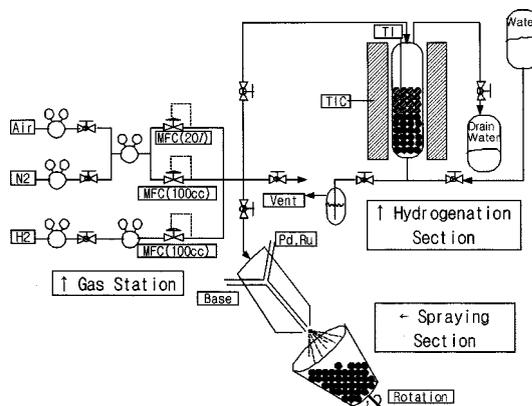


Fig. 1. Apparatus to prepare the PdRu/CCM catalyst.

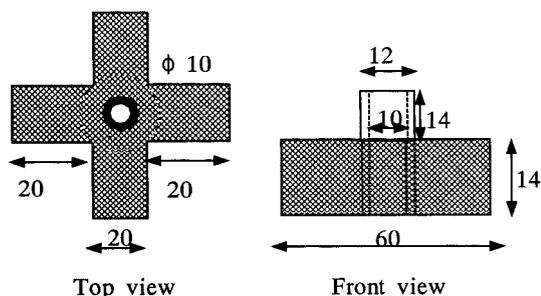


Fig. 2. Schematic diagram of reaction basket to prevent the breaking of the catalysts (unit in mm).

driving force for spraying and the vessel containing the support was rotated during spraying at a speed of 60~90 rpm. The total weight of palladium and ruthenium is 0.5 wt% of catalyst. The catalyst of (0.3%Pd-0.2%Ru)/CCM was usually used for this study and other PdRu/CCM with various metal composition was used for the synergetic effects between palladium and ruthenium. As a reference, a commercial 0.5%Pd/C catalyst for CTA hydropurification was also used for this study.

**Hydropurification reaction.** Hydropurification of CTA was conducted with 200 psi of hydrogen (at STP; about 14 times of the stoichiometry of hydrogenation) in a batch mode in a stirred autoclave (800 rpm) with 0.28 g of catalyst for 20 min, unless otherwise specified. The catalyst was loaded in a catalyst basket made of stainless steel 316 L of Fig. 2 to prevent the crushing of the catalyst. 25 g of CTA, which contains 3% of 4-CBA, and 250 g of water were charged as a substrate and solvent, respectively. To check the effect of reaction parameters, reaction time (10~30 min), catalyst weight (0.07~0.35 g), agitation speed (400~1000 rpm) and the amount of hydrogen (7~21 times of stoichiometry based on the hydrogenation) were varied.

To compare the residual activities, the catalysts were used for 41 days in a commercial reactor at 285 °C. After the aging of catalysts in commercial condition, the activity of each catalyst was measured with the hydropurification mentioned above.

**Analysis.** After the reactor was cooled to room temperature, the resulting product was subjected to a solid-liquid separation such as filtration. The recov-

ered solid product was washed, dried and analyzed with HPLC to determine the content of TPA, 4-CBA, p-tol and BA. The column and detector were C-18 (RP) and UV-DAD (254, 290 nm), respectively, and eluent was 1% acetic acid/acetonitrile (20/80% to 40/60%). Before analysis with HPLC, 0.5 g of solid was dissolved in 100 ml of 1%  $\text{NH}_4\text{OH}$ . Liquid component separated from solid product was also analyzed by HPLC to determine the concentration of TPA, 4-CBA, p-tol and BA.

The catalytic activity was calculated from the first-order plot of 4-CBA concentration with reaction time.

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.<sup>20</sup> In this case, alkali transmittance (AT) of PTA 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 PTA was dissolved in 50 ml of 2N KOH water solution and insoluble species were removed with centrifuging at 3000 rpm for 30 min. The optical density of mother liquor was also analyzed with the spectrophotometer.

## RESULTS AND DISCUSSION

**Effects of hydropurification conditions.** The effects of hydrogen pressure and agitation speed on the hydropurification are represented in Figs. 3 and 4. The conversion of 4-CBA increases with the hydro-

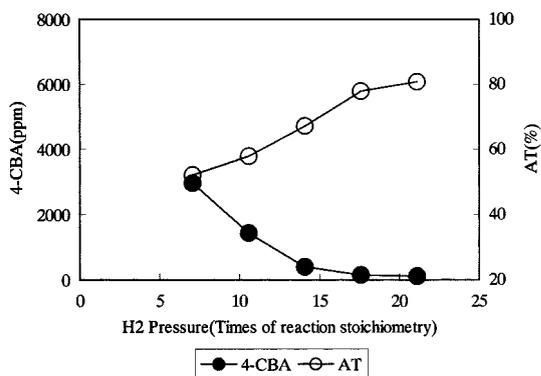


Fig. 3. Dependence of hydropurification with hydrogen pressure.

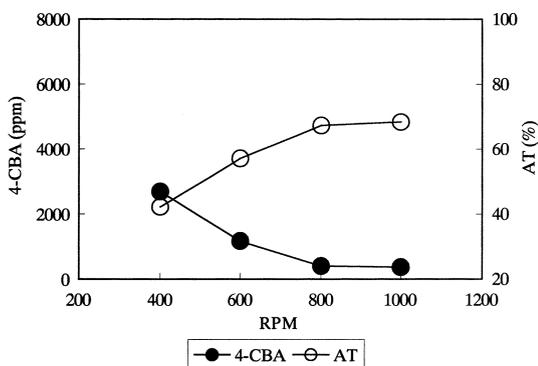


Fig. 4. Dependence of hydropurification with agitation speed.

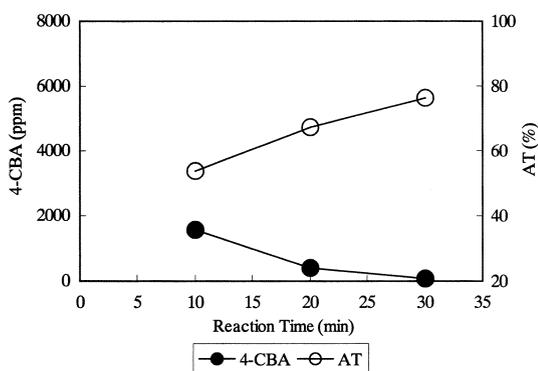


Fig. 5. Dependence of hydropurification with reaction time.

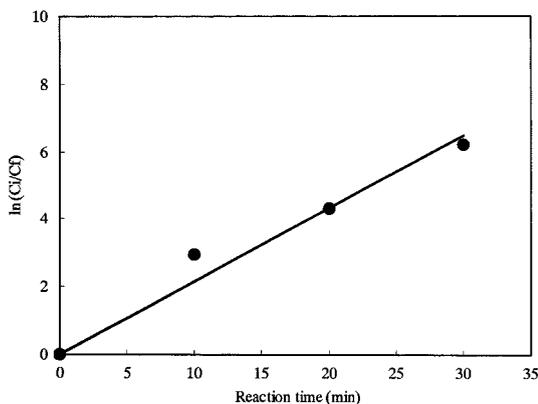


Fig. 6. Activity pattern of (0.3%Pd-0.2%Ru)/CCM catalyst for the hydropurification.  $C_i$  and  $C_f$  are initial and final concentrations of 4-CBA in TPA.

gen pressure and agitation speed as can be anticipated easily. However, the hydrogen pressure and agitation speed do not have noticeable effects on the hydropurification when hydrogen pressure is

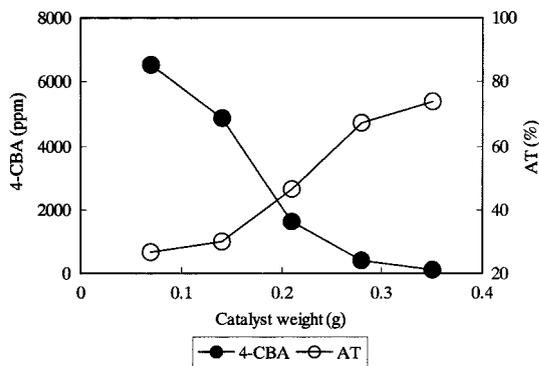


Fig. 7. Dependence of hydropurification on the weight of catalyst.

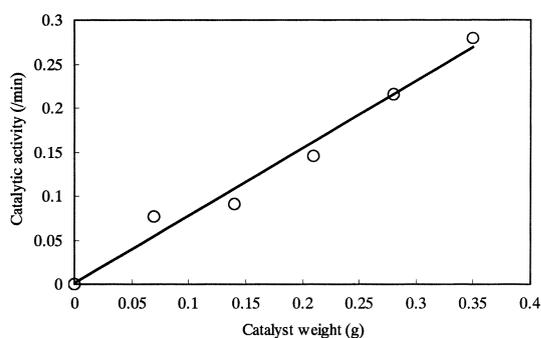


Fig. 8. Dependence of catalytic activity on the weight of catalyst.

higher than 200 psi (or 14 times of the stoichiometry of hydrogenation) and agitation speed is more than 800 rpm.

The effect of reaction time on the hydropurification is represented in Fig. 5. From Fig. 6, calculated from data of Fig. 5, it can be understood that the hydropurification reaction over (0.3%Pd-0.2%Ru)/CCM follows the first order kinetics similar to the result reported by Pernicone et al. for the Pd/C catalyst.<sup>2</sup>

To check whether the hydropurification reaction is governed by diffusion of reactants or not, the effect of catalyst weight on the conversion of 4-CBA was studied. From Figs. 7 and 8, it can be understood that the reaction does not depend on the diffusion of reactants. And the catalyst weight (up to 0.35 g) investigated in this report is not saturated in catalytic activity. Therefore, the relative activity of cata-

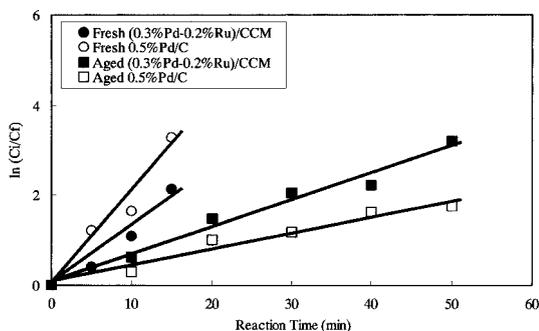


Fig. 9. Activity patterns of fresh catalysts and aged catalysts for 41 days in a commercial reactor.  $C_i$  and  $C_f$  are initial and final concentrations of 4-CBA in TPA.

lysts can be differentiated with the catalytic activity determined from first order kinetics.

Fig. 9 shows the activity pattern of fresh and aged catalysts in a commercial reactor for 41 days and it can be understood that the catalysts ((0.3%Pd-0.2%Ru)/CCM and 0.5%Pd/C) follow the first kinetic pattern even after the aging. The (0.3%Pd-0.2%Ru)/CCM catalyst shows larger activity than 0.5%Pd/C after the aging even though the fresh activity of the former is smaller than that of the latter. It can be understood that the (0.3%Pd-0.2%Ru)/CCM shows

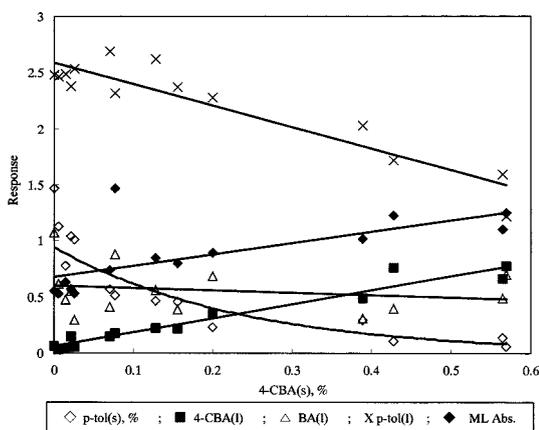


Fig. 10. Dependence of some parameters of PTA and mother liquor on the conversion of hydropurification or 4-CBA concentration of PTA. The 4-CBA(l), BA(l) and  $p$ -tol(l) mean the concentration of each compound in mother liquor in arbitrary unit. The  $p$ -tol(s) and ML abs represent the  $p$ -tol concentration (%) in solid PTA and absorbance of mother liquor at 300 nm, respectively.

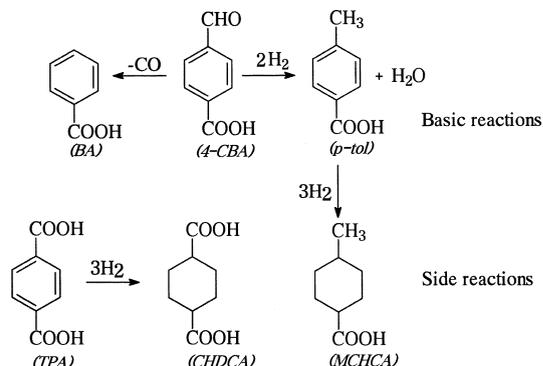


Fig. 11. Scheme of reactions in the hydropurification of CTA.

increased catalyst life. These effects are explained with the decreased sintering of metals due to the increased surface heterogeneity by incorporated ruthenium, and reported in detail elsewhere.<sup>17, 18</sup>

It can also be understood that the hydropurification reaction can be monitored crudely with the AT of the PTA, if 4-CBA is less than 0.15% (*vide infra*), because the AT and 4-CBA showed inverse trend in Figs. 3~5 and 7.

#### Dependence of quality of PTA on the conversion.

The effects of conversion or 4-CBA concentration in PTA on the concentration of  $p$ -tol in solid PTA and concentration of 4-CBA,  $p$ -tol and BA in mother liquor and absorbance of mother liquor were monitored. From Fig. 10, it can be understood that the  $p$ -tols in solid and liquid increase with the conversion of 4-CBA in agreement with the basic reaction of 4-CBA to  $p$ -tol (Fig. 11). However, the 4-CBA in liquid and absorbance of mother liquor decrease with the conversion. It can be understood that the removal of coloring materials accompanies with the removal of 4-CBA. However, the BA in mother liquor does not depend much on the conversion of 4-CBA. The BA in solid product was negligible. It was known that the decarbonylation of 4-CBA to BA and carbon dioxide depended on the hydrogen partial pressure. The decarbonylation was promoted in the deficiency of hydrogen<sup>21, 22</sup>. The constant concentration of BA may represent that the reaction of decarbonylation does not depend on the hydrogen pressure (7 to 21 times of stoichiometry of hydroge-

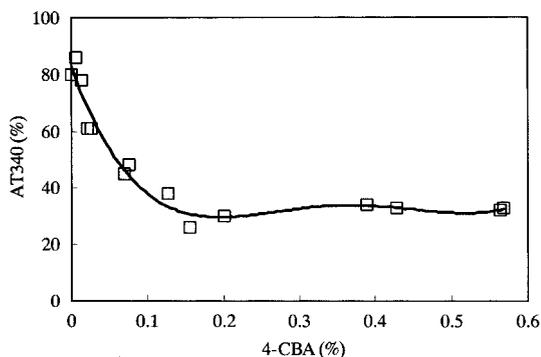


Fig. 12. Dependence of AT with the 4-CBA concentration.

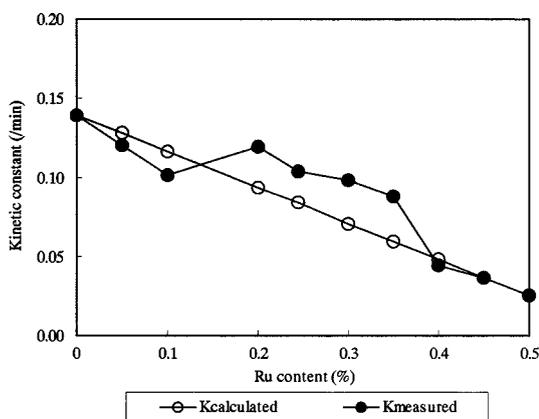


Fig. 13. Dependence of kinetic constant on the concentration of ruthenium in PdRu/CCM catalyst. The total concentration of palladium and ruthenium is 0.5 wt%.

nation) in this study. The hydrogen is not deficient for decarbonylation to occur much.

The AT of solid PTA depends inversely when the 4-CBA is less than about 0.15% as is shown in Fig. 12. This may show the coloring materials are removed in parallel with the hydrogenation of 4-CBA. However, the AT does not depend on the 4-CBA when the concentration is higher than about 0.2% which shows the 4-CBA, in itself, may not cause the coloring in CTA. And the reaction may be monitored crudely by the AT or color properties when the 4-CBA is not higher than 0.15%.

#### Synergetic effect between palladium and ruthenium.

The dependence of activity of PdRu/CCM catalyst with the concentration of palladium and ruthenium was checked and shows the activity generally

decreases with the replacement of palladium by ruthenium (Fig. 13). However, the activity shows a synergetic effect in the region of Ru=0.2~0.35 wt%. In that region of metal concentration, the activities are higher than the activities that calculated by the arithmetic summation of activities of x%Pd/CCM and (0.5-x)%Ru/CCM based on the activities of 0.5%Pd/CCM and 0.5%Ru/CCM. This synergetic effect increases even more after an aging or contacting of the catalyst with 4-CBA/hydrogen/water.<sup>23</sup> This synergetic effect should be studied in detail.

Considering the low cost of ruthenium compared with palladium<sup>24</sup>, increased stability and synergetic effect in activity, the PdRu/CCM can be a promising candidate to replace the commercial Pd/C catalyst.

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