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Effects of sodium promoter on the mechanism of biphenol hydrogenation over Pd/C catalyst

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Abstract

The effect of sodium promoter on the catalytic hydrogenation of biphenol (BP) was investigated. Several reaction products were identified and the change in their distribution with time was analyzed to find the reaction mechanism. Different amount of sodium salt was impregnated on Pd/C to observe its effect on the composing reactions of BP hydrogenation. The existence of sodium metal decreased the C=C bond hydrogenation, but accelerated the C=O bond hydrogenation resulting in the increase of the yield to bicyclohexyl-4,4′-diol (BHD). The promotional effect of Na on the supported palladium on carbon catalysts were explained by electronic and geometric factors.

Keywords: Biphenol hydrogenation; Sodium promoter; C=C and C=O bond; Electronic and geometric factors; Pd/C catalyst

1. Introduction

Bicyclohexyl-4,4′-diol (BHD) and bicyclohexyl-4,4′-dione (BHDN) are important intermediates in manufacturing polymeric resins and additives of plastic units including plasticizer, lubricant and antistatic agent. They are also useful raw materials for the production of pharmaceuticals, LCD and surfactant [1,2]. The first report on preparation of BHD was made by Wilds et al. [3] who performed hydrogenation of biphenol (BP) to produce BHD over Ni catalyst and produced BHDN through BHD oxidation over CrO_3. The related patent was released by Noboru who used Ni, Pd catalyst and various solvents in preparation of BHD [1]. Yasushi also filed a patent about preparation of BHDN by BP hydrogenation over alkali promoted Pd catalyst [2], but the detailed information on the reaction mechanism or the effects of catalyst promotion is not known.

On the promotional effects of alkali metal in BP hydrogenation, we may get some insight from the previous reports [4–9] on phenol hydrogenation and the effect of catalyst promotion since BP and phenol have similar structure of the molecules. Neri et al. found that the major reactions were hydrogenation of benzene ring and hydrogenolysis of the alcohol group [7]. It was found that Pd is an appropriate catalyst to selectively hydrogenate phenol to a ketone and that a small amount of sodium salt introduced into the reaction mixture increased the selectivity to ketone while larger amount of the additive increased the yield to alcohol [6]. In the investigation on the alkali promoters over Pd/Al_2O_3 catalyst, the enhancement of the selectivity to cyclohexanone was explained by the acid–base property of the catalyst [7–9].

This study was done to get a better understanding on the reaction mechanism of BP hydrogenation and the reason for the effect of alkali promotion of the metal catalysts. For this purpose, the changes in the product distribution which occurred due to catalyst promotion were analyzed regarding to the reaction mechanism. Here an interesting result is reported that the promoter affected the series reactions occurring in BP hydrogenation in different ways. This work also showed that the promoter can exert both of electronic and geometric effects on a catalytic reaction.

2. Experimental

2.1. Catalyst preparation

Pd/C (5 wt.% Pd) of commercial origin (Kawaken Fine Chemical Co., surface area = 1246 $m^2 g^{-1}$ and pore volu-

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Table 1
Characteristics of the investigated Pd/C catalysts

Catalyst code	Promoter salts	Pd loading (wt. %)	Na loading (wt. %)	Na/Pd (atomic ratio)
Pd	–	5	–	–
Na0.1Pd	Na_2CO_3	5	0.1	0.09
Na0.2Pd	Na_2CO_3	5	0.2	0.19
Na0.3Pd	Na_2CO_3	5	0.3	0.28
Na0.5Pd	Na_2CO_3	5	0.5	0.46
Na1.0Pd	Na_2CO_3	5	1.0	0.93
Na3.0Pd	Na_2CO_3	5	3.0	2.78

me = 0.7 ml/g) was oven-dried at 100 °C for 5 h before use. For catalyst promotion, aqueous solution of Na_2CO_3 was impregnated on the Pd/C catalyst (dry impregnation). The resulting solid was dried under vacuum at 100 °C for overnight and stored in a desiccator until use. Chemical compositions of the catalyst prepared are shown in Table 1.

2.2. Reaction apparatus and procedures

The BP hydrogenation reaction was carried out with a 200 mL Bűchi autoclave as shown in Fig. 1.

The reaction temperature was controlled by circulating a heating medium through the reactor jacket. The holes running top-to-bottom center of the shaft and at the side of impeller help H_2 gas introduced into the reaction media. A dip tube with two ball valves installed on the sampling line outside of reactor was inserted inside the reactor to extract product samples. 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 at 165 °C, 8 bar and 1000 rpm of agitation speed. 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 done using the mass fragmentation from the GC-MS (Fisons MD800).

3. Results

The characteristics of selective hydrogenation of 4,4′-biphenol (BP) over Pd/C were examined. The reaction products were composed of 4-(4-hydroxy-phenyl)-cyclohexanone (HPCN), 4-(4-hydroxy-cyclohexyl)-phenol (HCP), bicyclohexyl-4,4′-dione (BHDN), 4′-hydroxy-bicyclohexyl-4-one (HBN) and bicyclohexyl-4,4′-diol (BHD). HCP and HBN were obtained as two peaks in the chromatogram, which represented *trans* and *cis* isomers of the products, while BHD showed three peaks, which might correspond to *trans–trans*, *trans–cis*, *cis–cis* isomers. The hydrolysis products (designated as HP), which included 4-phenylcyclohexane et al., were obtained in less than 1%.

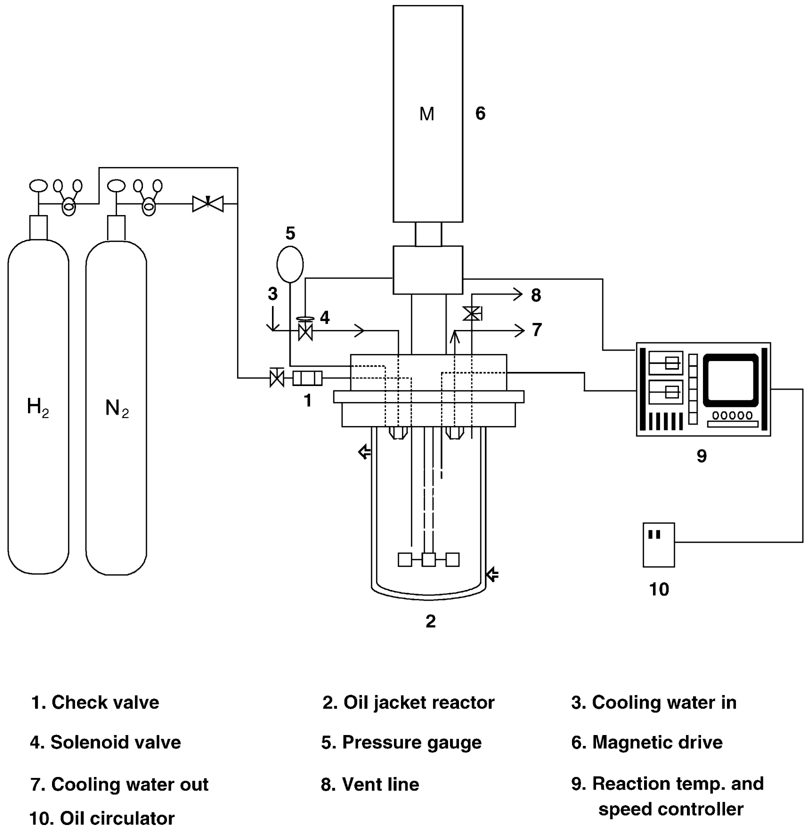


Fig. 1. Apparatus for the BP hydrogenation reaction.

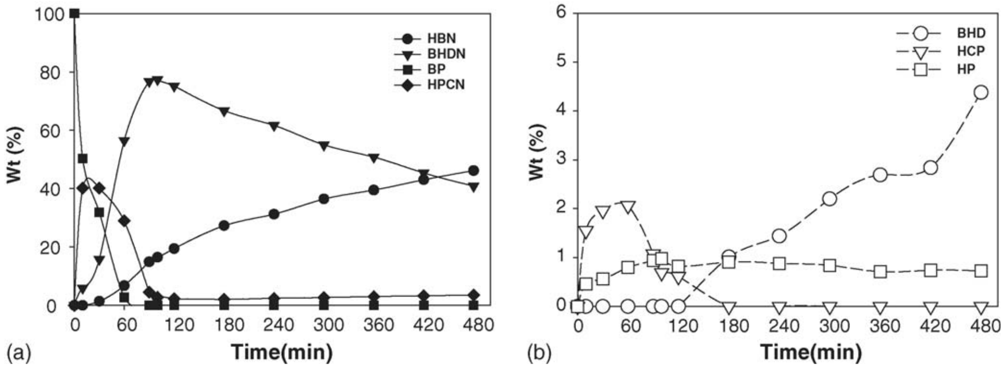


Fig. 2. Product distribution in BP hydrogenation (temperature 165 °C, pressure 25 bar, agitation speed 1000 rpm, catalyst loading 0.0125 gPd/BP 5 g): (a) major products; (b) minor products (HP: hydrogenolysis product).

The changes in the product distribution with time are shown in Fig. 2. The reactant (BP) was converted fully in 1 h but several compounds were produced and consumed sequentially. As BP reacted, HPCN, BHDN and HBN were obtained in large amounts, while HCP was produced in a much less amount. The fully saturated product, BHD, was obtained only in a small amount from 8 h reaction.

The rate of the composing reactions was found by comparing the slope of the concentration profile of each product (Fig. 2). We could find that the rate of BHDN consumption was much slower than those of hydrogenation of BP or HPCN. The formation of BHD was very low up to 2 h. The bottlenecks in the reaction to BHD seemed to be hydrogenation of BHDN and HBN.

The changes of the reaction characteristics with reaction temperature were examined and its results are shown in Fig. 3. The rates of BP hydrogenation and BHDN formation drastically increased with the increase of temperature. It also showed that the yield to BHD and HP increased significantly as the reaction temperature increased from 165 to 195 °C.

Alkali metals including Na_2CO_3 were doped on Pd/C catalyst in various amount and their effects on product distribution were examined (Fig. 4). The most significant effect of these promoters on the reaction was an enhancement of BHD yield. The yield of BHD with catalyst promoted with 3 wt.% Na was about 70% in 8 h in contrast to 6% yield with Pd/C. With Pd/C doped with 3 wt.% Na, all of BHDN was also consumed in 6 h, while 40% of BHDN was still left with

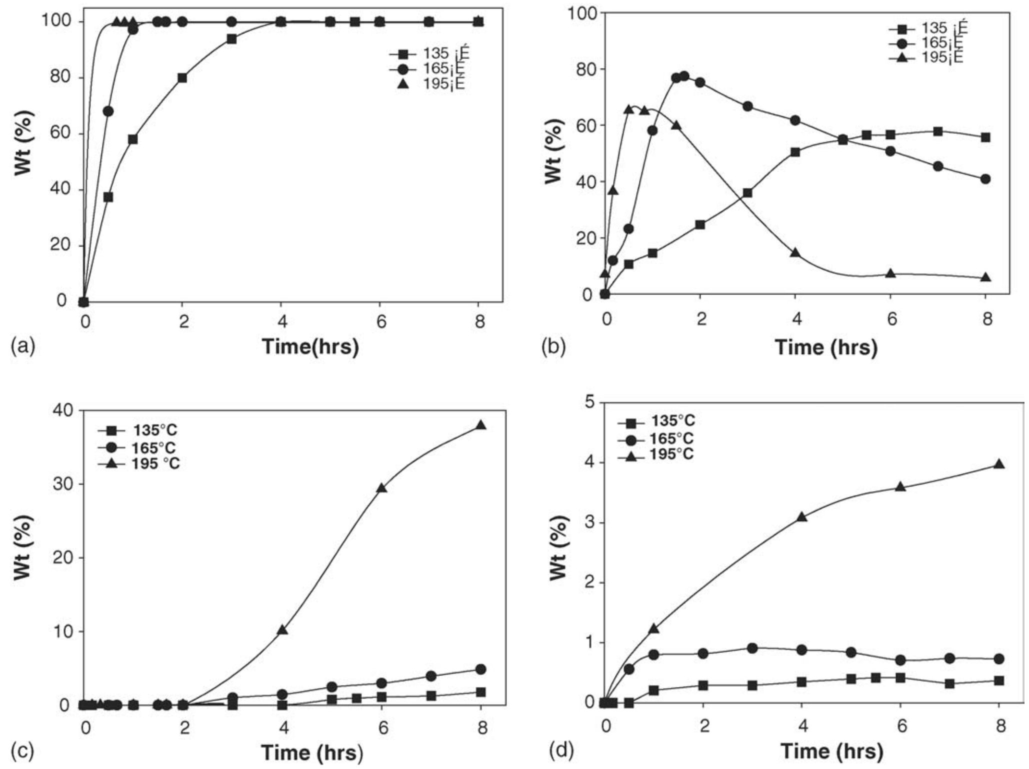


Fig. 3. The effect of temperature on conversion and product distribution (pressure 8 bar, agitation speed 1000 rpm, catalyst lading 0.0125 g Pd/BP 5 g): (a) BP conversion; (b) BHDN; (c) BHD; (d) HP (hydrogenolysis product).

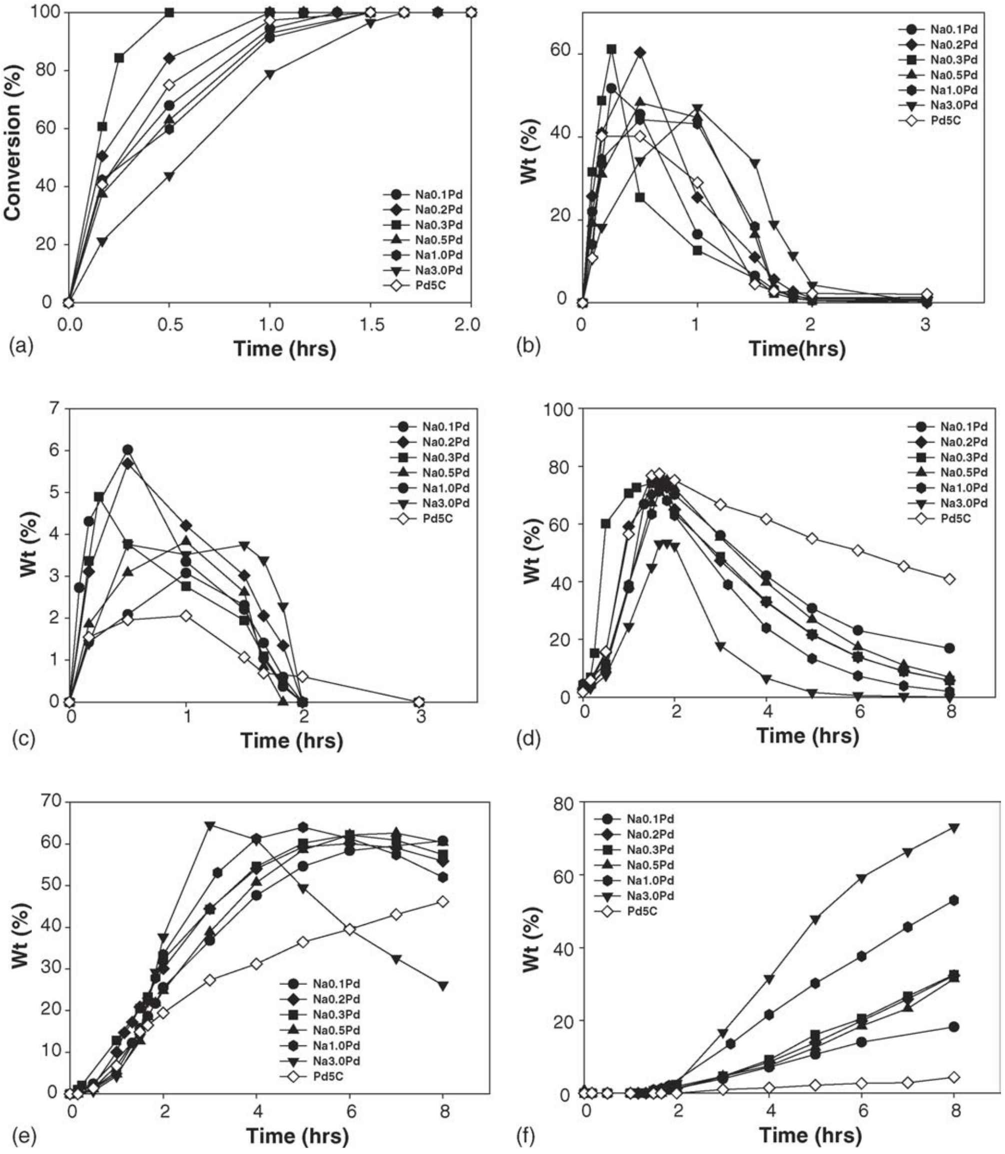


Fig. 4. The effect of Na promotion on BP hydrogenation (temperature 160 °C, pressure 8 bar, agitation speed 1000 rpm, catalyst loading 0.0125 Pd/BP 5 g): (a) BP conversion; (b) HPCN; (c) HCP; (d) BHDN; (e) HBN; (f) BHD.

monometallic Pd/C in 8 h of reaction. The rate of HBN consumption also became much higher with the catalyst of 3 wt.% Na promotion than other catalysts with lower sodium content. The apparent effect of Na promotion seems to be an enhancement of the rate of hydrogenation of BHDN and HBN, the bottleneck processes in BP hydrogenation, leading to a higher yield of BHD.

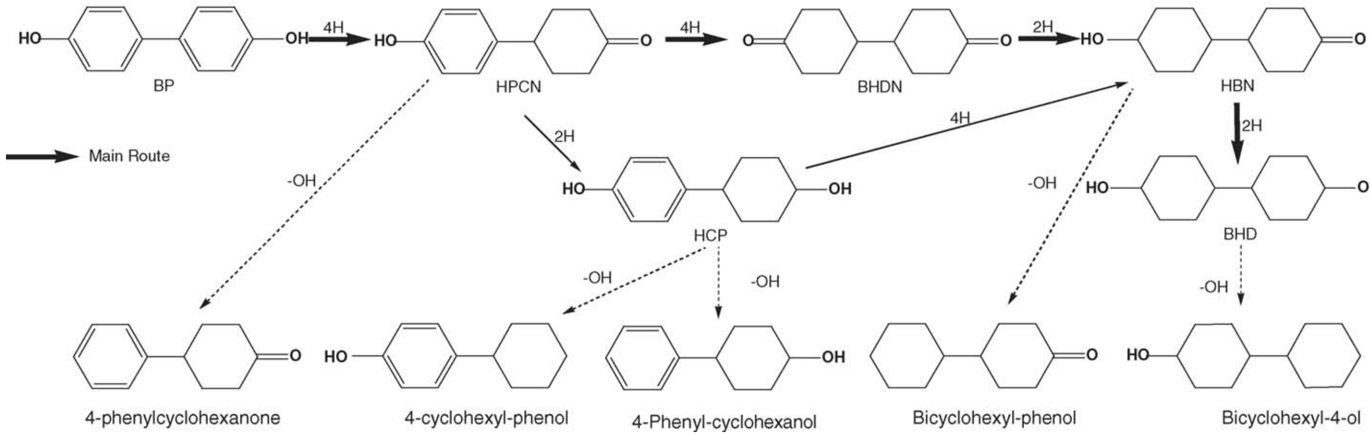
In contrast, the rate of BP conversion showed a different trend with catalyst promotion. While the rate increased as 0.1–0.3 wt.% of Na was added to the catalyst, it began to decrease as the sodium content increased further. When the content of Na reached 3 wt.%, the reaction rate of BP hydrogenation became much slower than that with Pd/C. The rate of HPCN hydrogenation and BHDN formation also decreased with the increase of Na content in the catalyst. These differences in the promotion effects on the rates of unit reactions during BP hydrogenation were notable and needed mechanistic analysis.

4. Discussion

In the hydrogenation of BP, various products were obtained and their distribution changed significantly with the change of reaction temperature and the alkali promotion of catalyst. Based on this information, it was attempted to find the reaction mechanism for BP hydrogenation and examine how the composing reactions were affected by the promotion of the catalyst.

From the changes of the product distribution with time (Fig. 2), the reaction pathway of BP hydrogenation was proposed as in Scheme 1.

The first product when BP was hydrogenated was HPCN, which means that two double bonds of the benzene ring of BP



Scheme 1. Reaction pathway of BP hydrogenation.

were hydrogenated and that the resulting product in an enol form was then converted to its isomer in a keto-form via tautomerization. It has been reported [7,9] that a ketone (cyclohexanone) was formed in the hydrogenation of phenol, a compound with a similar structure to BP. It was notable that no cyclohexadiene intermediates were observed during BP hydrogenation as in the case of benzene hydrogenation [10].

The major product from HPCN hydrogenation was BHDN (60% yield in 1 h) rather than HCP (2% yield in 1 h). This observation showed that the other benzene ring of HPCN (C=C bond) was hydrogenated preferentially over the ketone group of HPCN. It was also found that the rate of consumption of BP or HPCN (C=C bond hydrogenation) (Fig. 2) was much higher than that of consumption of BHDN (C=O bond hydrogenation). These results show that between the two kinds of hydrogenation reactions taking place during BP hydrogenation, the hydrogenation of C=C bond occurs more readily than that of the C=O bond.

When all of the C=C bonds had reacted, hydrogenation of the ketone groups of the BHDN slowly proceeded to give HBN and BHD as major products. BHD started to be formed only after 2 h had passed from the start of the reaction. Products from hydrogenolysis reaction were obtained in a small amount, which shows the little importance of hydrogenolysis reaction in BP hydrogenation at the given condition. Therefore, the major reaction steps in BP hydrogenation are considered to be hydrogenation of C=C bonds and C=O bonds as shown in Scheme 1.

As the reaction temperature was increased to 195 °C, the rate of BHDN consumption (C=O bond hydrogenation) became much higher so that a larger amount of BHD was formed in the reaction of 8 h (Fig. 3). It was also found that hydrogenolysis reaction became more important at a higher temperature.

The effects of the catalyst promotion on the rates of composing reactions were different according to the type of reactions. With increasing Na content, reactions of BP and HPCN (C=C bond hydrogenation) were first enhanced and then suppressed, while reactions of BHDN and HBN (C=O bond hydrogenation) were enhanced monotonously. The effects of sodium promotion on C=O bond reactions were much stronger than C=C bond reactions so that the yield of the final product (BHD) was highest with the catalyst of the largest amount of promoter. It is considered that the promoter effectively assisted to overcome the bottleneck processes (C=O bond hydrogenation) in BP hydrogenation.

Regarding to the possible reasons for the rate changes in BP hydrogenation, the reports on the hydrogenation of unsaturated aldehydes on the promoted Pt/C catalyst [11–13] are relevant since they contain reactions of the C=O bond and C=C bond in the substrate. The reason for the enhanced rate of hydrogenation of C=O bond over hydrogenation of C=C bond was explained by the formation of electrophilic or Lewis sites on the promoter metal where the carbonyl group can be adsorbed and activated via the lone pair of the oxygen atom [12]. Therefore, the enhanced reaction rates of BHDN and HBN in BP hydrogenation could be ascribed to the formation of additional sites on the sodium metal for C=O bond hydrogenation.

The increased rate of C=C bond hydrogenation with the catalyst of a lower Na content (Fig. 4a) may be ascribed to the increase in the electron density on the catalyst. It seems that sodium provided electron to palladium resulting in a decreased binding strength to the catalyst of the C=C bond and an enhancement of its reaction. On the other hand, the decreased rate of C=C bond reaction with the catalyst of higher Na content can be explained by blocking of palladium sites by sodium metal. It seems that site blocking effect overwhelmed the rate enhancement due to the electronic factor as the surface coverage of sodium increased.

It might sound strange that the rate of C=O bond hydrogenation could be increased even when Pd sites were significantly blocked to result in a decrease in the rate of C=C bond hydrogenation. This may indicate that there were the additional sites for C=O bond hydrogenation besides the metal sites used for C=C bond reaction, which support our theory on the additional sites on sodium metal for C=O bond hydrogenation.

The results obtained in this study were rather different from the previous work on phenol hydrogenation over alkali promoted Pd/Al_2O_3. Major product in that work was ketone and the enhanced selectivity to ketone with Na doping was explained by the changes in the acid–base distribution of support. These differences seem to come from the facts that the percentages of Pd and Na used in our work (5% Pd, 0.1–3% Na) were much higher than those in phenol hydrogenation experiments (1% Pd, ∼1% Na) and that a neutral support (activated carbon) was used in our work instead of acidic support (Pd/Al_2O_3).

The effects of catalyst promotion on BP hydrogenation can be explained as follows. In the initial stage of reaction, the rate of BP conversion increased at the Na content of 0.1–0.3 wt.%, due to electronic reasons, while it decreased significantly at higher content of Na as the geometric factor became dominant. When all of BP and HPCN had converted to either HBN or BHDN and at least one C═O bond had formed, the effect of sodium on the C═O hydrogenation reaction became more apparent. The rates of C═O hydrogenation were enhanced by adsorption and activation of C═O bond on the promoter sites, the number of which increased with addition of the promoter. As a result, rate of BHD formation was drastically enhanced by promoting sodium on Pd/C catalyst.

5. Conclusions

A study on the effect of sodium promoter on the mechanism of BP hydrogenation over Pd/C catalyst was performed and the following conclusions were obtained.

1. During BP hydrogenation, HPCN, BHDN, HBN and BHD were produced sequentially as major products and a reaction scheme was proposed based on the product distribution. The major reaction steps in BP hydrogenation were found to be hydrogenation of C═C bonds and C═O bonds and the hydrogenation of C═C bond occurred preferentially over to that of C═O bond.
2. With increasing Na content, C═C bond hydrogenation were first enhanced and then suppressed, while C═O bond hydrogenation were enhanced monotonously. The effects of sodium promotion on C═O bond reactions were much stronger than those on C═C bond reactions so that sodium promotion enhanced the BHD yield drastically.
3. Effects of the promoter on the catalytic hydrogenation of C═C bond seem due to the changes in the electronic and geometric properties of Pd site while the enhancement of C═O hydrogenation is considered to be due to formation of additional catalytic sites on sodium metal.

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