

Effects of Catalyst Promotion on the Selective Hydrogenation of Biphenol Using Various Pd/C Catalysts

Hong-Baek Cho,^{*,*} Bum-Eui Hong, Jai-Hyun Park, Sung-Hyun Ahn, and Yeung-Ho Park^{*}

Division of Materials and Chemical Engineering, Hanyang University, Ansan, Gyeonggi 425-791, Korea

**E-mail: parkyh@hanyang.ac.kr*

[†]Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan

**E-mail: hong-baekcho@etigo.nagaokaut.ac.jp*

Received July 12, 2008

The effect of sodium (Na) promotion was studied in the biphenol (BP) hydrogenation using various Pd/C catalysts. Different amounts of sodium metal were used for promotion with Pd/C and their effects on BP hydrogenation were observed. The promotion order was changed to compare the effect of the position of the promoter in relation to the palladium (Pd) metal on the catalytic activity and yield of the final product, bicyclohexyl-4,4'-diol (BIID). Pd/C catalysts prepared from different methods were also sodium-promoted and the changes of the reaction pathway according to the type of promoted Pd/C catalyst were compared.

Key Words : Sodium promotion, Pre-impregnation, Co-impregnation, Post-impregnation, Biphenol hydrogenation

Introduction

Bicyclohexyl-4,4'-diol (BHD), 4,4'-(hydroxyl-cyclohexyl)-phenol (HCP), and bicyclohexyl-4,4'-dione (BHDN) are produced in the selective hydrogenation of biphenol (BP), and are of importance in the manufacturing of fine chemicals used in pharmaceuticals, liquid crystal displays (LCD), and surfactants.^{1,2} BHD is obtained from the total hydrogenation of BP and is composed of three BHD isomers: *trans,trans*, *cis,trans*, and *cis,cis*. HCP and BHDN are obtained from the partial hydrogenation of BP. Hydrogenation of BP also involves many hydrogenolysis products. Therefore, the hydrogenation conditions of BP are critical to increase the selectivity of the desired compounds.

There are many ways to increase the activity and selectivity of products. Among those, ad Pd/C catalysts were observed. r effects on the change of reaction routes of BP hydrogenation. r all performance of differentlykali promoters are widely employed for catalytic reactions to improve activity, selectivity, and stability of catalysts.³⁻⁸ Addition of alkali compounds to the reaction enhances the rapid and selective hydrogenation of aromatic amines,⁹ though using alkali salt as a promoter additive is problematic because it necessitates further processing to recover the compounds produced from the alkali metals. The effect of a promoter as a second metal can be explained either in electronic or geometric terms; it can electronically activate the adsorption and desorption process between the reactant and catalyst metal, or it can geometrically protect the catalyst metal from sintering during catalyst reduction at higher temperature.^{7,10,11} Previous studies on the promotional effects of a second metal were carried out mainly by doping an alkali metal after preparation of the catalyst metal using a post-impregnation method¹²⁻¹⁴ that facilitated the location of the promoter metal either on or next to the catalyst metal. In a

liquid phase hydrogenation of cyclohexene, addition of a tin (Sn) promoter by co-impregnation was more advantageous than that by pre-impregnation.¹⁵ In phenol hydrogenation using an alkali-promoted Pd/Al₂O₃ catalyst, the catalytic activity and yield to cyclohexanol were increased by changing the acid-base property of the support using the pre-impregnation method.^{6,7} However, studies on the development of modified Pd/C catalysts for BP hydrogenation are limited, and some are patented.^{1,14} Moreover, the effect of promoter order on catalytic performance has not been thoroughly studied.

As part of the on-going research in our laboratory, we have been studying the reaction mechanism of BP hydrogenation and have found that the yield of BHD can be increased remarkably with sodium promotion.⁸ Furthermore, the reaction performance of BP showed large differences according to the method used to prepare the Pd/C catalysts.¹⁶ The present communication reports the influence of sodium promotion methods on the overall performance of differently-prepared Pd/C catalysts, and their effect on the BP hydrogenation reaction route.

Experimental Section

Preparation of sodium-promoted Pd/C. To compare different promotion order using sodium with a Pd/C catalyst, three different promotion orders were evaluated and sodium promotion and Pd impregnation were carried out by the incipient wetness method (IW). Sodium-promoted Pd/C catalysts were prepared as follows;

- 1) pre-impregnation: Sodium application before impregnation of Pd metal on activated carbon.
- 2) co-impregnation: Simultaneous impregnation of Pd and sodium on activated carbon.
- 3) post-impregnation: Sodium application after impreg-

nation of Pd metal on activated carbon.

The amount of sodium was varied from 0.2 wt% to 5.0 wt% and the incipient wetness method (IW) was adapted to both Pd impregnation and sodium promotion. When sodium promotion was performed by pre-impregnation, sodium was deposited on the carbon substrate and dried at 100 °C for 12 hours. Pd was then impregnated on the sodium-promoted carbon (Na/C) followed by drying at 100 °C for 12 hours and reduction at 100 °C for 2 hours under 50 mL/min H₂. The prepared 5Pd-(Na/C) catalysts were stored in a desiccator. To prepare co-impregnated sodium Pd/C catalysts, the precursor salts of Na and Pd were impregnated simultaneously, and the prepared (Na-5Pd)/C catalysts were dried, reduced, and stored in a desiccator under the same treatment conditions used for pre-impregnation. Finally, to prepare post-impregnated sodium Pd/C catalysts, the Pd/C catalyst prepared using the incipient wetness method (IW) was treated with sodium and dried. The Na-(5Pd/C) catalysts were dried and reduced using the same conditions as were used for pre-impregnation.

Catalyst preparations. Three kinds of Pd/C catalysts were sodium-promoted by post-impregnation to observe their differences in catalytic performance during BP hydrogenation. Pd/C (Kawaken) of commercial origin (Kawaken Fine Chemical Co., surface area = 1246 m²g⁻¹ and pore volume = 0.7 mL/g) was oven-dried at 100 °C for 5 hours before use for catalyst promotion. The other two Pd/C catalysts were prepared by the following methods.

1) Incipient wetness method: Pd/C(IW): A H₂PdCl₄ solution was prepared by dissolving 0.833 g PdCl₂ in 7 mL of a 3 M HCl solution, dropping the H₂PdCl₄ solution slowly into the activated carbon (9.5 g) solution, stirring, and then drying at 100 °C for 2 hours. The dried catalyst was stored in a desiccator after reduction at 100 °C under 50 mL/min of H₂ (g).

2) Precipitation and deposition method: Pd/C(PD): A H₂PdCl₄ solution was prepared by dissolving 0.833 g PdCl₂ in 85 mL of 0.067 M HCl in a flask (500 mL) while stirring at 1,500 rpm for 30 minutes. An activated carbon solution was prepared by introducing 9.5 g of activated carbon into 120 mL of 1 M Na₂CO₃ and stirring at 60 for 40 minutes in a flask (500 mL). Eighty five milliliters of the H₂PdCl₄ solution was then transferred into the activated carbon solution at a flow rate of 3 mL/min for 30 minutes while stirring vigorously (pH = 11). The catalyst prepared by PD was filtered by flushing with hot deionized water (DIW), dried (50, 12 hours), reduced (100, 50 mL/min H₂), and then stored in a desiccator (10 g Pd/C).

Sodium promotion by post-impregnation on different kinds of Pd/C catalysts. Pd/C catalysts prepared by precipitation and deposition (PD), the incipient wetness method (IW), and a commercial catalyst, Pd/C (Kawaken), were sodium-promoted through post-impregnation. The amount of sodium was varied from 0.3 wt%-3.0 wt% and the promoted catalysts were stored in a desiccator after drying at 100 °C for 12 hours and reduction at 100 °C for 2 hours under 50 mL/min H₂.

Dispersion of sodium-promoted catalysts was determined by oxygen-hydrogen titration cycles (OHTC), which were carried out at 100 °C, while increasing the titration gas (H₂) pressure in the range of 0-350 torr to eliminate the possibility of β-hydride generation as noted by Suh *et al.*¹⁷ The stoichiometric coefficient of Pd/H₂ in OHTC was 2/3 (Pd-O + 3/2 H₂ → Pd-H + H₂O), and the density of Pd was assumed to be 1.27 × 10¹⁹ atoms·m⁻².¹⁷

The BP hydrogenation reaction was carried out in a 200 ml Büchi autoclave semi-batch reactor.¹⁶ Dry catalyst (0.0125 g Pd) in a small amount of solvent was transferred into the reactor and reactant diluted with 1100 mL IPA was added afterwards. The reactor was purged with nitrogen gas and hydrogen gas sequentially. The reaction was performed for 8 hours, at 165 °C, 8 bar, and 1,000 rpm agitation speed. The initial activity of BP hydrogenation was determined by calculating the converted mole of BP after 30 minutes of reaction and the yield of each product was determined after 8 hours of reaction. The reaction sample taken regularly was filtered to remove catalyst, diluted with IPA and analyzed by a gas chromatograph Hewlett-Packard 6890 plus using a HP-5 5% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 μm). Identification of the product was achieved using the mass fragmentation from the GC-MS (Fisons MD800).

Results and Discussion

Sodium promotion on Pd/C with different promotion methods. To compare the effect of the promoter sequence, sodium was doped using three different promotion methods. The order of promotion was varied on the basis of Pd impregnation in the following three ways: pre-impregnation, co-impregnation and post-impregnation while changing the sodium content from 1.0-5.0 wt% based on the weight of Pd/C (Table 1).

Using sodium-promoted Pd/C catalysts prepared by pre-impregnation, the initial activity of BP was enhanced compared to unpromoted Pd/C. However the initial activity decreased with increasing sodium content. Using sodium-promoted Pd/C catalysts prepared by co-impregnation, the initial activity was increased with small amounts of sodium (1.0 wt% of Na), but decreased with further sodium addition. The yield of BHD produced from the sodium-promoted catalysts prepared by pre-impregnation and co-impregnation did not show proportional enhancement with increasing sodium content. Meanwhile, the hydrogenolysis products (HP) were decreased monotonously upon sodium promotion compared with the unpromoted Pd/C catalyst.

For the sodium-promoted Pd/C catalyst prepared by post-impregnation, not only the initial activity of the hydrogenation but also the yield to BHD was enhanced with all amounts of sodium promotion. The yield of BHD increased gradually with sodium content compared with other promotion methods and it was greatest with 5.0 wt% (95.7% BHD), which was three times greater than that with basic Pd/C (27.0% BHD). Furthermore, the amount of HP was

Table 1. Dispersion of Pd/C catalysts with different promotion methods

Promotion methods	Catalyst code	Na loading (wt%)	Dispersion (%)	Initial activity (mmol·g-cat ⁻¹ ·min ⁻¹)	Yield (%)	
					BHD	HP
basis	Pd/C(TW) ^a	–	41.07	19.07	27.0	23.1
pre-impregnation ^b	5Pd-(1Na/C)(TW)	1.0	45.43	24.31	26.9	17.9
	5Pd-(3Na/C)(TW)	3.0	55.75	21.70	18.1	17.2
	5Pd-(5Na/C)(TW)	5.0	20.17	21.38	32.4	17.2
co-impregnation ^c	(1Na-5Pd)/C(TW)	1.0	42.60	21.31	23.2	14.0
	(3Na-5Pd)/C(TW)	3.0	39.42	15.54	33.0	17.5
	(5Na-5Pd)/C(TW)	5.0	10.37	7.77	1.4	4.6
post-impregnation ^d	1Na-(5Pd/C)(TW)	1.0	42.40	21.31	28.4	16.8
	3Na-(5Pd/C)(TW)	3.0	28.57	28.23	43.5	4.3
	5Na-(5Pd/C)(TW)	5.0	38.18	27.02	95.7	1.6

^aPd/C (5 wt% Pd on carbon) prepared by the incipient wetness method (TW). ^bSodium promotion before Pd impregnation on carbon support. ^cSodium promotion and Pd impregnation simultaneously on carbon support. ^dSodium promotion after Pd impregnation on carbon support. Catalyst reduction: 2 hours, 50 mL/min H₂, 100 °C.

decreased to 1.6%, which was comparatively lower than that produced with unpromoted Pd/C. Sodium metal suppressed HP formation with increasing Na content to the greatest degree when post-impregnated Pd/C catalysts were used.

Sodium metal enhanced the initial activity of BP hydrogenation compared to unpromoted Pd/C with catalysts prepared by the post-impregnation method. Sodium promotion by pre-impregnation may result in sodium being located under the Pd metal, because it is deposited on the carbon surface prior to Pd impregnation. It is well known that alkali metal deposited on the platinum group metal catalysts is easily oxidized by donating electrons to the catalyst metal, and facilitates the adsorption and desorption procedure of reactant molecules by decreasing the binding strength between reactant molecule and catalyst metal. This resulted in rate enhancement or product yield increases.^{18,19} Based on the decreased amount of HP observed with pre-impregnation, sodium seems to donate its electron even when it is located under the catalyst metal on the carbon support, which is consistent with previous research on phenol hydrogenation.^{6,7} In the case of sodium promotion by co-impregnation and post-impregnation, the sodium metals may be mainly located either next to the Pd metal on the carbon support (co-impregnation) or on the surface of Pd metal thus covering the active metal site and hindering reactant molecules from adsorption (post-impregnation). The decreased number of active sites may cause the delay of BP conversion, which could become more serious with an increase in the amount of promoter metal. However, both the activity of BP hydrogenation and the yield of BHD were increased with sodium promotion by the post-impregnation method. In a previous study,⁸ we described how sodium formed additional sites on the surface of the Pd metal or on the surface of the carbon support near to palladium and enhanced C=O bonds hydrogenation.

The hydrogenation of C=C bonds, however, was differently influenced by sodium coverage on the surface of Pd active sites between the dominances of electrical and geometric effects compared with C=O bonds hydrogenation owing to

their differences in reaction rate. The slight decrease of the initial activity of BP resulted from the catalyst using 3.0 wt% sodium to 5.0 wt% sodium may show this turning point of promotional effect of sodium content on Pd metal. During C=C bonds hydrogenation, the electrical effect was dominant with 3.0 wt% sodium by facilitating the adsorption and desorption procedure of reactant, but it began to decrease with 5.0 wt% sodium because the geometrical blockage of exposed Pd active sites became overwhelming. It was thought that sodium metal can donate its electron without reference to the promotion order and reduce the amount of HP.

To determine the relationship between the catalyst promotion methods and catalytic performance in relation to initial activity and yield to final product, dispersion of each catalyst was measured by the OHTC method (Table 1). Among sodium-promoted catalysts prepared by the pre-impregnation method, the initial activity gradually diminished with increasing amounts of sodium, while the metal dispersion was greatest with a moderate amount of sodium (3.0 wt% Na). With catalysts promoted by the co-impregnation method, both Pd dispersion and the initial activity were decreased with increasing sodium content. Among the catalysts promoted by post-impregnation, the dispersion of 3.0 wt% sodium-promoted Pd was the lowest, while the reaction rate was the fastest.

The palladium dispersion with 1.0 wt% of sodium applied by three different methods resulted in a higher dispersion than basic Pd/C catalysts, which were not promoted. The dispersion of a monometallic catalyst usually inevitably decreases without reference to promotion order, because a certain portion of an active site will be occupied by the addition of the second metal on the carbon surface. However, addition of the second metal, sodium, seemed to have protected the catalyst metal from sintering during heat treatment when the catalyst was reduced. In this case, the promoter metal blocked metal migration on the support surface as reported by Margitfalvi *et al.*²⁰ Furthermore, an increased amount of sodium (3.0 wt%) seemed to decrease

Table 2. Effect of sodium promotion by post-impregnation on various Pd/C catalysts^a

Catalyst code	Intended metal content (wt%)		Metal content determined from ICP analysis (wt%)		Initial activity (mmol-g-cat ⁻¹ ·min ⁻¹)	Yield (%)	
	Na	Pd	Na	Pd		BHD	HP
Pd/C(IW) ^b	0	5	0.04	4.69	19.07	27.0	23.1
0.2Na(5Pd/C)(IW) ^b	0.3	5	0.07	4.95	18.78	24.5	15.5
1.0Na(5Pd/C)(IW) ^b	1	5	0.82	4.49	21.31	28.4	16.8
3.0Na(5Pd/C)(IW) ^b	3	5	2.39	4.35	28.23	43.5	4.3
Pd/C(PD) ^c	0	5	0	4.69	22.49	36.7	6.2
0.3Na(5Pd/C)(PD) ^c	0.3	5	0.32	4.73	22.67	39.3	1.10
1.0Na(5Pd/C)(PD) ^c	1	5	0.92	4.80	30.33	59.3	0.8
3.0Na(5Pd/C)(PD) ^c	3	5	2.65	4.56	29.83	69.2	0.5
Pd/C(Kawaken) ^d	0	5	1.07	5.00	34.67	4.4	0.7
0.3Na(5Pd/C)(Kawaken) ^d	0.3	5	1.37	4.71	35.60	32.6	1.4
1.0Na(5Pd/C)(Kawaken) ^d	1	5	1.96	4.66	32.49	53.0	1.2
3.0Na(5Pd/C)(Kawaken) ^d	3	5	3.52	4.52	28.10	73.1	0.8

^aSodium metal was promoted by the post-impregnation method. ^bPd/C prepared from the incipient wetness method, described as Pd/C(IW), was used as the basic catalyst. ^cPd/C prepared from the precipitation and deposition method, described as Pd/C(PD), was used as the basic catalyst. ^dPd/C from a commercial source (Kawaken Chemical Co.), described as Pd/C(Kawaken), was used as the basic catalyst. Catalyst reduction: 2 hours, 50 mL/min H₂, 100 °C.

dispersion because the amount of sodium metal was large enough to cover the active sites unveiled with 1.0 wt% sodium promotion. However, this phenomenon could not explain the effect of different promotion methods on BP hydrogenation. The dispersion of catalysts prepared from different promotion methods didn't show any specific relationship with initial activity of BP. Only the catalysts prepared from co-impregnation showed the increase of initial activity with the increase of sodium contents. There are a few possible factors which can affect to the initial activity of BP. The steric hindrance of bulky BP molecule (1.2-1.6 nm in kinetic diameter) may lead the initial rate different from the order of dispersion, which is calculated by relatively smaller molecules such as H₂(g) and O₂(g) by OHTC methods, especially in the liquid phase reaction.²¹ The bulky BP molecule is known to be highly affected by the micro porosity of the activated carbon support (Pd/C(IW); surface area 1,092 m²/g, micro pore volume 0.96 cc/g, maximum pore diameter 38.6 nm, ratio of micro pore/total pore 0.31). Therefore, there is great possibility that BP can not reach to the surface of palladium active site located inside the deeper micro pores, where other smaller molecules, H₂(g) and O₂(g), can reach during the dispersion measurement. Furthermore, because C=C bonds relatively react faster than C=O bonds, the initial activity of BP tends to be strongly affected by the palladium metals deposited on the surface of carbon pores near to the outer surface.¹⁶ The different order of sodium promotion can also change the geography among pre-, co-, and post- impregnations of palladium metal inside the micro porous carbon support. Therefore, for the explanation of the relationship between initial rate of BP and dispersion according to promotion methods, at least three factors need to be considered.

In the given experimental condition (165 °C, 8 bar, and 1,000 rpm of agitation speed), the reaction is optimized to obtain the final product, BHD, which is insignificantly

hydrogenated until the end of the reaction (8 hours). We therefore hypothesize that initial conversion of BP occurs too fast to be able to observe the effect of promotion methods. In contrast, the effect of promotion methods on the yield to BHD became distinct because the catalysts prepared by the post-impregnation method increased the yield of BHD more than any other method.

Accordingly, sodium-promoted catalysts prepared by post-impregnation remarkably increased the initial activity and yield of BHD compared to other promotion methods, and the catalytic performance became distinct as the sodium content increased. The post-impregnation method was also the most effective at suppressing HP production. Hence, for the enhancement of BHD production, the post-impregnation method, which creates additional adsorption sites on the surface of catalyst metal despite the decreased number of active sites, is regarded to be the most effective.

Sodium promotion by post-impregnation on different kinds of Pd/C catalysts. Sodium-promoted Pd/C catalysts exhibited advanced catalytic performance both in initial activity and BHD yield during BP hydrogenation. Moreover, their performance was further enhanced with sodium-promoted Pd/C prepared by post-impregnation. In this study, different kinds of Pd/C catalysts were prepared and sodium-promoted by post-impregnation, and their catalytic performances including reaction behaviors were observed (Table 2).

The initial activity varied according to the sodium content of the Pd/C catalyst. Nevertheless, all promoted Pd/C catalysts gradually showed an enhanced selectivity to BHD with increasing amounts of sodium. Among the prepared Pd/C catalysts, the Pd/C(PD) catalyst produced a higher amount of BHD than Pd/C(IW). Pd/C(PD) showed a higher BHD production ability even after its promotion with sodium. The commercial catalyst, Pd/C(Kawaken), decreased the initial conversion of BP with increasing sodium promotion, while

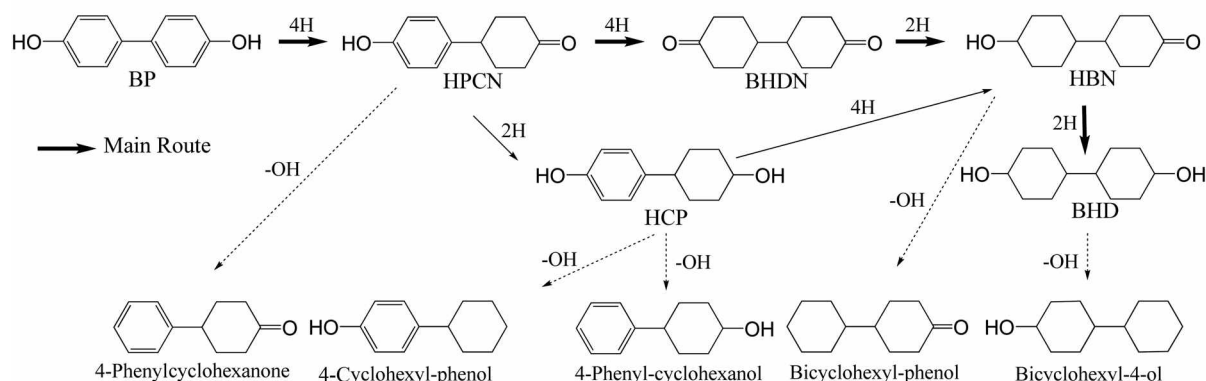


Figure 1. The reaction pathway scheme of BP hydrogenation over Pd/C (Kawaken).⁸

the yield of BHD was enhanced up to 73.1% with 3.0 wt% sodium promotion, 3.0 Na (5Pd/C)(Kawaken).

The initial activity of sodium-promoted Pd/C(PD) was enhanced over the range of sodium content used and 1.0 wt% sodium showed the highest activity at 30.33 mmol·g⁻¹·min⁻¹. The BHD yield was enhanced with increasing sodium content, and the largest amount (69.2%) was produced with 3.0 wt% sodium, which was greater than the 36.7% produced with Pd/C(IW). Considering all the Pd/C catalysts, the amount of HP was comparatively suppressed by sodium promotion and the yield was further decreased with increasing sodium content. With the help of sodium promotion, the catalysts prepared from the IW and PD methods suppressed the formation of HP more remarkably with higher amounts of sodium than unpromoted Pd/C.

The basic BP reaction behaviors using a Pd/C catalyst can be interpreted as reported in our previous study with the reaction pathways shown in Figure 1.⁸ As BP reacted, HPCN, BHDN, and HBN were obtained in large amounts, while HCP was produced in a much lower amount as a minor product. A much lower amount of BHD was produced as a fully saturated product in BP hydrogenation. The hydrogenolysis products (designated as HP) were obtained through each process of hydrogenation.

According to the product distribution of BP hydrogenation using promoted Pd/C catalysts (Figure 2), the majority of HPCN, which was formed through the hydrogenation of one benzene ring of BP, was hydrogenated to BHDN through C=C hydrogenation (Figure 2(d)), while the hydrogenation to HCP through C=O hydrogenation hardly occurred (Figure 2(c)). HPCN content increased to 40% within 1 hour and radically decreased upon further reaction (Figure 2(b)). HPCN was consumed to produce both BHDN and HCP, and 80% of BHDN was produced in 2 hours, while only 2% of HCP was produced.

In contrast, HPCN showed a different hydrogenation tendency in the reaction with Pd/C(PD). HPCN was not completely consumed until the end of the reaction, after 8 hours. Through HPCN hydrogenation, the maximum yield of BHDN was lower than 5%, while that of HCP was about 60%, which was remarkably higher than that of BHDN.

However, these reaction behaviors of BP obtained by unpromoted catalysts were changed upon sodium promotion. When sodium promoted Pd/C(PD) was used, the rate of HPCN hydrogenation was enhanced, the compound was completely consumed within 6 hours, and the yield of BHDN increased from 5% up to 20% (Figure 2(d)), while the maximum yield of HCP decreased from 60% to 15% (Figure 2(c)). Upon BP hydrogenation with Pd/C(PD), the hydrogenated HPCN molecules produced mainly HCP through C=O bond hydrogenation.

Using sodium promotion, all of the Pd/C catalysts mainly hydrogenated HPCN to BHDN, rather than HCP, which was produced through C=C bond hydrogenation. In addition, the rate of HBN (Figure 2(e)) formation and consumption through hydrogenation of both BHDN and HCP was enhanced, and accelerated the increased yield of BHD (Figure 2(f)), the final product.

When different Pd/C catalysts were promoted with sodium by post-impregnation, the major intermediates followed different routes depending on the catalysts. In the case of selectivity between HCP and BHDN through HPCN hydrogenation, the "HPCN to BHDN route" was the major route present with Pd/C (Kawaken), while the "HPCN to HCP route" was the major route with the prepared catalyst, Pd/C(PD). Furthermore the selectivity of BHDN was enhanced when the prepared catalyst was sodium-promoted.

In our previous report, we showed that a Pd/C catalyst can invoke a different reaction path in BP hydrogenation according to its preparation method and physical properties. Moreover, the different hydrogen delivery abilities of different catalysts was thought to shift the reaction to the "HPCN to HCP" or "HPCN to BHDN" routes.⁸ In the current study, we observed a change in HPCN hydrogenation rate upon sodium promotion (Figure 2). In addition, as the rate of HPCN consumption became faster, the selectivity of BHDN increased, while that of HCP decreased. With Pd/C (Kawaken), HPCN molecules were converted to BHDN within 2 hours and the yield to BHDN was almost 80%, while the sodium-promoted Pd/C (Kawaken) catalyst converted HPCN to BHDN rather slowly compared to unpromoted catalyst and decreased the yield of BHDN to 50%. Sodium-promoted Pd/

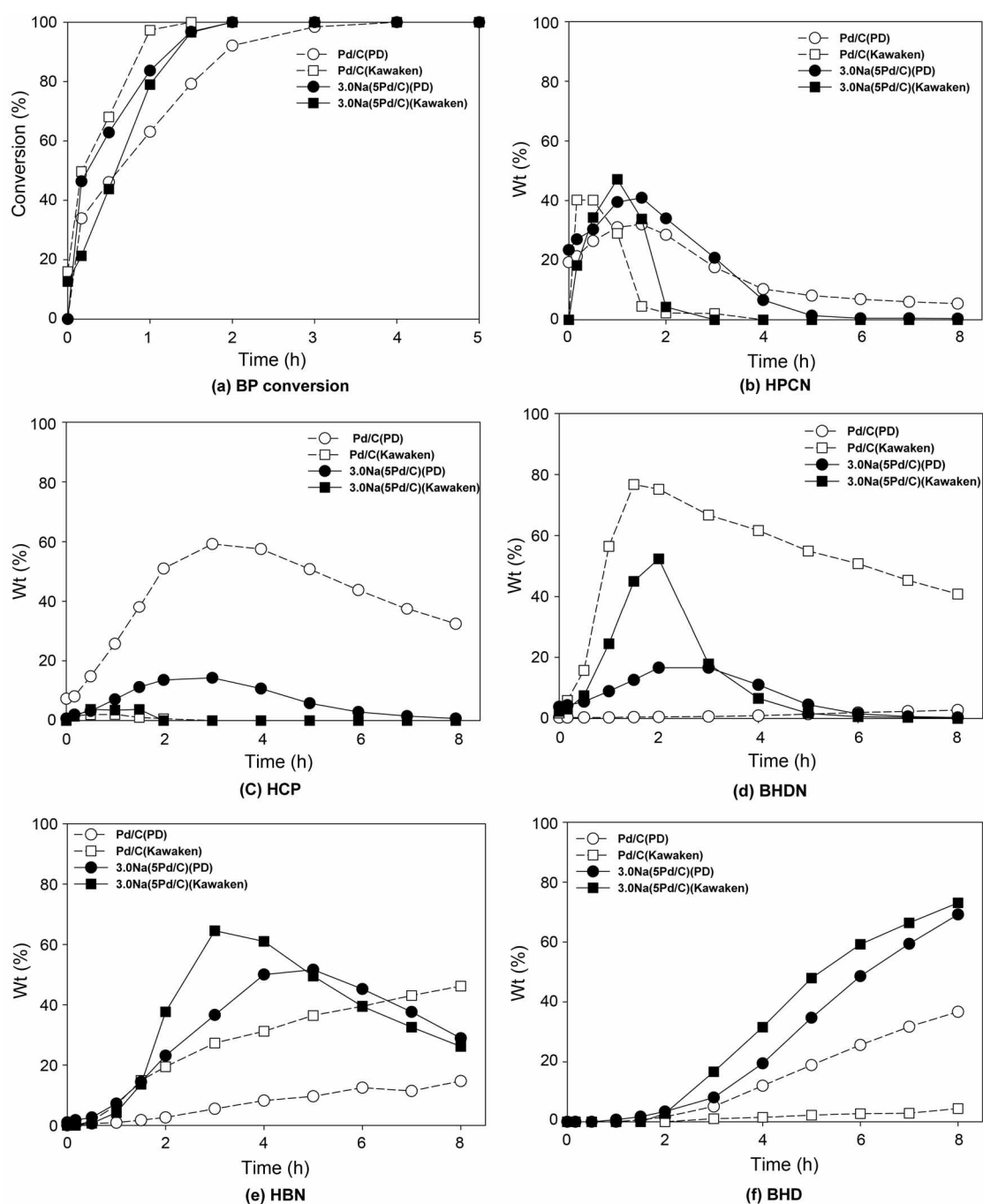


Figure 2. Product distribution of BP hydrogenation by sodium-promoted Pd/C catalysts.

C(Kawaken), however, did not change the major reaction route from “HPCN to BHDN” because the amount of HCP did not exceed that of BHDN. This tendency is very different from the prepared catalyst. With Pd/C(PD), HPCN was not completely consumed until the end of the reaction, and the yield of BHDN was less than 5%. However, upon sodium promotion of Pd/C(PD), HPCN was consumed within 6 hours and the yield to BHDN was enhanced to 20%, while decreasing the yield of HCP from 60% to 15%. The selectivity of BHDN seems to have increased compared with that of HCP with the help of the facilitated hydrogen delivery of Pd through sodium metal. It is believed that

addition of sodium metal on palladium increased the adsorption and desorption rate of hydrogen molecules (hydrogen delivery) by changing the nature of the prepared catalyst, Pd/C(PD). In contrast, the sodium metal hardly affected the enhancement of C=C bond hydrogenation at the initial BP conversion as described in Table 2, which indicates that C=C bond hydrogenation is not a rate determining step. It has been reported that sodium produces another C=O bond adsorption site which results in the rate enhancement of C=O bond hydrogenation during BP hydrogenation.⁸ It is also known that differently prepared Pd/C catalyst changes the rate of hydrogen delivery, which alters the major

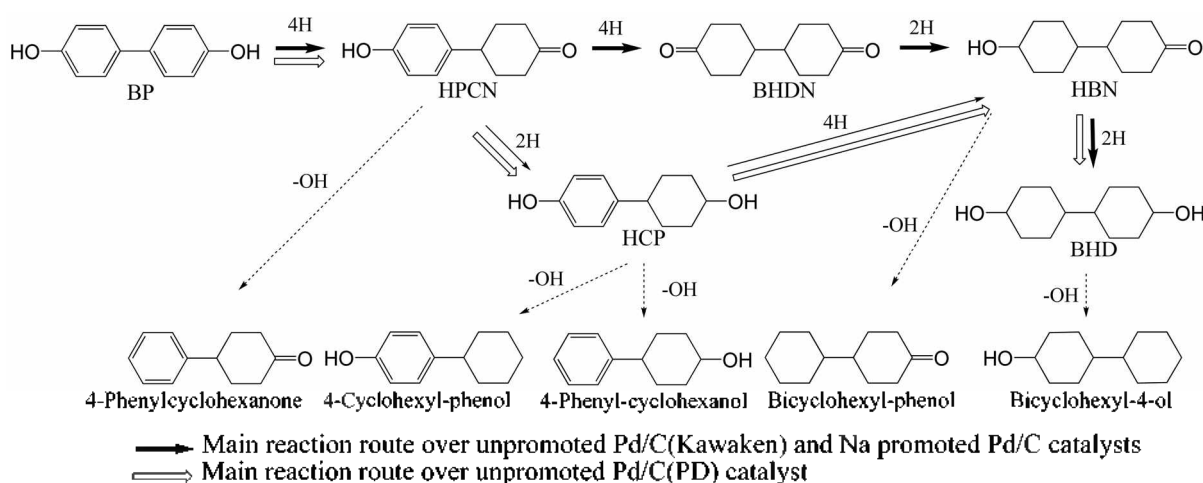


Figure 3. The reaction pathway scheme of BP hydrogenation using promoted Pd/C catalysts.

reactions of BP hydrogenation.¹⁶

Therefore, it is believed that the sodium promoter not only produces additional adsorption sites for C=O bonds, but also enhances hydrogen delivery during C=C bond hydrogenation and leads to a different reaction pathway.

Effect of sodium-promoted Pd/C catalysts on the reaction pathways of biphenol hydrogenation. The effect of sodium-promoted Pd/C catalysts on the product distribution of BP hydrogenation showed different reaction behaviors according to reaction time. Based on these results, the previously-proposed reaction network (Figure 1) was altered slightly depending on the type of Pd/C catalyst and sodium promotion as illustrated in Figure 3. The sodium promoter accelerates the rates of hydrogenation of both HCP and BHDN without reference to the type of Pd/C. The major reaction pathway when prepared catalyst is present proceeds via the "HPCN to HBN route" yielding HCP as a major intermediate. The reaction is thought to be caused by the surface status of the catalyst metal, which has difficulty transferring hydrogen molecules during liquid phase hydrogenation of BP, but, with the help of sodium promotion, converts HPCN to BHDN rather than to HCP.

Conclusions

Sodium-promoted Pd/C catalysts prepared by the post-impregnation method were the most effective at increasing the yield and selectivity to BHD in BP hydrogenation. The catalysts prepared by three different promotion methods showed no promotional relevance of sodium content for boosting the initial activity of BP. The initial stage of BP hydrogenation was not a rate determining step; this seemed to minimize the effect of the promotion methods. On the contrary, the post-impregnation method was the most effective method for enhancement of BHD yield and selectivity. The greatest yield and selectivity to BHD through C=O bond hydrogenation occurred when the sodium metal was applied after catalyst preparation (Pd/C) resulting in the presence of promoter metal on the surface of the catalyst metal.

Various Pd/C catalysts were sodium-promoted by post-

impregnation and changes in reaction pathways were observed. In BP hydrogenation, the major reaction routes between the hydrogenations of C=O bonds (hydrogenation of HPCN to HCP) and C=C bonds (hydrogenation of HPCN to BHDN) was changed by sodium promotion depending on the type of Pd/C catalyst. It is believed that a sodium promoter not only facilitates C=O bond hydrogenation,⁸ but also leads to an enhancement of hydrogen delivery on the surface of the catalyst metal resulting in a change in reaction pathways (Figure 3). However, the surface status of the catalyst metal should also be considered when attempting to increase selectivity for desired compounds in BP hydrogenation.

References

1. Yasushi, I. *JP Patent* 2001, 002616.
2. Wilds, A. L.; Shunk, C. H.; Hoffman, C. H. *J. Am. Chem. Soc.* 1954, 76, 1733.
3. Mross, W. D. *Catal. Rev. Sci. Eng.* 1983, 25, 591.
4. van der Lee, G.; Ponc, V. *Catal. Rev. Sci. Eng.* 1987, 29, 183.
5. Ponc, V. *Catal. Today* 1992, 12, 227.
6. Mahata, N.; Vishwanathan, V. *Indian J. Chem.* 1998, 37A, 652.
7. Mahata, N.; Raghavan, K. V.; Vishwanathan, V. *Appl. Catal. A* 1999, 182, 183.
8. Cho, H.-B.; Lee, J.-C.; Park, Y.-H. *Catal. Today* 2006, 111, 417.
9. Hara, Y.; Endou, K. *Appl. Catal. A: Gen.* 2003, 239, 181.
10. Gallezot, P.; Richard, D. *Catal. Rev.-Sci. Eng.* 1998, 40, 81.
11. Neri, G.; Visco, A. M.; Donato, A.; Milone, A.; Malentacchi, M.; Gubitosa, G. *Appl. Catal. A* 1994, 110, 49.
12. Richard, D.; Ockelford, J.; Giroir-fendler, A.; Gallezot, P. *Catal. Lett.* 1989, 3, 53.
13. Nishimura, S.; Shu, T.; Hara, T.; Takagi, Y. *Bull. Chem. Soc. Jpn.* 1966, 39, 329.
14. Noboru, Y.; Shizuo, N. *JP Patent* 1991, 279539.
15. Pillai, U. R.; Sahle-Demessie, E. *Appl. Catal.* 2005, 281, 31.
16. Cho, H.-B.; Hong, B.-E.; Park, J.-H.; Park, Y.-H. *Bull. Kor. Chem. Soc.* 2008, 29, 328.
17. Suh, D. J.; Park, T.-J.; Ihm, S.-K. *J. Catal.* 1994, 149, 486.
18. van Santen, R. A. *Surf. Sci.* 1991, 251/252, 6.
19. Lee, D. W.; Kim, H. G.; Kang, M.; Kim, J. M.; Lee, I.-M. *Bull. Kor. Chem. Soc.* 2007, 28(11), 2034.
20. Margitfalvi, J. L.; Jalett, H. P.; Talas, E.; Baiker, A.; Blaser, H. U. *Catal. Lett.* 1991, 10, 325.
21. Okhlopkova, L. B.; Lisitsyn, A. S.; Likholobov, V. A.; Gurrath, M.; Boehm, H. P. *Appl. Catal. A: Gen.* 2000, 204, 229.