Catalysis Science & Technology

Accepted Manuscript

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ARTICLE

Significant effect of base on the selectivity improvement in the hydrogenation of benzoic acid over NiZrB amorphous alloy supported on γ–Al_2O_3

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

This study presents a facile way to improve the selectivity for cyclohexane carboxylic acid by adding base in the hydrogenation of benzoic acid over non-noble metal NiZrB amorphous alloy supported on γ–Al_2O_3. It is found that alkali metal carbonates exhibited an excellent selectivity improvement from 50.3% to a range of 93.5–95.7%, with the conversion of benzoic acid higher than 92.3%. Even very small amount of K_2CO_3 (1 mol % of benzoic acid) was efficient for improving the selectivity for cyclohexane carboxylic acid. In addition, lower reaction temperature was beneficial to the selectivity improvement. Based on the results of temperature programmed desorption of NH_3 and inductively coupled plasma analysis, the selectivity improvement in the presence of base was attributed to the neutralization of acidic sites on the surface of catalyst by the *in-situ* generated potassium benzoate, inhibiting the hydrodeoxygenation of carbonyl and resulting in a high selectivity for cyclohexane carboxylic acid.

1. Introduction

Selective hydrogenation of a targeted functional group in a molecule having several reducible functional groups is of great utility in chemical processes.[1–5] Particularly, the hydrogenation of aromatic substrates aiming at manufacturing saturated or partially saturated molecules has attracted much interest in the field of chemical and pharmaceutical industry, due to their environmentally benign, the ready availability of suitable feedstocks and the most straightforward approach.[5–10] In general, aromatic ring hydrogenation usually requires harsh reaction conditions, increasing the potential to the hydrogenation of other reducible moieties, and then leads to low chemoselectivity.[11,12] One approach to enhance the selectivity is to modify the surface of catalysts.[13] For instance, the selective hydrogenation of aromatic and hetero-aromatic compounds, such as quinoxalines,[14] quinolines and indoles,[15,16] in order to obtain their relative saturated or partially saturated molecules, can be achieved by using ligand-controlled ruthenium-based catalysts.[17] Another approach is to select suitable support to apply the interaction between catalyst and support, thus improving the selectivity for the hydrogenation of aromatic ring. For example, the hydroxy aromatic derivatives, such as phenol, could be selectively hydrogenated to the corresponding ketones by palladium nanoparticles supported on hydrophilic carbon,[18] mesoporous graphitic carbon nitride[19] or nitrogen-functionalized ordered mesoporous carbons.[20,21] It is noteworthy that a simple way to enhance the selectivity for cyclohexanone in the hydrogenation of phenol has been established by Han and his coworkers.[22] Lewis acid ($AlCl_3$, $ZnCl_2$ or $InCl_3$) was added as a dual-functional additive to increase the selectivity and activity of Pd/C catalyst, because Lewis acid could not only activate the phenyl ring but also suppress its further hydrogenation.

Selective hydrogenation of benzoic acid (BA) to cyclohexane carboxylic acid (CCA), which is an important organic intermediate for the synthesis of praziquantel and ansatrienin, has been studied in previous works.[23–26] Most of the catalysts used in this transformation were noble metal catalysts.[24–26] However, their high price has limited their further industrial applications. Recently, we have prepared a non-noble metal catalyst Ni–Zr–B–PEG(800), which showed both good activity and selectivity for CCA in the selective hydrogenation of BA using water as solvent.[23] However, the turnover number of Ni–Zr–B–PEG(800) was relatively low due to the following two reasons: (i) the Ni active species were leached into water during the long time stirring at high temperatures;[27] (ii) the formation of nickel hydroxide during the reaction caused a rapid deactivation of the Ni-based catalyst.[28,29] Whereas if we selected aprotic solvents in the selective hydrogenation of BA to CCA, the selectivity for CCA was markedly lowered due to the decrease of the solvent polarity.[23]

In a continuing attempt to achieve higher selectivity using the non–noble metal catalyst in the selective hydrogenation of BA to CCA, we herein demonstrate a facile and effective approach to improve the selectivity for CCA over NiZrB amorphous alloy supported on γ–Al_2O_3 [NiZrB/Al_2O_3] just by adding small amounts of bases in cyclohexane. To the best of our knowledge, this might be the first report on the selectivity improvement by tuning the catalyst *via* the *in-situ* generated intermediate during

Table 1 Structural properties of the amorphous alloy catalysts and γ-Al_2O_3

Catalyst	Composition (atomic ratio)[a]	Ni loading (wt %)	H_2-Chemisorption (cm^3/g)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
NiZrB/Al_2O_3	$Ni_{1.00}Zr_{0.026}B_{0.30}$	11.0	0.15	154	0.25	6.5
NiZrB[b]	$Ni_{1.00}Zr_{0.025}B_{0.40}$	90.2	0.45	50	0.14	10.9
γ−Al_2O_3	–	0	0	202	0.42	8.3

[a]Based on ICP results. [b]According to the results of Ni–Zr–B–PEG(800) in reference 23.

the reaction. Therefore, a possible mechanism was proposed based on necessary characterizations. Furthermore, the influence of parameters such as solvent, reaction temperature, and ratio of base to BA was also investigated.

2. Experimental

2.1. Catalyst Preparation

Unless otherwise noted, all chemicals were analytical reagent grade and used without further purification. NiZrB/Al_2O_3 was prepared by an impregnation-reduction method. The support γ−Al_2O_3 (2.7 g) was first heated at 773 K for 4 h and then impregnated with an mixed solution of 1.234 g $NiCl_2·6H_2O$, 0.055 g $Zr(NO_3)_4·5H_2O$ (molar ratio Ni : Zr = 40 : 1), 0.5 g poly(ethylene glycol) (average molecular weights: 800 g mol^{-1}, PEG800) and 2 mL water under ultrasound for 20 min. After the resulting paste was dried at 393 K for 2 h, the light yellow precursor was ground into powder and then placed in an ice-bath, reduced by adding 20 mL of 1.0 M aqueous KBH_4 containing 0.25 M NaOH dropwise under vigorous stirring. When bubbles ceased to appear, the precipitate was filtered, washed with water several times until the washings were pH 7, and then further washed with absolute ethanol three times to replace residual water. Furthermore, unsupported NiZrB amorphous alloy modified with PEG(800) was prepared by a chemical reduction method as described previously.[23]

2.2. Catalyst Characterization

Brunauer–Emmett–Teller (BET) surface area was estimated on a Micromeritics Tristar II 3020 surface area and pore analyzer. H_2-chemisorption and temperature programmed desorption of NH_3 (NH_3-TPD) was tested using a TP-5000 instrument supplied by Xianquan Ltd. X-ray diffraction (XRD) patterns were recorded on a Bruker D8-ADVANCE X-ray diffractometer. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 microscope. Fourier transform infrared spectroscopy (FTIR) was carried out on a Bruker Vertex 70 spectrometer. Inductively coupled plasma analysis (ICP) was measured on a Varian Vista-MPX spectrometer.

2.3. Catalyst Activity Test

Selective hydrogenation of BA was conducted as follows: BA (3.0 g), solvent (60 mL), catalyst (1.0 g), and base were mixed in a stainless steel autoclave (100 mL) equipped with an electric heating system and a magnetically driven mechanical stirrer. The reaction system was filled with H_2 to 3.0 MPa several times by evacuation to displace residual air, and then pressured with H_2 to 5.0 MPa and heated to the requisite temperature. On reaching the temperature, the reaction was performed by stirring the reaction mixture vigorously. When the reaction was complete, the reaction mixture allowed to cool to room temperature, and separated by filtration. The solution was analyzed by gas chromatography (GC) using a 30-m SE-54 capillary column. The product was identified using gas chromatography–mass spectroscopy (GC–MS) on a Thermo Finnigan Polaris-Q spectrometer. The used catalyst was denoted as "NiZrB/Al_2O_3–u–base". When base was not added, the used catalyst was denoted as "NiZrB/Al_2O_3–u".

2.4. Comparative Experiments

Comparative experiments were carried out using the same method as that of BA hydrogenation but without adding any catalyst, instead of using excess additive – half of the amount of BA. For a typical run: BA (3.0 g), cyclohexane (60 mL), K_2CO_3 or K_2SO_4 (50 mol % of BA) were reacted on 423 K under 5 MPa hydrogen pressure for 4 h, and then treated by the same process as described above. The experiments were denoted as CE–K_2CO_3 and CE–K_2SO_4, respectively.

3. Results and discussion

3.1. Catalyst Characterization

Physical properties of NiZrB/Al_2O_3, NiZrB and γ−Al_2O_3 were summarized in Table 1. From the ICP analysis, it was found that the contents of Ni and Zr in both NiZrB/Al_2O_3 and NiZrB were about 40 : 1, which was almost identical with the feed ratio. The Ni loading of NiZrB/Al_2O_3 was only 11.0 wt %, much lower than that of NiZrB. Thus, it is reasonable that NiZrB/Al_2O_3 has a lower H_2-chemisorption value than NiZrB. In fact, it has a higher H_2-chemisorption value for each Ni atom due to the dispersive effect of γ−Al_2O_3. The BET surface area, pore volume and pore size of NiZrB/Al_2O_3 markedly decreased compared with the pure γ−Al_2O_3 support, indicating that some NiZrB amorphous alloy particles should occupy on the surface and in the pores of the γ−Al_2O_3 support due to its porous nature.[30]

XRD analysis of the prepared NiZrB/Al_2O_3 catalyst showed three characteristic peaks, which were all attributed to γ−Al_2O_3 (Fig. 1); in contrast, no peak related to amorphous alloy was detected in this catalyst, probably because that the diffraction peak of NiZrB in the NiZrB/Al_2O_3 has been obscured by the peaks of γ−Al_2O_3 at about 45 °C.[30–33]

TEM image of NiZrB/Al_2O_3 was shown in Fig. 2a. It was obvious that NiZrB amorphous alloy was well dispersed on the γ−Al_2O_3 support with the particle sizes in a range of 7.0–21.0 nm (Fig. 2b). The mean particle size of NiZrB amorphous alloy was

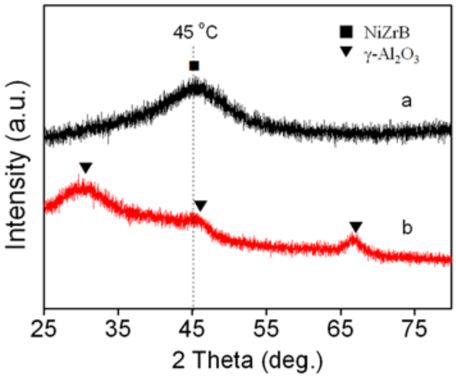

Fig. 1 XRD patterns of amorphous alloy catalysts (a) NiZrB and (b) $NiZrB/Al_2O_3$.

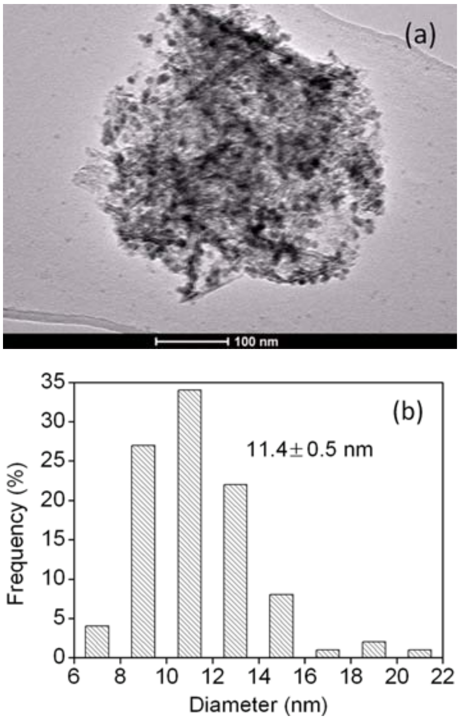

Fig. 2 TEM image (a) and size distribution (b) of $NiZrB/Al_2O_3$.

11.4 nm, which was much smaller than that of the unsupported NiZrB amorphous alloy (20.8 nm), as reported in our previous work.[23] On the other hand, no evidence for the existence of PEG(800) on the surface of $NiZrB/Al_2O_3$ can be found from the TEM result. Thus, we suggest that most of the PEG(800) has been removed during the washing process of preparation, as supported by the FTIR spectra (Fig. S1, ESI†) and in agreement with our previous work.[34] Its main role was to prevent agglomeration of the amorphous alloy particles in the reduction process, which resulted in more active Ni species.

3.2. Effect of Bases

Table 2 shows the results of the selective hydrogenation of BA for CCA over $NiZrB/Al_2O_3$ under different conditions. As can be seen, the conversion of BA was 99.9%, but the selectivity for CCA was only 50.3% in cyclohexane without any additive (entry 1). Although the selectivity for CCA was increased to 82.5% in water, the conversion was only 29.6% (entry 2), which might be due to the low Ni content in the catalyst. According to the observation of Han and his coworkers, the coordination of Lewis basic C=O group and Lewis acid inhibited further hydrogenation of cyclohexanone in the hydrogenation of phenol.[22] Thus, for our reaction system, the carboxyl group of BA and Lewis acid might form a complex, protecting carboxyl group from hydrogenation and then improving the selectivity for CCA. Unfortunately, a terribly low conversion (1.1%) was obtained when $AlCl_3$ was added in cyclohexane, though the selectivity for CCA can reach 99.9% (entry 3). Subsequently, some bases and salts were also tested as additives to improve the selectivity in cyclohexane. Interestingly, bases showed remarkable effect on the selectivity for CCA. In the case of alkali metal carbonates (entry 4-7), the selectivities for CCA were markedly improved from 50.3% to a range of 93.5–95.7%. In the case of other bases (entry 8-14), the selectivities for CCA were also over 80% except triethylamine, which was only 56.7%, just a little higher than that of no additive used. In contrast, in the case of a neutral salt, such as K_2SO_4, the selectivity for CCA was only 47.7% (entry 15), much lower than those of alkali metal carbonates. Thus, we can conclude that bases, especially for alkali metal carbonates, favored the selectivity for CCA in cyclohexane over $NiZrB/Al_2O_3$.

To further study the effect of base on the selectivity for CCA in the hydrogenation of BA, K_2CO_3 was chosen in consideration of the catalytic efficiency and cost. The effects of solvent, reaction temperature, and the amount of K_2CO_3 were then investigated. The effect of solvent on the selectivity for CCA was first studied and the results are shown in Fig. 3. With the addition of K_2CO_3, no matter what kind of solvents was used, the selectivities for CCA were higher than 95%. Thus, the catalytic system involving both base and $NiZrB/Al_2O_3$ displays a good solvent profile for selectivity. On the other hand, the best conversion of BA was

Table 2 Effect of additives in the selective hydrogenation of BA over $NiZrB/Al_2O_3$

Entry	Additives	Conversion of BA (%)	Selectivity for CCA (%)	Yield of CCA (%)
1	–	99.9	50.3	50.2
2^a	–	29.6	82.5	24.4
3	$AlCl_3$	1.1	99.9	1.1
4	Li_2CO_3	99.9	93.5	93.4
5	Na_2CO_3	99.9	93.8	93.7
6	K_2CO_3	99.9	95.3	95.2
7	Cs_2CO_3	92.3	95.7	88.3
8	KOAc	96.7	93.9	90.8
9	$NaHCO_3$	99.4	89.3	88.8
10	C_6H_5COOK	99.9	93.7	93.6
11	NaOH	99.9	80.3	80.2
12	KOH	99.9	90.3	90.2
13	PAAS^b	99.9	86.5	86.4
14	$N(C_2H_5)_3$	99.9	56.7	56.6
15	K_2SO_4	99.9	47.7	47.7

Reaction conditions: BA (3.0 g), cyclohexane (60 mL), $NiZrB/Al_2O_3$ (1.0 g, 11.0 wt % of Ni), additive (5 mol % of BA), 423 K, initial P (H_2) = 5 MPa, and reaction time 4 h. ^{a}Water as the solvent. ^{b}Polyacrylic acid sodium.

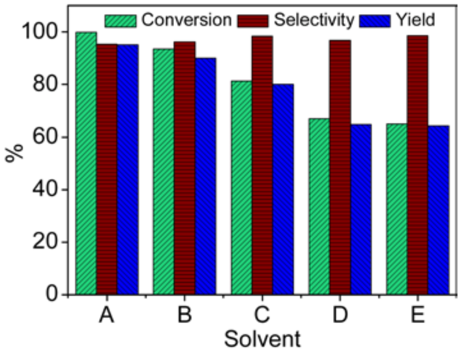

Fig. 3 Effect of different solvents (A) cyclohexane, (B) *tert*-butanol, (C) tetrahydrofuran, (D) ethyl acetate, and (E) dioxane. Reaction conditions: BA (3.0 g), solvent (60 mL), NiZrB/Al_2O_3 (1.0 g, 11 wt % of Ni), K_2CO_3 (5 mol % of BA), 423 K, initial *P* (H_2) = 5 MPa, and reaction time 4 h.

obtained in cyclohexane, probably due to its aprotic and non-polar nature. Thus, cyclohexane was the solvent of choice for hydrogenation of BA.

The effect of reaction temperature on the selectivity for CCA in the presence of K_2CO_3 is shown in Table 3. The selectivity for CCA was nearly 100% with the reaction temperature decreasing from 423 K to 373 K; at the same time, the conversion of BA decreased to 30.5% (entry 1-3), and it can reach 82.7% if prolonging the reaction time to 16 h (entry 4). These results indicated that lower temperature would be benefit for the orientation of aromatic ring facing towards catalyst or decrease the reaction rate towards the carboxyl hydrodeoxygenation product, thus inhibiting the generation of toluene. Finally, 423 K was chosen as the optimal reaction temperature in view of the transformation efficiency.

Figure 4 shows the effect of amount of K_2CO_3 in the hydrogenation of BA. It was found that when the amount of K_2CO_3 decreased from 15 mol % to 1 mol %, the conversion of BA kept over 98.0% and the selectivity for CCA remained over 95.0%, higher than the observation in our previous work both in water (93.6%) and cyclohexane (42.7%) over the NiZrB catalyst.[23] With further decrease of the amount of K_2CO_3 to 0.1 mol %, the selectivity for CCA decreased to 75.8%, which was still higher than that of no additive added (50.3%). Thus, we can conclude that even small amount of K_2CO_3 (1 mol %) is efficient for improving the selectivity for CCA in the hydrogenation of BA in cyclohexane.

Furthermore, the turnover number (molar ratio of transformed BA to Ni atom) of NiZrB/Al_2O_3 was 13.1, much higher than that (3.0) of NiZrB catalyst.[23] We ascribed this to the more well-dispersive Ni active sites in NiZrB/Al_2O_3, as demonstrated by TEM and H_2-chemisorption results. Therefore, the observation of this phase of studies led to a conclusion that the addition of base and γ−Al_2O_3 support exhibited a robust effect in improving the selectivity and activity of NiZrB/Al_2O_3 in the hydrogenation of BA, respectively. It must be noted that the activity of catalyst gradually decreased during the recycle in cyclohexane (Fig. S2 and S3, ESI†), although it was still much better than that in water. We can deduce that the decrease of catalyst activity in cyclohexane should be due to the transformation of the active nickel species from the unstable amorphous alloy to the relatively stable crystalline, as proven by the TEM (Fig. S4, ESI†) and XRD (Fig. S5, ESI†) results. In contrast, the Ni leaching,[27] formation of nickel hydroxide[28,29] and hydrate boehmite[35,36] are believed as the main reasons for the deactivation of the nickel-based catalysts in water. On the other hand, it is necessary to clarify the role of K_2CO_3 in the selectivity improvement of BA hydrogenation.

Table 3 Effect of reaction temperature

Entry	Temperature (K)	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)
1	423	4	99.9	95.3	95.2
2	398	4	82.8	99.5	82.4
3	373	4	30.5	100	30.5
4	373	16	82.7	99.8	82.5

Reaction conditions: BA (3.0 g), cyclohexane (60 mL), NiZrB/Al_2O_3 (1.0 g, 11 wt % of Ni), K_2CO_3 (5 mol % of BA), initial *P* (H_2) = 5 MPa, and reaction time 4 h.

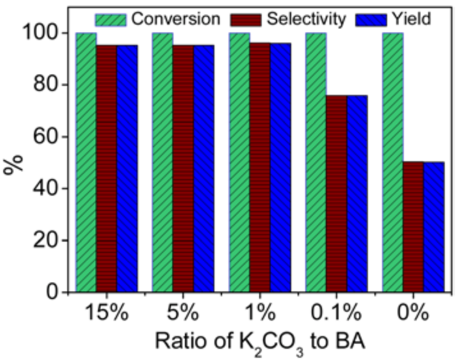

Fig. 4 Effect of amount of K_2CO_3. Reaction conditions: BA (3.0 g), cyclohexane (60 mL), NiZrB/Al_2O_3 (1.0 g, 11 wt % of Ni), base (K_2CO_3), 423 K, initial *P* (H_2) = 5 MPa, and reaction time 4 h.

3.3. Mechanism Insight of the Selectivity Improvement by Bases

FTIR spectroscopy measurements were first carried out to investigate the mechanism of selectivity improvement. As can be seen, the FTIR spectra of NiZrB/Al_2O_3, NiZrB/Al_2O_3–u, and NiZrB/Al_2O_3–u–K_2CO_3 were markedly different (Fig. 5). For the fresh NiZrB/Al_2O_3, the peaks at about 3400 cm^{-1} and 1641 cm^{-1} were assigned to the stretching and deformation vibration absorption of water, and the peaks at about 1397 cm^{-1} and 816-568 cm^{-1} were assigned to absorption of Al–O. For the NiZrB/Al_2O_3–u catalyst, which underwent hydrogenation in the absence of K_2CO_3, some new peaks at 2931 cm^{-1}, 1582 cm^{-1}, 1446 cm^{-1} and 980 cm^{-1} appeared, which can be assigned to the adsorbed CCA on the used catalyst. Interestingly, apart from these new peaks, other new peaks at 3075 cm^{-1}, 1610 cm^{-1}, 1390 cm^{-1} and 709 cm^{-1} appeared in the FTIR spectrum of NiZrB/Al_2O_3–u–K_2CO_3, which was used in the presence of K_2CO_3. These new peaks were similar to the characteristic peaks of potassium benzoate (PB).[37] So, some PB might be *in-situ* generated under the reaction conditions.

To confirm the formation of PB, a comparative experiment was then carried out using excess K_2CO_3 under the same reaction conditions in the absence of catalyst (CE–K_2CO_3). The FTIR spectrum of the precipitation of CE–K_2CO_3 (Fig. 6, curve a) is in consistent with that of pure PB (Fig. 6, curve b),[37] together with the disappearance of the characteristic peaks of BA (Fig. 6, curve

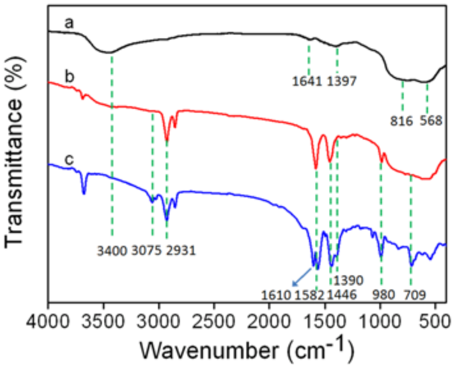

Fig. 5 FTIR spectra of (a) $NiZrB/Al_2O_3$, (b) $NiZrB/Al_2O_3$–u, and (c) $NiZrB/Al_2O_3$–u–K_2CO_3.

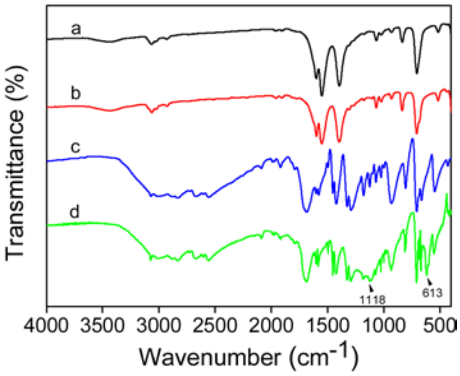

Fig. 6 FTIR spectra of (a) precipitation of CE–K_2CO_3, (b) PB, (c) BA, and (d) precipitation of CE–K_2SO_4.

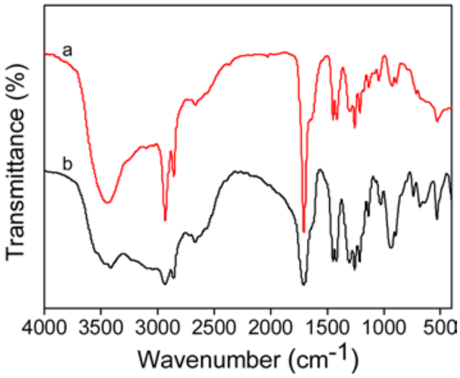

Fig. 7 FTIR spectra of products obtained from hydrogenation of BA in the absent (a) and in the presence of K_2CO_3 (b) in cyclohexane.

c). Thus, PB can be *in-situ* generated from BA and K_2CO_3 under the reaction conditions. In contrast, in a comparative experiment using excess K_2SO_4 instead of K_2CO_3 (CE–K_2SO_4), no PB can be identified from the FTIR spectrum of its precipitation (Fig. 6, curve d). The curve d was believed as a combination of the characteristic peaks of BA and K_2SO_4 (typical at 1118 cm^{-1} and 613 cm^{-1}), proving that PB could not be generated from BA and K_2SO_4.

On the other hand, FTIR spectra of the products prepared in the presence (Fig. 7, curve a) and absence (Fig. 7, curve b) of K_2CO_3 are similar, suggesting that the addition of K_2CO_3 did not affect the purity of product. Further ICP analysis showed that the content of potassium in the obtained product was only 0.025 mol % of CCA, which can be ignored and in agreement with the FTIR results (Fig. 7). Combined with the above results, we can conclude that PB was *in-situ* generated from BA and K_2CO_3 under the reaction conditions, and then adsorbed on the catalyst surface. Then, it will probably tune the acid-base properties of the catalyst and improve the selectivity for CCA.

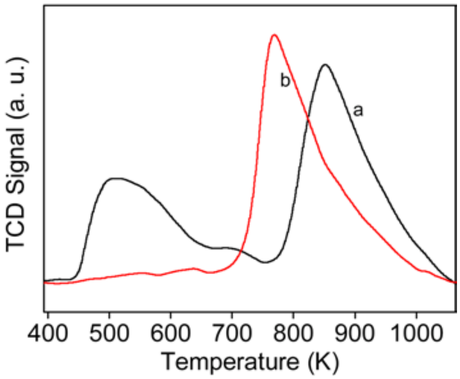

Fig. 8 NH_3-TPD profiles of amorphous alloy catalysts (a) $NiZrB/Al_2O_3$–u and (b) $NiZrB/Al_2O_3$–u–K_2CO_3.

Figure 8 shows the NH_3-TPD profiles of $NiZrB/Al_2O_3$–u and $NiZrB/Al_2O_3$–u–K_2CO_3. For $NiZrB/Al_2O_3$–u (Fig. 8, curve a), there were two peaks at about 510 K and 850 K; whereas the peak at 510 K disappeared and the peak at 850 K moved to a lower temperature (770 K) when K_2CO_3 was used during the hydrogenation process (Fig. 8, curve b), so that $NiZrB/Al_2O_3$–u–K_2CO_3 has nearly no weakly acidic sites and lower acidity of strong acidic sites compared with $NiZrB/Al_2O_3$–u. In combination with the FTIR results, we ascribed this to the neutralization of acidic sites by the *in-situ* generated PB, which then accounted for the high selectivity for CCA in cyclohexane. Although there have been some reports on the selectivity improvement by the modulation of the acid-base properties of the catalysts during their preparation,[38–40] it might be the first observation that the selectivity improvement can be achieved by tuning the catalyst *via* the *in-situ* generated intermediate during the reaction.

It is really interesting that high selectivity for CCA was obtained in cyclohexane, a non-polar solvent, by the addition of base in this reaction system, in comparison with our prvious study.[23] Indeed, the orientation of BA molecule is irregular on the surface of $NiZrB/Al_2O_3$ in cyclohexane,[23,24] as shown in Fig. 9. In the case of no base added, both benzene ring and carbonyl of BA will be adsorbed on the surface of catalyst. Thus, BA can be hydrodeoxygenated to form toluene, as proven by GC-MS (Fig. S6, ESI†), in the presence of twin oxygen vacancies,[41,42] resulting in a low selectivity for CCA (Fig. 9). On the contrary, if some base like K_2CO_3 was added during the reaction, PB will be *in-situ* generated from BA and K_2CO_3, and loaded on the surface of γ–Al_2O_3. It can neutralize some acidic sites on the catalyst surface, and then inhibiting the hydrodeoxygenation of carbonyl[38–40] and resulting in a high selectivity for CCA (Fig. 9). It can be further proved by the poor selectivity improvement performace of K_2SO_4 (Table 2, entry 15), which can not generate PB with BA, as demonstrated by the previous CE–K_2SO_4 comparative experiment. Thus, the formation of PB and its neutralization of the acidic sites on the catalyst surface should play an important role on the CCA selectivity improvement in the hydrogenation of BA.

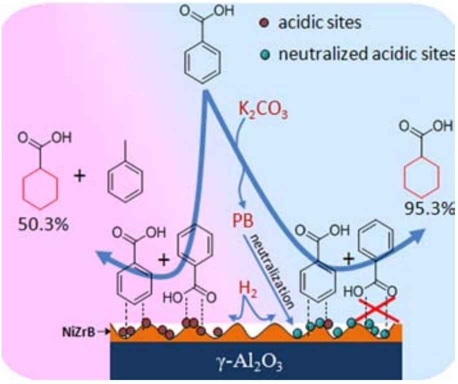

Fig. 9 Proposed mechanism for the hydrogenation of BA with or without K_2CO_3.

4. Conclusions

In summary, we have first shown appreciable positive effect of bases on the selectivity improvement of CCA in the selective hydrogenation of BA over a NiZrB/Al_2O_3 catalyst. The presence of even very small amount of K_2CO_3 in the hydrogenation of BA resulted in a substantial increase in the selectivity for CCA. PB was proven to be *in-situ* generated from BA and K_2CO_3 under the reaction conditions, and then adsorbed on the catalyst surface. Thus, it can neutralize of acidic sites on the catalyst surface, inhibiting the hydrodeoxygenation of carbonyl and resulting in a high selectivity for CCA. The selective hydrogenation of BA exhibited a better solvent profile by the base addition over NiZrB/Al_2O_3 catalyst. These observations will also be helpful for selectivity improvement in other reactions.

Acknowledgements

Financial support by the National Natural Science Foundation of China (21376060), the Natural Science Foundation of Hebei Province (B2014201024), and the Youth Foundation of Hebei Educational Committee (QN2014069) are gratefully acknowledged.

Notes and references

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† Electronic supplementary information (ESI) available: FTIR analysis of catalysts, time-conversion plot, data of recycle runs, characterization of used catalyst (TEM and XRD) and GC-MS analysis of products.

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