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Significant effect of base on the improvement of selectivity in the hydrogenation of benzoic acid over NiZrB amorphous alloy supported on γ -Al₂O₃†

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This study presents a facile way to improve the selectivity for cyclohexanecarboxylic acid by adding a base in the hydrogenation of benzoic acid over a non-noble metal NiZrB amorphous alloy supported on γ -Al₂O₃. It is found that alkali metal carbonates exhibit 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 a very small amount of K₂CO₃ (1 mol% benzoic acid) was efficient for improving the selectivity for cyclohexanecarboxylic acid. In addition, a lower reaction temperature was beneficial to the improvement of selectivity. Based on the results of temperature programmed desorption of NH₃ and inductively coupled plasma analysis, the improvement of selectivity in the presence of a base was attributed to the neutralization of the acidic sites on the surface of the catalyst by the *in situ* generated potassium benzoate, inhibiting the hydrodeoxygenation of carbonyl and resulting in a high selectivity for cyclohexanecarboxylic acid.

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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 chemical and pharmaceutical industry, due to it being environmentally benign, having readily available suitable feedstocks and being the most straightforward approach.^{5–10} In general, aromatic ring hydrogenation usually requires harsh reaction conditions, increasing the potential for the hydrogenation of other reducible moieties, which 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 heteroaromatic 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 a suitable support to apply the interaction between the catalyst and the support, which improves the selectivity for the hydrogenation of the aromatic ring. For example, 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 nitride¹⁹ or nitrogen-functionalized ordered mesoporous carbon.^{20,21} It is worth noting that a simple way to enhance the selectivity for cyclohexanone in the hydrogenation of phenol has been established by Han and his coworkers.²² A Lewis acid (AlCl₃, ZnCl₂ or InCl₃) was added as a dual-functional additive to increase the selectivity and activity of the 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 cyclohexanecarboxylic acid (CCA), which is an important organic intermediate for the synthesis of praziquantel and ansatrienin, has been studied in previous reports.^{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 leached

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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 when we selected aprotic solvents in the selective hydrogenation of BA to CCA, the selectivity for CCA was markedly lowered due to the decrease in solvent polarity.²³

In a continuing attempt to achieve a higher selectivity using a 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 a NiZrB amorphous alloy supported on γ -Al₂O₃ [NiZrB/Al₂O₃] just by adding small amounts of bases in cyclohexane. To the best of our knowledge, this might be the first report on selectivity improvement by tuning the catalyst *via* the *in situ* generated intermediate during the reaction. Therefore, a possible mechanism was proposed based on the necessary characterization. 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 of analytical reagent grade and used without further purification. NiZrB/Al₂O₃ was prepared by an impregnation–reduction method. The support γ -Al₂O₃ (2.7 g) was first heated at 773 K for 4 h and then impregnated with a mixed solution of 1.234 g of NiCl₂·6H₂O, 0.055 g of Zr(NO₃)₄·5H₂O (molar ratio Ni:Zr = 40:1), 0.5 g of poly(ethylene glycol) (average molecular weight: 800 g mol⁻¹, PEG800) and 2 mL of 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 and reduced by adding 20 mL of 1.0 M aqueous KBH₄ 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, an unsupported NiZrB amorphous alloy modified with PEG(800) was prepared by a chemical reduction method as described previously.²³

2.2. Catalyst characterization

The Brunauer–Emmett–Teller (BET) surface area was estimated using a Micromeritics Tristar II 3020 surface area and pore analyzer. H₂-chemisorption and temperature programmed desorption of NH₃ (NH₃-TPD) were performed 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 using a FEI Tecnai G2 F20 microscope. Fourier transform infrared spectroscopy (FTIR) was carried out using a Bruker Vertex 70 spectrometer. Inductively coupled plasma analysis (ICP) was performed using 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 H₂ to 3.0 MPa several times by evacuation to displace residual air, and then pressured with H₂ to 5.0 MPa and heated to the requisite temperature. Upon reaching the required temperature, the reaction was performed by stirring the reaction mixture vigorously. When the reaction was complete, the reaction mixture was 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/Al₂O₃-u-base.” When a base was not added, the used catalyst was denoted as “NiZrB/Al₂O₃-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 excess additive was used – half of the amount of BA. For a typical run: BA (3.0 g), cyclohexane (60 mL), and K₂CO₃ or K₂SO₄ (50 mol% BA) were allowed to react at 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-K₂CO₃ and CE-K₂SO₄, respectively.

3. Results and discussion

3.1. Catalyst characterization

The physical properties of NiZrB/Al₂O₃, NiZrB and γ -Al₂O₃ are summarized in Table 1. From the ICP analysis, it was found that the contents of Ni and Zr in both NiZrB/Al₂O₃ and NiZrB were about 40:1, which was almost identical to the feed ratio. The Ni loading of NiZrB/Al₂O₃ was only 11.0 wt%, much lower than that of NiZrB. Thus, it is reasonable that NiZrB/Al₂O₃ has a lower H₂-chemisorption value than NiZrB. In fact, it has a higher H₂-chemisorption value for each Ni atom due to the dispersive effect of γ -Al₂O₃. The BET surface area, pore volume and pore size of NiZrB/Al₂O₃ markedly decreased compared with those of the pure γ -Al₂O₃ support, indicating that some NiZrB amorphous alloy particles occupied the surface and the pores of the γ -Al₂O₃ support due to its porous nature.³⁰

XRD analysis of the prepared NiZrB/Al₂O₃ catalyst showed three characteristic peaks, which were all attributed to γ -Al₂O₃ (Fig. 1); in contrast, no peak related to the amorphous alloy was detected in this catalyst, probably because the diffraction peak of NiZrB in NiZrB/Al₂O₃ was obscured by the peaks of γ -Al₂O₃ at about 45 °C.^{30–33}

Table 1 Structural properties of the amorphous alloy catalysts and γ -Al₂O₃

| Catalyst | Composition ^a (atomic ratio) | Ni loading (wt%) | H ₂ -chemisorption (cm ³ g ⁻¹) | Surface area (m ² g ⁻¹) | Pore volume (cm ³ g ⁻¹) | Pore size (nm) |
|--|--|---------------------|---|---|---|-------------------|
| NiZrB/Al ₂ O 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 ₂ O 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 ref. 23.

The TEM image of NiZrB/Al₂O₃ is shown in Fig. 2a. It was obvious that the NiZrB amorphous alloy was well dispersed on the γ -Al₂O₃ support with the particle size in the range of 7.0–21.0 nm (Fig. 2b). The mean particle size of the NiZrB amorphous alloy was 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/Al₂O₃ can be found from the TEM results. 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 the 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 to CCA over NiZrB/Al₂O₃ 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 the Lewis basic C=O group and Lewis acid inhibited further the hydrogenation of cyclohexanone in the hydrogenation of phenol.²² Thus, for our reaction system, the carboxyl group of BA and the Lewis acid might form a

complex, protecting the carboxyl group from hydrogenation and then improving the selectivity for CCA. Unfortunately, a terribly low conversion (1.1%) was obtained when AlCl₃ was added in cyclohexane, although 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 a remarkable effect on the selectivity for CCA. In the case of alkali metal carbonates (entries 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 (entries 8–14), the selectivities for CCA were also over 80% except for triethylamine, which was only 56.7%, just a little higher than that obtained when no additive was used. In contrast, in the case of a neutral salt, such as K₂SO₄, 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/Al₂O₃.

To further study the effect of base on the selectivity for CCA in the hydrogenation of BA, K₂CO₃ was chosen in

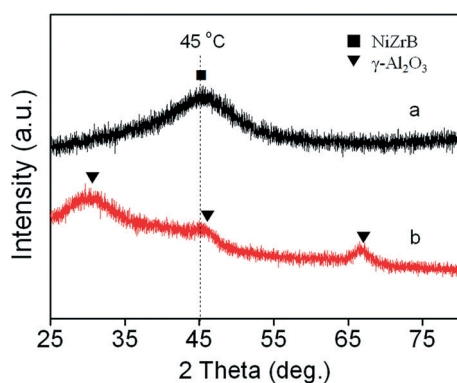


Fig. 1 XRD patterns of amorphous alloy catalysts (a) NiZrB and (b) NiZrB/Al₂O₃.

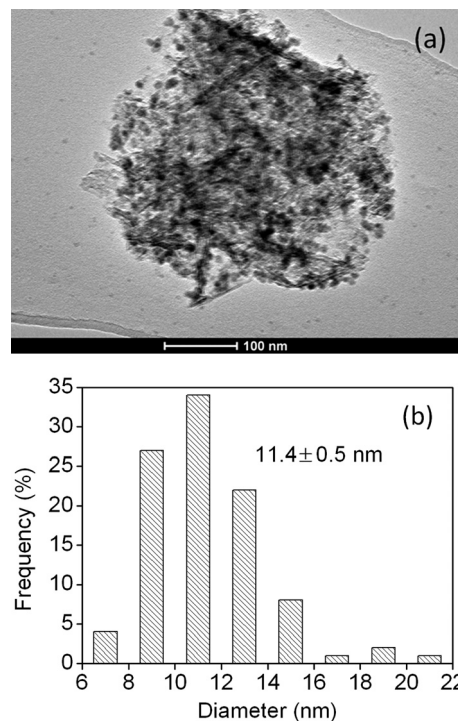


Fig. 2 TEM image (a) and size distribution (b) of NiZrB/Al₂O₃.

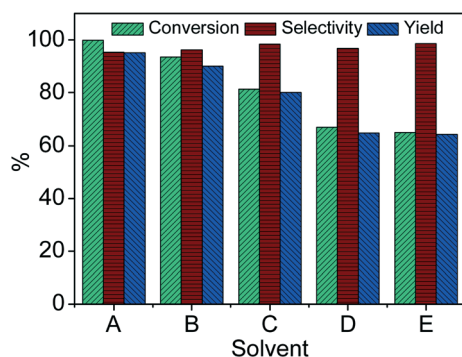
Table 2 Effect of additives in the selective hydrogenation of BA over NiZrB/Al₂O₃

| 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 ₂ CO ₃ | 99.9 | 93.5 | 93.4 |
| 5 | Na ₂ CO ₃ | 99.9 | 93.8 | 93.7 |
| 6 | K ₂ CO ₃ | 99.9 | 95.3 | 95.2 |
| 7 | Cs ₂ CO 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 ₆ H ₅ COOK | 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 ₂ H ₅) ₃ | 99.9 | 56.7 | 56.6 |
| 15 | K ₂ SO ₄ | 99.9 | 47.7 | 47.7 |

Reaction conditions: BA (3.0 g), cyclohexane (60 mL), NiZrB/Al₂O₃ (1.0 g, 11.0 wt% Ni), additive (5 mol% BA), 423 K, initial $P(\text{H}_2) = 5$ MPa, and reaction time 4 h. ^a Water as the solvent. ^b Polyacrylic acid sodium.

consideration of its catalytic efficiency and cost. The effects of solvent, reaction temperature and amount of K₂CO₃ 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 K₂CO₃, no matter what kind of solvent was used, the selectivities for CCA were higher than 95%. Thus, the catalytic system involving both base and NiZrB/Al₂O₃ displays a good solvent profile for selectivity. On the other hand, the best conversion of BA was obtained in cyclohexane, probably due to its aprotic and non-polar nature. Thus, cyclohexane was the solvent of choice for the hydrogenation of BA.

The effect of reaction temperature on the selectivity for CCA in the presence of K₂CO₃ 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% (entries 1–3), and it can reach 82.7% if the reaction time is prolonged to 16 h (entry 4).

**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/Al₂O₃ (1.0 g, 11 wt% Ni), K₂CO₃ (5 mol% BA), 423 K, initial $P(\text{H}_2) = 5$ MPa, and reaction time 4 h.**Table 3** Effect of reaction temperature

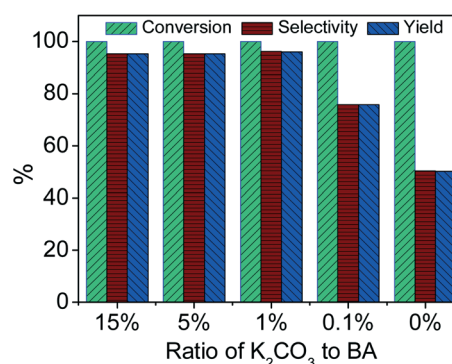
| Entry | Temperature (K) | Time (h) | Conversion (%) | Selectivity (%) | Yield (%) |
|-------|-----------------|----------|----------------|-----------------|-----------|
| 1 | 423 | 4 | 99.9 | 95.3 | 95.2 |
| 2 | 398 | 4 | 82.8 | 99.5 | 82.4 |
| 3 | 373 | 4 | 30.5 | 100 | 30.5 |
| 4 | 373 | 16 | 82.7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

Reaction conditions: BA (3.0 g), cyclohexane (60 mL), NiZrB/Al₂O₃ (1.0 g, 11 wt% Ni), K₂CO₃ (5 mol% BA), initial $P(\text{H}_2) = 5$ MPa, and reaction time 4 h.

These results indicated that a lower temperature would benefit the orientation of the aromatic ring facing towards the 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.

Fig. 4 shows the effect of the amount of K₂CO₃ in the hydrogenation of BA. It was found that when the amount of K₂CO₃ decreased from 15 mol% to 1 mol%, the conversion of BA remained over 98.0% and the selectivity for CCA remained over 95.0%, higher than that observed in our previous work both in water (93.6%) and cyclohexane (42.7%) over the NiZrB catalyst.²³ With a further decrease in the amount of K₂CO₃ to 0.1 mol%, the selectivity for CCA decreased to 75.8%, which was still higher than that observed when no additive was added (50.3%). Thus, we can conclude that even a small amount of K₂CO₃ (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/Al₂O₃ was 13.1, much higher than that of the NiZrB catalyst (3.0).²³ We ascribed this to the more well-dispersed Ni active sites in NiZrB/Al₂O₃, as demonstrated by the TEM and H₂-chemisorption results. Therefore, the observation of this phase of study led to a conclusion that the addition of base and the γ -Al₂O₃ support exhibited a robust effect on improving the selectivity and activity of NiZrB/Al₂O₃ in the hydrogenation of BA, respectively. It must

**Fig. 4** Effect of the amount of K₂CO₃. Reaction conditions: BA (3.0 g), cyclohexane (60 mL), NiZrB/Al₂O₃ (1.0 g, 11 wt% Ni), base (K₂CO₃), 423 K, initial $P(\text{H}_2) = 5$ MPa, and reaction time 4 h.

be noted that the activity of the 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, Ni leaching,²⁷ the formation of nickel hydroxide^{28,29} and hydrate boehmite^{35,36} are believed to be 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 improvement of selectivity of BA hydrogenation.

3.3. Mechanism insight into 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 $816\text{--}568\text{ cm}^{-1}$ were assigned to the 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 the catalyst (CE- K_2CO_3). The FTIR spectrum of the precipitate of CE- K_2CO_3 (Fig. 6, curve a) is consistent with that of pure PB (Fig. 6,

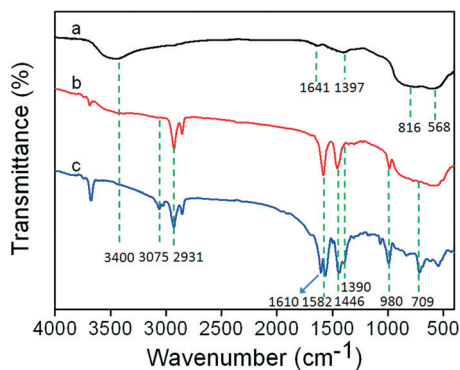


Fig. 5 FTIR spectra of (a) $NiZrB/Al_2O_3$, (b) $NiZrB/Al_2O_3-u$, and (c) $NiZrB/Al_2O_3-u-K_2CO_3$.

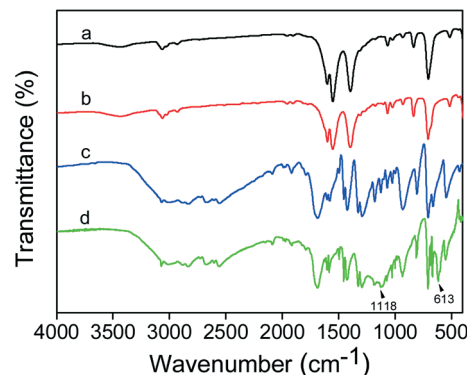


Fig. 6 FTIR spectra of (a) the precipitate of CE- K_2CO_3 , (b) PB, (c) BA, and (d) precipitate of CE- K_2SO_4 .

curve b),³⁷ together with the disappearance of the characteristic peaks of BA (Fig. 6, curve 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 precipitate (Fig. 6, curve d). Curve d was believed to be 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, the FTIR spectra of the products prepared in the absence (Fig. 7, curve a) and presence (Fig. 7, curve b) of K_2CO_3 are similar, suggesting that the addition of K_2CO_3 did not affect the purity of the 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 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

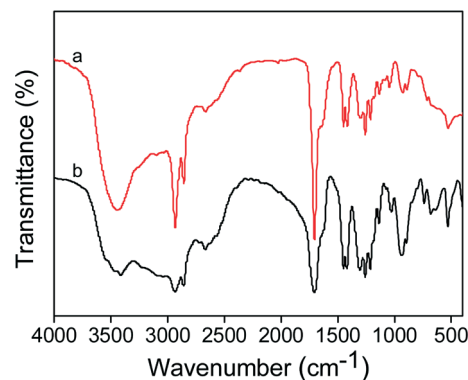


Fig. 7 FTIR spectra of the products obtained from the hydrogenation of BA in the absence (a) and in the presence of K_2CO_3 (b) in cyclohexane.

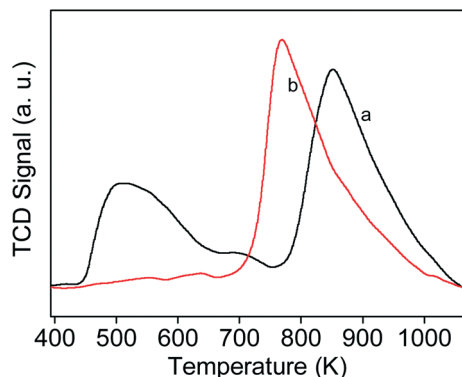


Fig. 8 NH_3 -TPD profiles of amorphous alloy catalysts (a) $\text{NiZrB}/\text{Al}_2\text{O}_3\text{-u}$ and (b) $\text{NiZrB}/\text{Al}_2\text{O}_3\text{-u-K}_2\text{CO}_3$.

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 $\text{NiZrB}/\text{Al}_2\text{O}_3\text{-u-K}_2\text{CO}_3$ has nearly no weakly acidic sites and has a lower acidity of strong acidic sites compared with $\text{NiZrB}/\text{Al}_2\text{O}_3\text{-u}$. In combination with the FTIR results, we ascribed this to the neutralization of the 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 selectivity improvement can be achieved by tuning the catalyst *via* the *in situ* generated intermediate during the reaction.

It is really interesting that a 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 previous study.²³ Indeed, the orientation of the BA molecule is irregular on the surface of $\text{NiZrB}/\text{Al}_2\text{O}_3$ in cyclohexane,^{23,24} as shown in Fig. 9. In the case when no base is added, both the benzene ring and carbonyl of BA will be adsorbed on the surface of the 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 the base like K_2CO_3

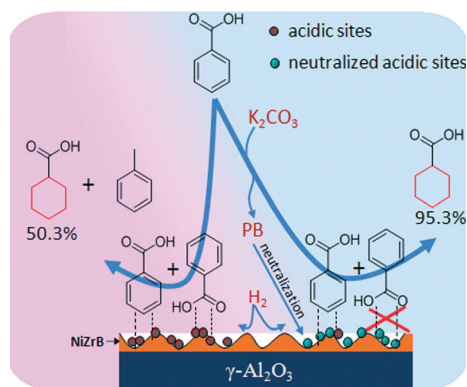


Fig. 9 Proposed mechanism for the hydrogenation of BA with or without K_2CO_3 .

was added during the reaction, PB will be *in situ* generated from BA and K_2CO_3 , and loaded on the surface of $\gamma\text{-Al}_2\text{O}_3$. It can neutralize some acidic sites on the catalyst surface, 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 performance of K_2SO_4 (Table 2, entry 15), which cannot generate PB with BA, as demonstrated by the previous $\text{CE-K}_2\text{SO}_4$ comparative experiment. Thus, the formation of PB and its neutralization of the acidic sites on the catalyst surface should play an important role in the CCA selectivity improvement in the hydrogenation of BA.

4. Conclusions

In summary, we have first shown the appreciable positive effect of bases on the improvement of selectivity for CCA in the selective hydrogenation of BA over the $\text{NiZrB}/\text{Al}_2\text{O}_3$ catalyst. The presence of even a 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 the 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 base addition over the $\text{NiZrB}/\text{Al}_2\text{O}_3$ catalyst. These observations will also be helpful for the improvement of selectivity in other reactions.

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