Selective hydrogenation of 4-isobutylacetophenone over a sodium-promoted Pd/C catalyst

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Abstract−The effect of sodium promotion on the selective hydrogenation of 4-isobutylacetophenone, 4-IBAP, was investigated over a Pd/C catalyst. A precipitation and deposition method was used to prepare the catalyst, and sodium was promoted on the Pd/C catalyst via post-impregnation while varying the sodium content. The sodium-promoted Pd/C catalyst resulted in a significantly improved yield greater than 96% of the desired product, 1-(4-isobutylphenyl) ethanol (4-IBPE), compared with the non-patented literature results under a mild hydrogenation condition. A detailed hydrogenation network over the Pd/C catalyst was suggested. The reaction mechanism for the yield and selectivity enhancement of 4-IBPE induced-by the promoted Pd/C was elucidated in relation to the geometric and electronic effects of reactant molecules in the microporous support depending on the reaction steps.

Key words: Selective Hydrogenation, 1-(4-Isobutylphenyl)ethanol, Pd/C Preparation, Sodium Promotion, 4-Isobytylac-etophenone

INTRODUCTION

Selective hydrogenation of an aromatic ketone to an aromatic alcohol is an important reaction in a variety of chemical processes used for the synthesis of fine chemicals, pharmaceuticals and agrochemicals [1]. One representative example is the selective hydrogenation of 4-isobutylacetophenone, 4-IBAP, to 1-(4-isobutylphenyl) ethanol, 4-IBPE (Fig. 1) [2], which is an important intermediate in the production of ibuprofen, a well-known non-steroidal anti-inflammatory drug. 4-IBPE is further carbonylated to synthesize ibuprofen via a catalytic reaction. Moreover, this process is an excellent example of complex multi-step catalytic hydrogenation. In addition, many processes are applied for the production of ibuprofen using 4-IBAP as a starting compound [3-5]. This reaction is usually carried out commercially over supported metal catalysts in a liquid phase semi-batch hydrogenation process. Most of the early research on this reaction has been patented (Table 1), and only a few reports deal with its catalytic aspects such as the reaction mechanism and the effects of catalysts [3,4,6-12]. For example, the Hoechst Celanese Co. described the carbonylation of 4-IBPE in their ibuprofen preparation method in their patent [3]. They only mentioned the hydrogenation of 4-IBAP to 4-IBPE as one example of the reaction steps using a relatively large weight ratio of 4-IBAP : Pd/C catalyst of 7 : 1 by weight percent.

The information provided by the patents is very limited and general. Supported metal catalysts consisting of Ni [8,9], Pd [2,7,8,10, 12] and Ru [6] have been suggested for use in the selective hydrogenation of 4-IBAP. A different type of Pd has been tested with a variety of solvents [2,11,12]. Silylation of the SiO_2 support was used to produce a hydrophobic catalyst system and to aid the fast adsorption of 4-IBAP [7]. The use of Ru/Al_2O_3 increased the initial conversion, but it also enhanced the saturation of ketones and benzene rings, leading to the formation of byproducts [6]. Among the previous works, the highest yield (~60%) of the desired 4-IBPE product was obtained using Pd/SiO_2 catalyst [7], although the catalytic system is still not satisfactorily stable due to the large amount of by-
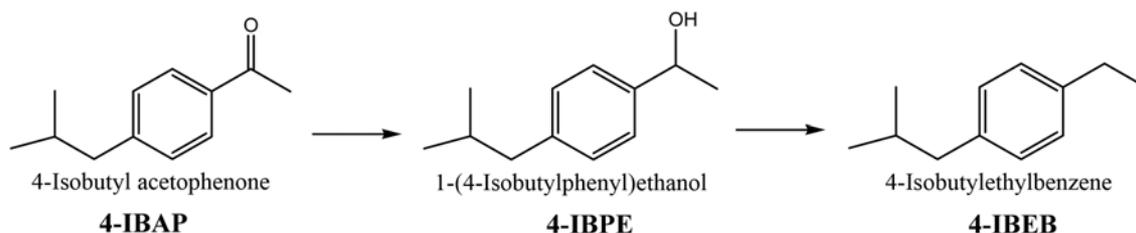

Fig. 1. The basic reaction scheme of 4-IBAP hydrogenation over supported Pd catalysts.

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Table 1. Literature survey for 4-IBAP hydrogenation

Catalyst	Promoter		PH_2 (bar)	Conversion 4-IBAP (%)	Selectivity 4-IBPE (%)	Yield 4-IBPE (%)	Year	Ref.
Pd/C	-	MeOH	303	68	99	97		1990	[3]*
Raney Ni	Molybdenum	MeOH	335	82	97	100		1989	[5]*
Pd/C	Aq. NaOH	n-Hexane	373	105	99	92	92	1990	[3]*
Ni	-	MeOH	393	59	90	50	50	1996	[9]
Ru/Al$_2$O$_3$	-	MeOH	373-398	34-62	100	20	20	1999	[6]
Pd black	-	Cyclohexane	373	20	90	58	52	2007	[12]
Pd/SiO$_2$	-	n-Decane	373	20	90	69	44	2007	[2]
Pd/SiO$_2$	-	n-Decane	373	10	90	60	80	2008	[7]

*Patent research

※ Note that the selectivity and yield of 4-IBPE in the Table are recalculated based on the equations given in the text using the values in the references

products.

Addition of alkali compounds to a reaction media enhances the rapid and selective hydrogenation of aromatic amines [12]. The promotion effect when using an alkali compound as a second metal on a primary catalyst metal can be explained either in electronic or geometric terms, as it can electronically activate the adsorption and desorption processes between the reactant and catalyst metal or can geometrically protect the catalyst metal from sintering during catalytic reduction at higher temperatures [13,14]. In the Hoechst Celanese patent, aqueous NaOH was applied as an additive in 4-IBAP hydrogenation and improved the 4-IBPE selectivity to 92% over a Pd/C catalyst, although no further information about the function of alkali was provided [3]. The alkali salt can provide a promotion effect via direct introduction into the reactor in the presence of additive solvents. The simple procedure allows for observation of the additive effect, but is problematic because it necessitates further processing to recover the compounds and additional introduction of the salt whenever the catalyst is reused in commercial applications. On the contrary, the promotion of a second metal on the surface of the catalyst metal can be repeatedly used for as long as the catalyst maintains its activity.

In the previous research, Pd-supported catalyst showed a comparatively high selectivity for 4-IBPE, and reaction routes and mechanisms using aprotic solvents have been suggested [2,10]. However, the detailed reaction mechanism describing the distribution of reaction products over Pd/C using a polar protic solvent has not been clearly explained. In addition, the promotional effects of a second metal have not been studied with selective hydrogenation of 4-IBAP.

The aim of this work was to obtain a better understanding of the reaction network in the hydrogenation of 4-IBAP over Pd/C catalyst in an ethanol solvent in order to develop a method to increase the yield and selectivity of 4-IBPE via sodium promotion. Another goal was to explain the mechanism of the effect of sodium on the Pd catalyst. The changes in the product distribution which occurred due to the Pd/C catalyst were evaluated and compared with the previous results performed over other catalysts including Ru and Ni. Various amounts of sodium were promoted on Pd/C using the post-impregnation method, and the effect of sodium content on the product selectivity in 4-IBAP hydrogenation was evaluated. Here, a suitable function of sodium as a promoter in the selective hydrogenation

of 4-IBAP over Pd/C using an ethanol solvent is suggested and compared with the reaction routes over other previously released catalyst systems. The sodium promoter leads to remarkable enhancements in yield and selectivity of 4-IBPE in the series reactions.

EXPERIMENTAL

The Pd/C catalysts were prepared using a precipitation and deposition (PD) method and were sodium promoted using the post-impregnation (sodium application after impregnation of Pd metal on activated carbon) method to investigate their different catalytic performances during 4-IBAP hydrogenation.

1. Preparation of Pd/C Catalyst

For the preparation of Pd/C catalyst, activated carbon from Aldrich (Dcrco-60, surface area of 1,305 m^2/g, pore volume of 1.04 ml/g) was used as the carbon support. An H$_2$PdCl$_4$ solution was prepared by dissolving 0.833 g PdCl$_2$ in 85 ml of 0.067 M HCl in a flask (500 ml) while stirring at 1,500 rpm for 30 min. An activated carbon dispersed Na$_2$CO$_3$ solution was prepared by introducing 9.5 g of activated carbon into 120 ml of 1 M Na$_2$CO$_3$ under stirring at 60 °C for 40 min in a flask (500 ml). Eighty-five milliliters of the H$_2$PdCl$_4$ solution was then transferred into the solution at a flow rate of 3 ml/min for 30 min while being vigorously stirred (pH=11). The catalyst prepared using the PD method was filtered by flushing with hot deionized water (DIW), dried (50 °C, 12 h), reduced (100 °C, 50 ml/min H$_2$), and then stored in a desiccator (10 g Pd/C).

2. Preparation of Sodium-promoted Pd/C

To compare the effect of the sodium-promoted Pd/C catalyst, different amounts of sodium were promoted on the Pd/C catalyst. Na$_2$CO$_3$ was used as the sodium salt and the amount of sodium was varied from 0.5 to 3.0 wt%. The incipient wetness (IW) method was adapted to carry out the sodium promotion. An aqueous solution of sodium salt with the same volume as the pore volume of the Pd/C catalyst was deposited onto the catalyst, dried at 100 °C for 12 h and reduced at 100 °C for 2 h under 50 ml/min H$_2$.

3. Characterization and Measurements

Dispersion of the sodium-promoted catalysts was determined using oxygen-hydrogen titration cycles (OHTC), which were carried out at 100 °C while increasing the titration gas (H$_2$) pressure in the range of 0-350 torr. The stoichiometric coefficient of Pd/H$_2$ in

OHTC was 2/3 (Pd-O+3/2 $H_2\rightarrow$Pd-H+H_2O), and the density of Pd was assumed to be 1.27×10^{19} atoms m^{-2} [15]. X-ray diffraction (XRD; Rigaku D/MAX-2500 18KW) and transmission electron micrograph (TEM; FEI Technai G2 F30) were used for characterization of promoted- and nonpromoted-catalysts.

4. 4-IBAP Hydrogenation

The 4-IBAP hydrogenation reaction was carried out in a 200 ml Bûchi autoclave semi-batch reactor. Dry catalyst (0.15 g Na-Pd/C) was suspended in 1,100 ml ethanol and transferred into the reactor with 0.028 mol 4-IBAP. The reactor was purged sequentially with nitrogen and hydrogen gases. The reaction was performed for 2-9 h until 100% conversion was achieved at a temperature of 303-343 K, a pressure of 20 bar, and an agitation speed of 1,000 rpm. The initial activity of the 4-IBAP hydrogenation was determined by calculating the number of converted moles of 4-IBAP after 30 min of reaction, while the yield and selectivity of 4-IBPE were calculated as a function of the 4-IBAP conversion. The regularly collected reaction samples were filtered to remove catalyst, diluted with IPA and analyzed using a gas chromatograph (Hewlett-Packard 6890 plus) equipped with an 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 MD 800).

RESULTS AND DISCUSSION

1. The Reaction Network of 4-IBAP Hydrogenation over Pd/C in Ethanol

The surface properties and the particle size distribution of the Pd/C catalyst, prepared using the PD method, are shown in Table 2 and Fig. 2. The surface area of the catalyst was increased before the deposition of Pd compared to that of the activated carbon (see Table 2). Also, the micropores occupied almost 40% of the total volume, resulting in a large surface area of 1,615 m^2/g. The TEM images indicate that the Pd metals were widely distributed on the carbon surface, with sizes of about 10 nm. The partial collapse of the micro structure of carbon (surface area=1,305 m^2/g, pore volume=1.04 ml/g) during Pd deposition in a base solution under vigorous mixing up to 1,500 rpm is believed to increase the surface area along with the pore volume of Pd/C in the PD process.

The product distribution of the 4-IBAP hydrogenation over Pd/C is shown in Fig. 3. The reaction products are divided into major products and minor products; 4-IBPE and 4-isobutylethylbenzene (4-IBEB) were obtained as major products, while 4-isobutylstyrene (4-IBS), 1-(1-ethoxyethyl)-4-isobutylbenzene (EEIB) and isobutylbenzene (IBB) were obtained as minor products. During hydrogenation, 4-IBAP was rapidly consumed for 30 min after the start of the reaction and 88% was hydrogenated after reaction for 6 h. The
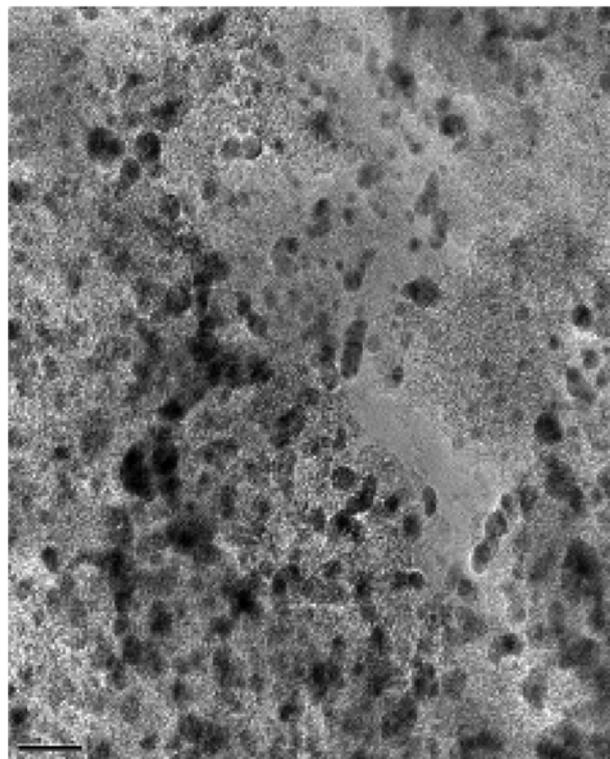

Fig. 2. TEM image of Pd/C prepared using the PD method (space bar: 20 nm).

formation of 4-IBPE increased proportionally with the decreasing rate of 4-IBAP during the initial reaction (1 h from the beginning of hydrogenation), reaching its highest concentration of 64% at 5 h and then decreasing. The 4-IBEB gradually increased with reaction time and maintained its tendency even after the 4-IBPE concentration started decreasing after 5 h. The minor products of 4-IBS, EEIB, and IBB were produced in very small amounts less than 2%, but continuously increased as the reaction proceeded.

The 4-IBAP hydrogenation process can be summarized using a quite complex reaction scheme (Fig. 4). During the hydrogenation of 4-IBAP, the reaction can follow four different routes, depending on the kind of catalyst, the acidity of the support, and the solvents used. One conspicuous route is reaction over Ru/Al$_2$O$_3$ catalyst [10]. Since the Ru catalyst shows a high selectivity for the C=C double bond hydrogenation of aromatic ketones [15], the reaction to 4-IBCHE is preferably preceded as a major route even at a low reaction temperature, which conversely results in the low selectivity of 4-IBPE.

Another two routes result from reactions over Pd catalysts, which depend on the acidity of the support: the formation of 4-IBEB via dehydration-hydrogenation (4-IBPE→4-IBS→4-IBEB over Pd/

Table 2. Surface properties of Pd/C catalysts

Catalyst	Surface area[a] (m^2/g)	Micro pore volume (cc/g)	Average pore diameter (Å)	Micro pore/ total pore (cc/min)	Pd content[b] (wt%)	Pd dispersion[c] (%)
Pd/C	1,615	1.15	42.76	0.39	3.68	19.87

[a]Surface area was determined based on the Langmuir isotherm
[b]Pd loading was measured using ICP analysis
[c]Pd dispersion was measured using the OHTC method
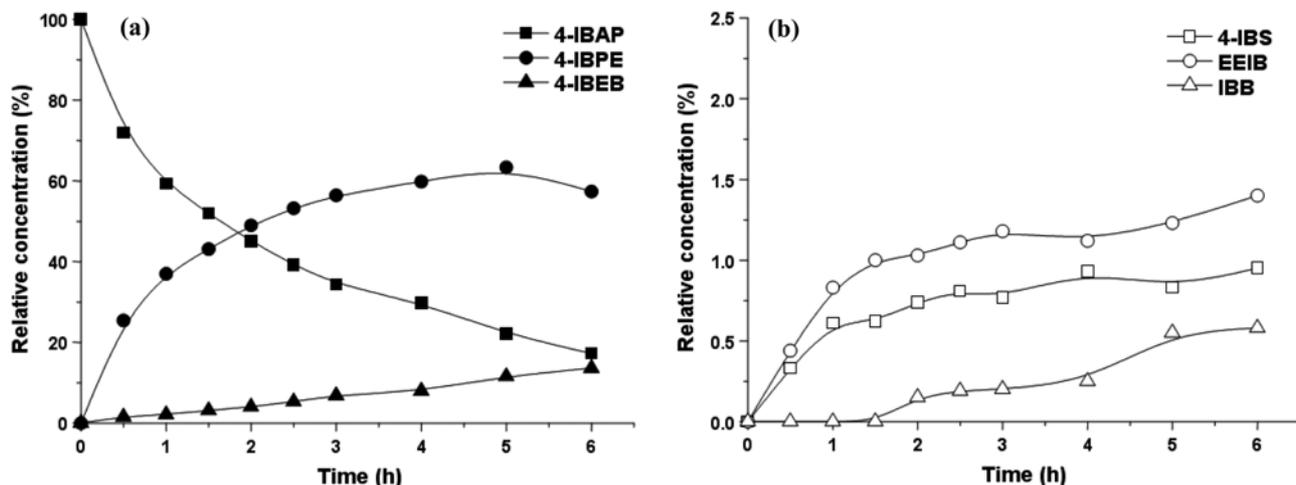
Fig. 3. Product distribution obtained from the hydrogenation of 4-IBAP over Pd/C as a function of the reaction time: (a) major products and (b) minor products. The reaction conditions were $C_{4\text{-}IBAP}$=0.028 mol/L, T=303 K, pressure=20 bar, an ethanol solvent, agitation rate=1,000 rpm, and Pd/C=3 wt% of the substrate (0.15 g).
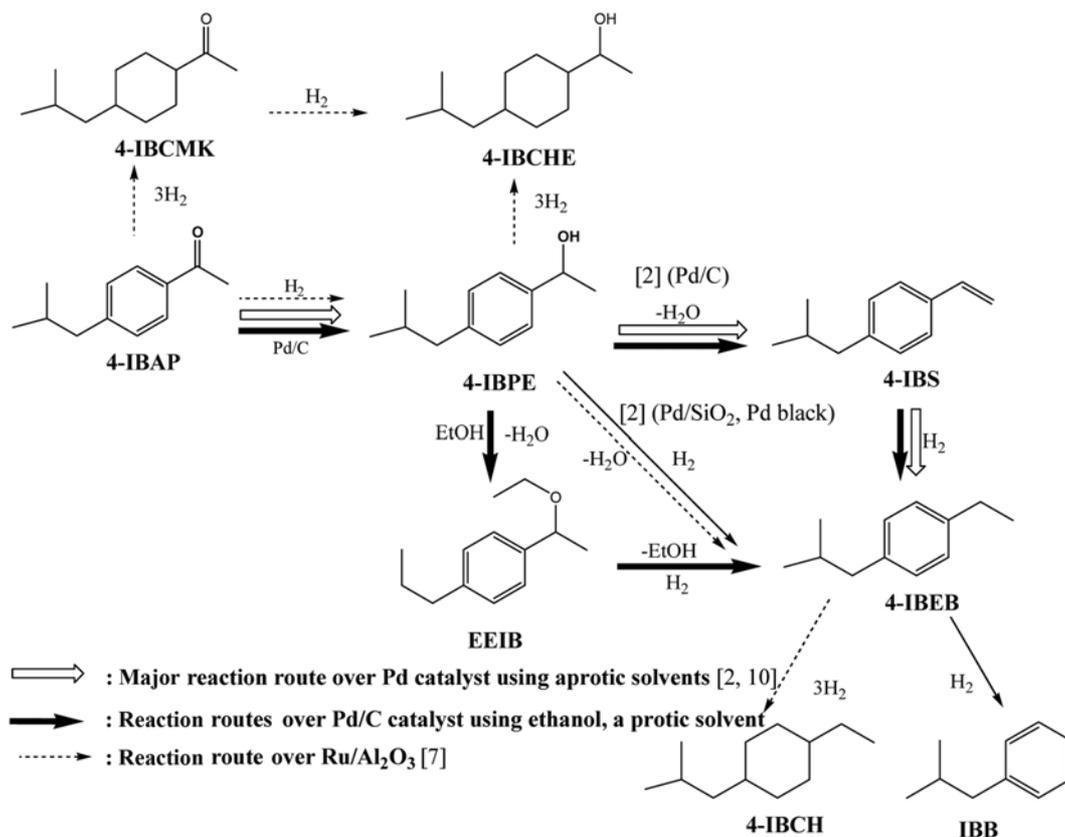

Fig. 4. Reaction scheme of 4-IBAP hydrogenation using the 5% Pd/C catalyst in an ethanol solvent.

C) and via direct hydrogenolysis (4-IBPE→4-IBEB over Pd/SiO$_2$ and Pd black). The acidic sites on the carbon support motivate the dehydration of 4-IBPE via C-O bond scission [2], which is regarded as facilitating the reaction following the 4-IBPE→4-IBS→4-IBEB route. The other route is the formation of an ether derivative and scission of ethanol, which proceeded through the 4-IBPE→EEIB→ 4-IBEB route. It has been found that polar protic alcohol solvents yield better rates than do aprotic solvents [16]. During hydrogena-

tion, the -OH group of alcohol is a strong electron donor which stabilizes the formed carbocation, leading to the formation of the ether derivative. This indicates that EEIB can be produced through a reaction between ethanol and 4-IBPE, followed by dehydration.

Meanwhile, ether derivatives were not formed when aprotic solvents such as cyclohexane [2] and n-hexane [7] were used in the same reaction. Thus, when a polar protic alcohol such as methanol, ethanol, or iso-propanol is used in the reaction, 4-IBPE hydrogena-

tion occurs via two simultaneous routes. Even though the relative concentrations of two compounds, EEIB and 4-IBS, are low in this catalytic system (Fig. 3), the amount of EEIB produced through reaction with ethanol is significantly higher than the amount of 4-IBS produced during hydrogenation. This demonstrates that the role of the protic solvent is more important than the support acidity in determining the reaction route during 4-IBAP hydrogenation over Pd/C. The trace amount of IBB formed is one characteristic of hydrogenolysis of 4-IBEB over Pd-supported carbon catalyst compared with the reaction over Ru/Al$_2$O$_3$, which showed a higher selectivity to C=C bond hydrogenation. This hydrogenolysis may occur due to the presence of acidic sites on the carbon support [2] or to a small amount of acidic compounds remaining during catalyst preparation [13].

2. Effect of Sodium Promotion on the Selective Hydrogenation of 4-IBAP

Using alkali salt as a promoter additive is one representative way to enhance the selectivity of a desired compound during hydrogenation of an aromatic ketone. The prepared Pd/C catalyst was promoted by various amounts of sodium via post-impregnation, and the effects on the yield and selectivity were evaluated. The amount of sodium was varied to 0.5 wt%, 1.0 wt%, and 3.0 wt% on Pd/C (3 wt% Pd) and are denoted as 0.5Na-Pd/C, 1.0Na-Pd/C and 3.0Na-Pd/C, respectively. The sodium-promoted Pd/C catalysts were characterized according to their X-ray diffraction patterns, as shown in Fig. 5. The existence of sodium can be identified as crystalline forms of Na$_2$CO$_3$, Na$_2$O$_2$ and Na$_2$O when the amount reaches 3.0 wt%.

The overall selectivity to 4-IBPE (S$_{4\text{-}IBPE}$=mole of 4-IBPE produced), yield (Y$_{4\text{-}IBPE}$) of 4-IBPE, and conversion (X$_{4\text{-}IBAP}$=mole of 4-IBAP reacted) of 4-IBAP were calculated using the following respective equations:

$$X_{4\text{-}IBAP} = \frac{C^0_{4\text{-}IBAP} - C_{4\text{-}IBAP}}{C^0_{4\text{-}IBAP}} \qquad (1)$$

$$S_{4\text{-}IBPE} = \frac{C_{4\text{-}IBPE}}{C^0_{4\text{-}IBAP} - C_{4\text{-}IBAP}} \qquad (2)$$

$$Y_{4\text{-}IBPE(\%)} = X_{4\text{-}IBAP} \cdot S_{4\text{-}IBPE} \qquad (3)$$
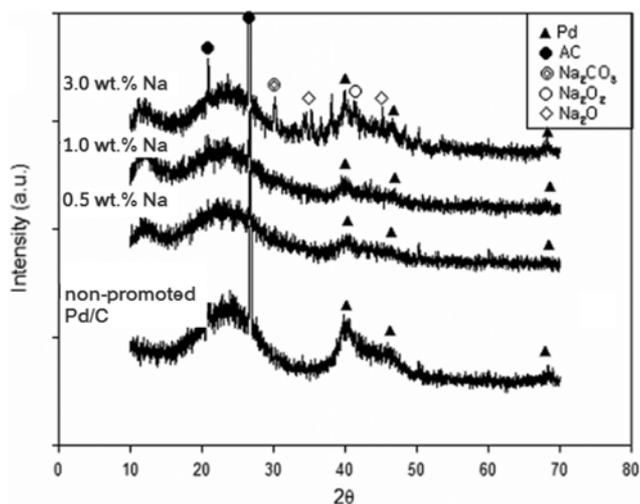

Fig. 5. X-ray diffraction of promoted Pd/C catalysts with various sodium contents.

The influence of sodium on the yield and selectivity of 4-IBPE production is shown in Fig. 6. The Pd/C catalyst promoted with 1.0 wt% sodium, 1.0Na-Pd/C, was used to analyze the relative con-
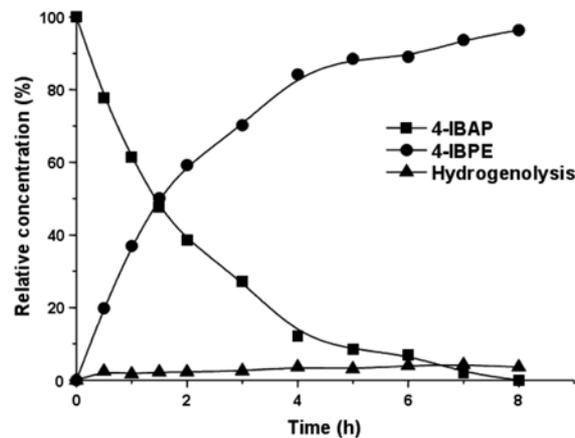

(a)
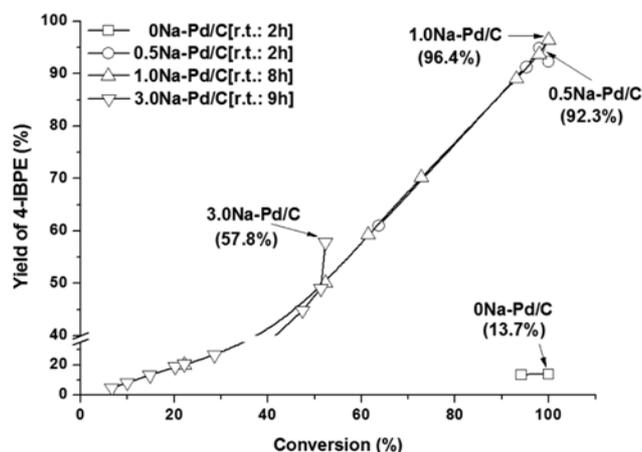
(b)
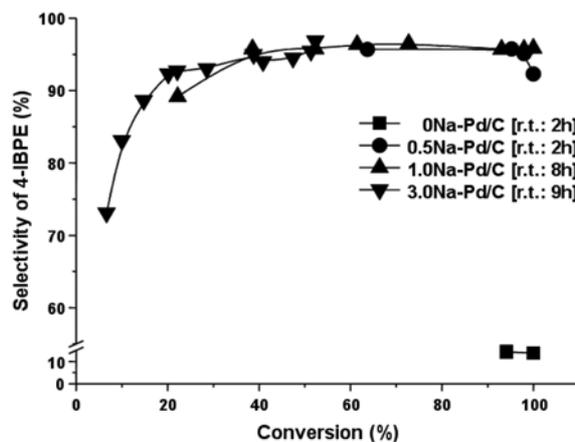
(c)

Fig. 6. (a) Relative concentrations as a function of reaction time over 1.0Na-Pd/C. (b) Overall yield and (c) selectivity of 4-IBPE as a function of the 4-IBPE conversion over Na-promoted Pd/C catalysts. The reaction conditions included C$_{4\text{-}IBAP}$ =0.028 mol/L, T=343 K, pressure=20 bar, an ethanol solvent, agitation rate=1,000 rpm, Pd/C=3 wt% of substrate (0.15 g) and a reaction time of 2-9 h.

centrations of reaction products in Fig. 6(a). According to the 4-IBAP consumption, the concentration of 4-IBPE monotonously increased to 96.4% (Fig. 6(b)) after 100% conversion (8 h), resulting in less than 4% hydrogenolysis products. This yield is an outstanding increase rather than those obtained when using non-promoted Pd/C catalysts at the same temperature of 343 K (13.7%) of Fig. 6(b) and at a lower temperature of 303 K (Fig. 3(a)). Although the reaction temperature was lowered in an attempt to enhance the selectivity of the alcohol substrate by decreasing the conversion rate, the concentration of 4-IBPE began to decrease after 5 h due to the increase in hydrogenolysis product (Fig. 3). This indicates that the Pd/C catalyzes the hydrogenation of C=O bonds as well as the dehydration or hydrogenolysis of the corresponding alcohol, resulting in the lower yield and selectivity of 4-IBPE, which is a typical observation in 4-IBAP hydrogenation over palladium-supported catalyst [2,7,11,12]. With sodium promotion, the conversion rate of the reactants gradually decreased with increasing sodium content. Two hours were required to achieve 100% conversion with over non-promoted Pd/C, while only 59.7% of the reactant was converted over 3.0Na-Pd/C, even after 9 h. However, the promoted catalyst with 0.5-1.0 wt% sodium enhanced the yield of 4-IBPE to around 95% (92.3% over 0.5Na-Pd/C and 96.4% over 1.0Na-Pd/C). All three sodium-promoted catalysts increased the 4-IBPE selectivity and maintained highly over 90% after the 4-IBAP conversion exceeded 40%, while the highest selectivity was obtained over 1.0Na-Pd/C (96.9%). Consequently, the sodium-promoted Pd/C catalyst retarded the conversion of reactant compared to that with the un-promoted Pd/C, while it enhanced the yield (96.9%) and selectivity (96.4%) of 4-IBPE with the 1.0Na-Pd/C catalyst.

3. Elucidation of Sodium Promotion on the Reaction Mechanism for the Selective Hydrogenation of 4-IBAP

The effect of sodium promotion on Pd/C was noticeable. The sodium delayed the rate of ketone hydrogenation and inhibited the reaction of the corresponding alcohol, resulting in higher production of 4-IBPE than with Pd/C. To explain the reaction rate of the C=O bonds in 4-IBAP hydrogenation, the hydrogenation of an aromatic ketone on the promoted Pd/C catalyst [13] is relevant since they contain a ring of C=C and C=O bond in the substrate. The rate of C=O bond hydrogenation was affected by the formation of electrophilic or Lewis sites on the promoter metal where the ketone group could be adsorbed and activated via the lone pair of oxygen atoms [17,18].

On the contrary, in the present study, the reverse effect was observed during 4-IBAP hydrogenation because the total hydrogenation time and rate of conversion decreased with sodium promotion, and the selectivity to 4-IBPE was decreased with increasing sodium content. The different effect of alkali promotion on the hydrogenation of aromatic ketone may be explained by considering the microporous structure of palladium-supported carbon. The surface area of the un-promoted Pd/C was 1,615 m^2/g, and the micro pore distribution occupied almost 40% of the total pores with an average pore diameter of 42.76 (Table 2). When the bulky structure of 4-IBAP (length of molecule=10.66 Å) is diffused from the external surface to the micro pores inside the support and adsorbs onto a Pd active site, the C=O bond of 4-IBAP should be horizontally located on the Pd surface, with other parts in a slant-like orientation, as shown in Fig. 7(a). In addition, the C=O bond of 4-IBAP must overcome the steric hindrance of two bulky groups, iso-butyl benzene and the methyl group, which are connected to the ketone group when the molecule diffuses inside the narrower micro pores of the carbon support. The larger amount of sodium promoter will narrow the free diffusion space of the reactant molecule inside the carbon micro pores. The lowest 4-IBAP conversion over Pd/C, promoted by 3.0 wt% Na, supports this explanation in which the conversion was less
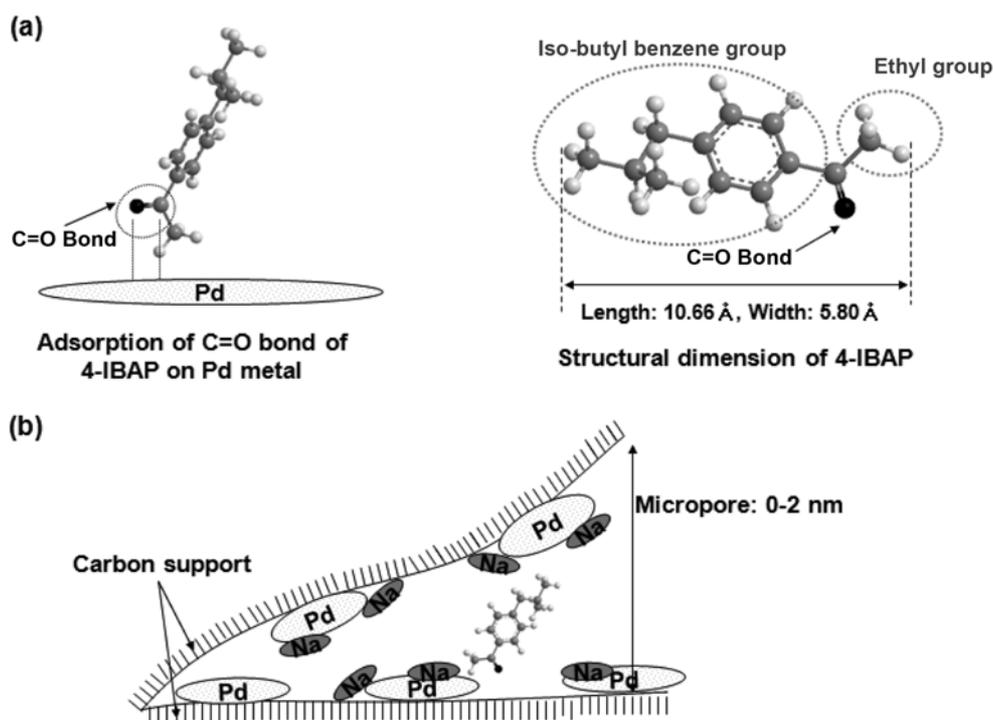

Fig. 7. Diffusional limitation of 4-IBAP molecules in the pores of the Pd/C catalyst.

than 60% even after the longest reaction time of 9 h. Owing to the limited diffusion of molecules and narrowed space for the slant-like orientation of C=O bond adsorption induced by promoted sodium on Pd, accessibility to the Pd metal located on the microporous carbon surface is prevented. Thus, this diffusion limitation induced by the steric hindrances will allow reduced amounts of 4-IBAP to reach and adsorb onto Pd active sites located in micro pores, thus decreasing the rate of consumption compared to that of un-promoted Pd/C, as shown in Fig. 7(b). The report that the diffusion of reactant molecules into microporous media was highly affected by steric hindrance, especially in a liquid phase reaction [19], supports the notion that the geometric effect of sodium promotion is dominant in determining the rate of C=O conversion in 4-IBAP hydrogenation compared to the electronic effect [18].

However, it is noticeable that the Pd/C catalyst greatly enhanced the yield and selectivity to 4-IBPE after sodium promotion. The decreased yield of 4-IBEB over promoted Pd/C was another reason for the enhanced production of 4-IBPE, and understanding the mechanism will elucidate the function of sodium in the Pd/C catalyst system. During hydrogenation of 4-IBAP over Pd/C (Fig. 3), the relative concentration of 4-IBPE first increased and then decreased, with the highest concentration after 5 hr of reaction, while those of the by-products produced from the consumption of 4-IBPE continuously increased with time, which indicates that the selectivity gradually decreased with reaction time. In the case of 0.5 and 1.0 wt% sodium, the selectivity was maintained at greater than 95% until 100% conversion of the reactant molecules. This demonstrates that the dehydration of the alcohol substrate, 4-IBPE, was inhibited by the existence of sodium.

It has been reported that the presence of a base eliminates the dehydration route, resulting in the highest selectivity to secondary alcohol. The KCl improved the selectivity of alcohol by inhibiting dehydration of alcohol to alkenes and by slowing the hydrogenation of the alkenes to alkanes [20,21]. Also, the addition of NaOH neutralized the acidic sites present on the Ni-Pt/HT catalyst, which inhibited the dehydration of the secondary alcohol [18]. It seems that the sodium promoter contributed to neutralization of a trace amount of acidic sites on the active carbon, which eliminates the dehydration route of the secondary alcohol. Considering the overwhelming geometric effect of sodium during 4-IBPE hydrogenation, the 4-IBEB dehydration was prominently decreased by the electronic effect of sodium rather than due to geometric effects.

Two related mixed effects explain the stronger electronic effect of sodium during 4-IBEP consumption. The amount and formation rate of the dehydration product from 4-IBEB are minor and very slow (Fig. 3), respectively. In addition, when 4-IBEB adsorbs onto the Pd surface, it experiences less steric hindrance than does 4-IBAP, which needs to be absorbed on a slant-like structure. Consequently, the sodium promoter prepared via post-impregnation on Pd/C enhanced the yield and selectivity to 4-IBPE. Sodium inhibited the rate of reaction during C=O hydrogenation through a geometric effect, while it enhanced the yield and selectivity of 4-IBPE by neutralizing the trace amount of acidic sites remaining on the catalyst. The rate of individual reaction may attribute to determine the overwhelming effects of sodium promotion for the selective hydrogenation of 4-IBAP to 4-IBPE over Pd/C; during 4-IBAP hydrogenation, which exhibits fast reaction over non-promoted Pd/C, the

diffusion of reactant molecules from bulk liquid to the palladium active site inside the carbon pore, was not restricted. By sodium promotion on Pd, which has high occupancy of microporosity, however, the diffusion limitation and steric hindrance against C=O bond adsorption of 4-IBAP became preponderant. In contrast, the very slow reaction of 4-IBPE implies the diffusion limitation by steric and geometric effects of internal pore structure induced-by sodium promotion became weaker. Instead, the electronic effects by sodium on Pd surface were overwhelming. The existence of acidic sites on the carbon support facilitates the dehydration of 4-IBPE [2] resulting in the reduction of 4-IBPE selectivity. The basic property of sodium promoter may retard this reaction by neutralization of those acidic sites. In addition, the polar protic solvent, ethanol, is reported to facilitate a formation of an ether derivative of 4-IBPE by strong electron donation from -OH groups [16]. It is considered that the existence of sodium deposited on the Pd surface or a trace amount of resolved sodium in solvent lessens those electronic effects of hydroxyl group of the solvent. Furthermore, when sodium is deposited on the surface of Pd/C, its electronic effect will be direct, which is different from the use of alkali metal as an additive because additives are introduced to the reactant solution and can affect the catalytic system.

CONCLUSIONS

The effect of sodium on the selective hydrogenation mechanism of 4-IBAP was investigated over a Pd/C catalyst. The distribution of reaction products was identified, and the hydrogenation routes over Pd/C using an ethanol solvent were suggested. The desired product, 4-IBPE, was produced via hydrogenation of the C=O bond of 4-IBAP and was further consumed following four different routes depending on the kind of catalyst and solvent present. Inhibition of these consecutive reactions was the prime focus of this research. The sodium-promoted Pd/C catalyst simultaneously decreased the consumption of 4-IBAP and 4-IBPE, which led to a remarkable increase in the 4-IBPE production compared with that of the non-promoted catalyst. Among the sodium-promoted Pd/C catalysts, 1.0Na-Pd/C resulted in the highest yield (96.9%) and selectivity (96.4%) of 4-IBPE, which was significantly higher than values reported in the non-patented literature. Sodium affected the diffusion limitations via its geometric effect during C=O hydrogenation and neutralized the trace amount of acidic sites remaining on the catalyst, which resulted in the highest yield and selectivity of 4-IBPE.

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