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Catalytic Behaviors of Amorphous Co-B Catalysts in Hydroformylation of 1-Octene

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Abstract An amorphous Co-B catalyst was prepared by chemical reduction method and characterized by isothermal N_2 adsorption/desorption, XRD, ICP-AES and HR-TEM. The catalytic activity of the Co-B catalyst in the hydroformylation of 1-octene was evaluated in a 100 mL stainless autoclave. Fresh amorphous Co-B catalyst showed a relatively high activity in the hydroformylation of 1-octene. The thermal stability of fresh Co-B catalyst was also examined. When fresh Co-B catalyst was thermally treated in N_2 or H_2 atmosphere at 200–500 °C for 2 h, the specific surface area and the catalytic activity of the Co-B catalyst decreased. When Co-B was supported on SiO_2, the activity of the catalyst increased obviously. Compared with conventional supported Co/SiO_2 catalyst, Co-B/SiO_2 showed much higher activity than Co/SiO_2. The influences of solvents and reaction conditions on the catalytic activity of the amorphous Co-B catalyst were also studied. The recycle test of the amorphous Co-B catalyst was done.

Keywords Hydroformylation · 1-Octene · Nonyl aldehyde · Amorphous Co-B

1 Introduction

The hydroformylation of olefins has been an important industrial catalytic process for producing aldehydes/alcohols and it constitutes the most important homogeneous catalytic process in industry today [1, 2]. Co-based and Rh-based homogeneous catalysts have been used as effective catalysts in the hydroformylation [3–6]. Homogeneous catalysts and homogeneous processes have their own advantages, such as uniform active sites, easy adjusting of catalytic properties by ligands, mild reaction conditions, high catalytic activity and selectivity and less influence of mass diffusion. However, it is not easy to separate homogeneous catalysts from products and to recycle the catalysts. On the other hand, heterogeneous catalysts are easy for the separation of catalysts from products and reactants. Up to now, a great of efforts have been made to improve the catalyst-product separation in homogeneous catalytic processes by combining the advantages of homogeneous and heterogeneous catalysis, such as water soluble catalysts [7, 8], biphasic catalysis [9], immobilizing complex catalysts [10], and also solid state catalysts [11].

Recently, several Co or Rh metal catalysts supported on inorganic supports have also been investigated for the hydroformylation of olefins [12–18]. It has been reported that Co/activated carbon catalysts showed good catalytic performance in hydroformylation of 1-hexene in alcoholic solvents [13]. Among Rh/AC, Pd/AC, Ru/AC and Pt/AC catalysts, Rh/AC catalyst exhibited the best performance in the low-pressure hydroformylation of 1-hexene. Zhang et al. [15] reported that a Co/CNTs catalyst, which was prepared by metal organic chemical vapor deposition technique, showed high activity and region selectivity in the hydroformylation of 1-octene [17]. Although some progress on the research works in the application of solid catalysts to the

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hydroformylation of olefins has been achieved, the activity and stability of the supported Co catalysts are still not satisfactory and the further efforts are necessary.

On the other hand, metal-metalloid amorphous catalysts like Ni-B, Cu-B and Co-B, etc., which possess the structures with long-range disorder and short-range order, have recently attracted much attention due to their superior activity and selectivity in some catalytic hydrogenation processes [19–22]. It has been reported that NiB and CoB amorphous catalysts exhibited high activity and selective in the selective hydrogenation of citral. Liaw et al. [19] revealed that supported NiB-SiO_2 also showed high activity for citral hydrogenation at low temperature [20].

However, there are still few detailed reports about the application of metal-metalloid amorphous catalysts to the hydroformylation of olefins so far. Employing this kind catalyst in the hydroformylation reaction could create a new application of the metal-metalloid amorphous catalysts. Perhaps, the metal-metalloid amorphous catalysts could be an alternative of conventional supported catalysts in the heterogenizing of homogeneous hydroformylation processes. Considering cobalt being an active component for the hydroformylation of olefins, we have recently employed an amorphous Co-B catalyst in the hydroformylation of 1-octene. Our research objective is to investigate the behaviors of the Co-B catalyst in the hydroformylation of olefins and explore the possibility of the Co-B catalyst in the recycle use in olefin hydroformylation, and then to further develop a highly active and stable Co-B catalyst for the hydroformylation of olefins.

2 Experimental

2.1 Preparation of Catalysts

An amorphous Co-B sample was prepared by chemical reduction method, using $CoCl_2$ and $NaBH_4$ as starting materials, according to the procedure described in literature [23]. A typical preparation procedure is as follows. 100 mL aqueous solution of $NaBH_4$ and NaOH mixture (2.0 M $NaBH_4$ and 2.5 M NaOH) was added dropwise into a well-stirred aqueous solution of $CoCl_2$ (0.5 mol L^{-1}, 100 mL) in an ice-water bath. Obtained Co-B black powder was repeatedly washed with deionized water until pH of mother liquor was 7, and then washed with ethanol and stored in ethanol. This Co-B sample is denoted as fresh Co-B. For testing the thermal stability of Co-B sample in inert gas atmosphere or H_2 gas atmosphere, as-prepared fresh Co-B was further treated in N_2 or H_2 gas at different temperatures for 2 h, the obtained Co-B samples are denoted as Co-B-N_2-T or Co-B-H_2-T, and here T represents the treating temperature.

The Co-B/SiO_2 catalyst was also prepared by the same method using impregnated Co/SiO_2 and $NaBH_4$ [20]. Firstly, 2 g SiO_2 powder ($S_{BET} = 300$, obtained from Tianjin Chemical Institute) was impregnated in a $CoCl_2$ aqueous solution (10 mL, 0.5 M $CoCl_2$) for 12 h, and then the water was removed by evaporation. The obtained powder was further dried at 110 °C for 12 h and calcined in air at 200 °C for 3 h, and then reduced at 0 °C (under ice-water bath) by an aqueous solution of $NaBH_4$ and NaOH mixture (20 mL solution, 2.0 M $NaBH_4$ and 2.5 M NaOH). The other washing procedures were same as the preparation of pure Co-B. For comparison, supported Co/SiO_2 catalyst was also prepared by conventional impregnation method (calcined at 200 °C in air and reduced at 500 °C by H_2 gas). $Co_2(CO)_8$ was purchased from Strem Company and used a homogeneous catalyst for comparison. Co metal powder sample was prepared by decomposing cobalt acetate at 500 °C in air atmosphere for 3 h and then reducing at 500 °C in H_2 gas for 3 h.

2.2 Characterization of Catalysts

The specific surface areas (S_{BET}) of the Co-B and Co-B/SiO_2 catalysts were measured by N_2 adsorption/desorption isotherm with the BET method on a Micromeritics ASAP 2010C analyzer. The phase structures of the catalysts were determined by X-ray diffraction (XRD) with a Bruker D8 advance X-ray powder diffractometer with Cu $K\alpha$ ($\lambda = 0.15406$ nm).

The bulk compositions of the Co-B catalysts were measured by Inductive coupling plasma-atomic emission spectroscopy (ICP-AES) with a IRIS Intrepid II XSP ICP-AES of Thermo Electron Corporation (the work condition of apparatus: RF Power: 1150W, Nebulizer Flow: 26.0 PSI, Auxiliary gas: 1.0 LPM).

The surface morphologies, microstructure and the particle size distribution of the Co-B catalysts were analyzed by high-resolution transmission electron microscopy (HR-TEM, JEM-2010 of JEOL). The accelerating voltage of the HR-TEM was 120 kV. X-ray microanalysis (EDS) was conducted to analyze elements. The selected-area electron diffraction (SAED) was done to confirming the amorphous structure of the samples.

2.3 Hydroformylation

The olefin hydroformylations were carried out in a stainless steel autoclave of 100 mL with a magnetic stirrer. After Co-B catalyst, solvent and 1-octene were placed into the autoclave, the reactor was sealed and placed in water-ice bath. The air in the reactor was replaced three times with 3.0 MPa syngas and then the pressure in the reactor was released to 0.1 MPa. Then the reactor was placed in the electric furnace, heated to the reaction temperature, and then pressurized with syngas to desirable pressures. Then, the stirrer was turned on to start the reaction. After the hydroformylation reaction finished, the autoclave was removed from the electric furnace, the reactor was cooled to room temperature and then placed in a water-ice bath. After being depressurized, the liquid and the solid catalyst were separated by centrifugation and filtration. The liquid phase mixture were analyzed qualitatively by GC-Mass (GCMS-G1530A, HP Corporation) and analyzed quantitatively with a gas chromatography (HP 4890D, capillary column HP-5 30 m × 0.25 mm; 60–200 °C; 10 °C min^{-1}; FID detector).

3 Results and Discussion

3.1 Characterization of Catalysts

Table 1 lists the S_{BET} and the bulk composition of the fresh and thermal-treated Co-B catalysts. The specific surface area of fresh Co-B was 52 $m^2\ g^{-1}$. However, when fresh Co-B was treated in N_2 at 200–500 °C or in H_2 at 300 °C, the S_{BET} of Co-B samples sharply decreased (Table 1). It is clear that the thermal treatment had a great influence on the specific surface area of the amorphous Co-B. Co-B/SiO_2 catalyst showed high specific surface area (327 $m^2\ g^{-1}$). On the other hand, for the composition of fresh Co-B and thermal-treated Co-B samples, ICP analysis showed that the bulk ratios of Co/B were in the range of 1.94–2.08 (atom ratio), indicating no great difference in the bulk ratio of Co/B between fresh Co-B and thermal-treated Co-B samples.

The typical amorphous structure of fresh Co-B sample prepared in present study was confirmed by XRD characterization, as shown in Fig. 1a. One broad peak around $2\theta \approx 45°$ was obtained from fresh Co-B sample, indicating the formation of amorphous Co-B [24]. Furthermore, from TEM (Fig. 2a), the pattern of SAED of fresh Co-B showed only diffuse Debye rings (a series of successive diffraction rings) rather than distinct dots, as shown in Fig. 2a (inserted), also confirming the amorphous nature of Co-B sample.

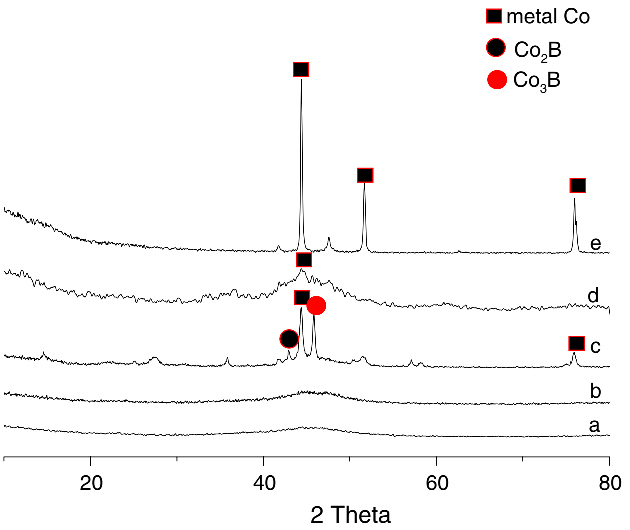

Fig. 1 XRD patterns of fresh and thermal-treated Co-B samples. *a* Fresh Co-B, *b* Co-B-N_2-300, *c* Co-B-N_2-500, *d* Co-B-H_2-300, *e* metal Co

The thermal stability of prepared Co-B was examined by treating fresh Co-B sample either in N_2 or H_2 atmosphere at elevated temperatures. As it can be seen from Fig. 1b, XRD pattern of the Co-B sample still exhibited the amorphous character after treated at 300 °C in flowing N_2 gas for 2 h, indicating that Co-B amorphous structure was stable in N_2 atmosphere below 300 °C. The pattern of SAED of Co-B-N_2-300 (Fig. 2b, inserted) also showed only diffuse Debye rings, further confirming it being amorphous structure. When the fresh Co-B was treated at 300 °C in flowing H_2 gas for 2 h, the structure of Co-B-N_2-

Table 1 Specific surface areas and bulk compositions of Co-B catalysts

No.	Catalyst	S_{BET} ($m^2\ g^{-1}$)	Bulk composition (atom %)[a]		Co/B[a] (atomic ratio)	Average particle size of Co-B or Co (nm)
			Co	B		
1	Fresh Co-B	52	67.5	32.5	2.08	41[b]
2	Co-B-N_2-200	31	67.1	32.9	2.04	–
3	Co-B-N_2-300	20	66.0	34.0	1.94	44[b]
4	Co-B-N_2-500	2	–	–	–	–
5	Co-B-H_2-300	11	67.3	32.7	2.06	–
6	Co-B/SiO_2	327	59.2	40.8	1.45	16[b]
7	Co/SiO_2	250	–	–	–	31[c]

[a] Analyzed by ICP

[b] Analyzed by TEM

[c] Calculated from XRD

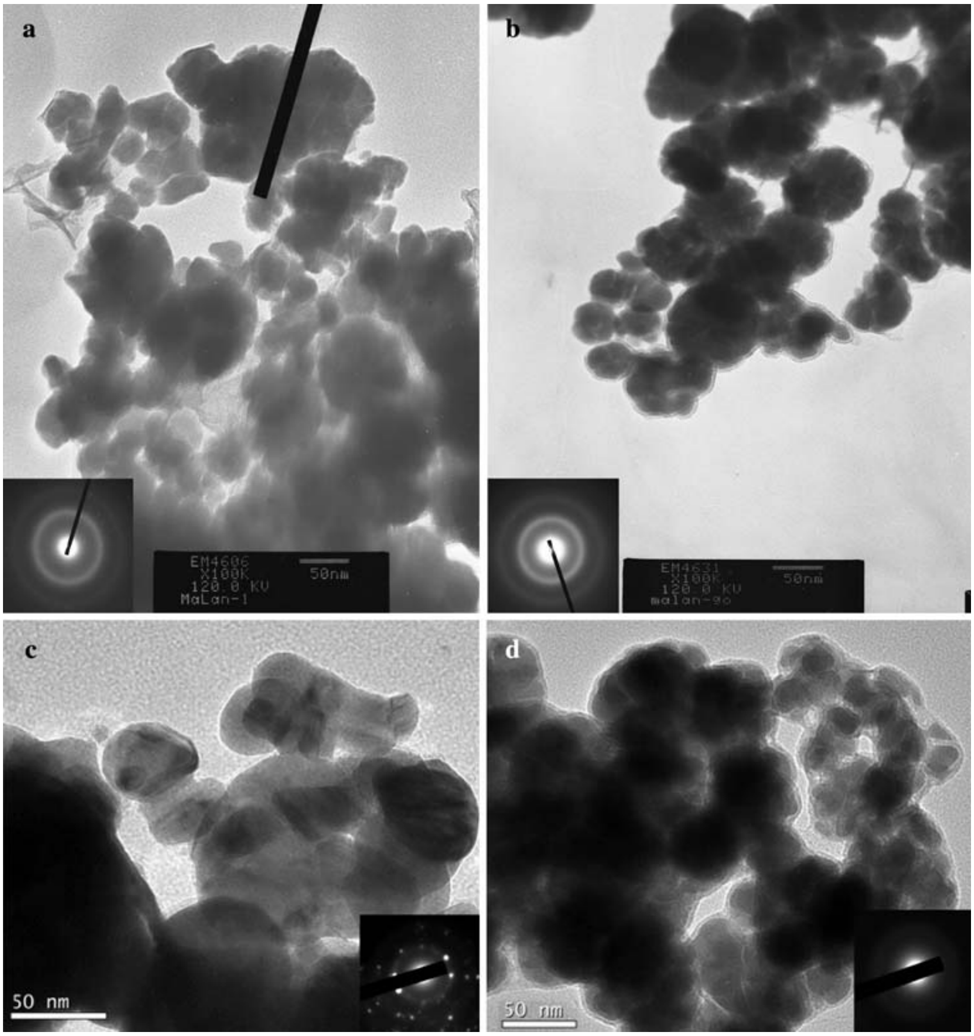

Fig. 2 TEM images and typical SAED patterns (*inserted*) of Co-B samples. **a** Fresh Co-B; **b** Co-B-N_2-300; **c** Co-B-N2-500; **d** Co-B-H2-300

300 was basically amorphous, and only a very weak diffraction peak at around $2\theta \approx 45°$ (Fig. 1d), which could be assigned to Co metal crystalline phase (Co111), was observed. This indicates that a small quantity of the sample was reduced and crystallized after being treated at 300 °C in H_2 for 2 h.

With the increase of the treating temperature of fresh Co-B to 500 °C in N_2 gas, the diffraction peaks of metal Co phase (Co111, Co200 and Co220) became clearer and sharper, and the diffraction peaks assigned to CoB crystalline phase (Co_2B and Co_3B) were also detected (Fig. 1c). For comparison, XRD profile of Co metal powder, which was obtained by decomposing $Co(Ac)_2 \cdot 4H_2O$ at 500 °C in air atmosphere and followed treating in a H_2 atmosphere at 500 °C, is also presented in Fig. 1e.

The microstructures of fresh Co-B, Co-B-N_2-300, Co-B-N_2-500 and Co-B-H_2-300 samples were analyzed by HR-TEM, as shown in Fig. 2. As it can be seen from the images of TEM, fresh Co-B sample comprised of approximately sphere-shaped particles, and the self-aggregation of particles in this sample existed. A wide distribution of particle size of fresh Co-B, ranged approximately from 30 to 60 nm, could be observed from TEM image. In the case of Co-B-N_2-300 sample, the self-aggregation of particles (Fig. 2b) was more serious than in fresh Co-B. However, no great change in the amorphous structure was observed for Co-B-N_2-300 sample, compared with fresh Co-B sample. This was confirmed by the SAED pattern (Fig. 2b, inserted) and XRD profile (Fig. 1b) of Co-B-N_2-300. The TEM image of Co-B-N_2-500 sample showed that it has crystallized and aggregated seriously after being treated in flow N_2 at 500 °C (Fig. 2c), and the SAED pattern (Fig. 2c, inserted), which showed bright distinct dots, confirmed the crystallization structure of Co-B-N_2-500. For Co-B-H_2-300, which was treated in flow H_2 at 300 °C, TEM characterization (Fig. 2d) showed that the self-aggregation was more serious than Co-B-N_2-300. However, the amorphous state of Co-B-H_2-300 was still kept, and this was confirmed by SAED (Fig. 2d, inserted). For Co-B/SiO_2 sample, the

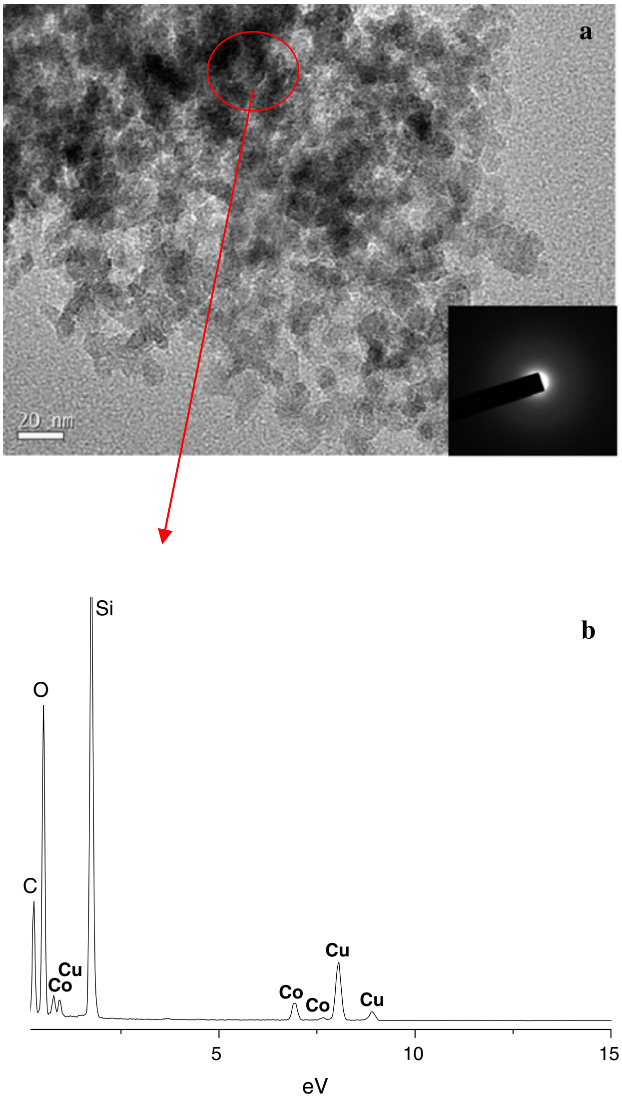

Fig. 3 TEM image (**a**), EDS (**b**) and typical SAED pattern [*inserted* in (**a**)] of Co-B/SiO_2 sample

characterizations of HR-TEM combined with EDS and SAED were also done and the results are shown in Fig. 3. It can be seen that both Co-B and SiO_2 were fine particles (Fig. 3a), and the black particles shown in the TEM micrograph (Fig. 3a, circled area) were confirmed to be Co-B particles by EDS analysis (Fig. 3b), here, B element is out of the measurable range in EDS instrument). It seems that Co-B was dispersed very well on the surface of SiO_2 support. The SAED pattern (Fig. 3a, inserted) of Co-B/SiO_2 revealed that the amorphous structure of Co-B on SiO_2 was kept.

3.2 Hydroformylation Reaction

3.2.1 Catalytic Performance of Co-B Catalysts

The catalytic activities of fresh amorphous Co-B and thermal-treated Co-B catalysts as well as Co-B/SiO_2 were tested in the hydroformylation of 1-octene. Nonyl aldehydes (including *n*-nonyl aldehyde and iso-nonyl aldehyde) were the dominant products over the Co-B catalysts (Table 2), and a very small quantity of dimmer of aldehydes was detected as the by-product of the reaction. For comparison, the activity of the conventional supported Co/SiO_2 was also examined in the hydroformylation reaction and the results are also listed in Table 2.

As shown in Table 2, under the reaction conditions of 120 °C and 5 MPa, fresh Co-B catalyst showed an activity of 71.1% conversion and high selectivity to C_9 aldehydes (98.7%). The heat treatment of Co-B samples had an influence on the catalytic activity of the catalyst. After treating fresh Co-B at 200 and 300 °C in N_2 for 2 h, the activities of Co-B-N_2-200 and Co-B-N_2-300 decreased to low levers (Table 2). Similarly, when treating Co-B in H_2 at 300 °C, the activity of Co-B-H_2-300 also dropped down to a low level (Conv. 28.3%). Furthermore, the activity of

Table 2 Catalytic performance of Co-B catalysts in 1-octene hydroformylation

Catalyst (g)	Co content in catalyst (wt %)[a]	Co/Olefin (mol. ratio)	1-Octene conv. (%)	C_9-aldehydes selectivity (%)	Ratio of *n*/iso
Fresh Co-B (0.240)	74.9	0.096	71.1	98.7	1.4
Co-B-N_2-200 (0.240)	68.1	0.087	42.9	97.9	1.7
Co-B-N_2-300 (0.240)	67.5	0.086	12.9	97.0	1.4
Co-B-N_2-500 (0.240)	–	–	0.1	–	–
Co-B-H_2-300 (0.240)	65.1	0.083	28.3	97.9	1.4
Co-B/SiO_2 (0.480)	10.0	0.025	88.3	97.8	1.4
Co/SiO_2 (0.450)	15.0	0.036	22.7	65.5	1.6
$Co_2(CO)_8$ (0.0482)	34.5	0.0088	81.8	95.5	1.5

1-Octene = 5 mL; *n*-butyl ether (solvent) = 15 mL; 120 °C, 5 MPa, 150 min

[a] Analyzed by ICP

Co-B-N_2-500 was even approximate to nil when fresh Co-B was treated at 500 °C in N_2 for 2 h.

It has been reported that amorphous alloy materials usually show low thermal stability [25, 26]. Thermal treatment might result in the crystallization of amorphous alloy catalysts, and subsequently cause the decrease of catalytic activities [27]. Here, we compared the characterization results of XRD, TEM and BET of thermal-treated Co-B samples (Co-B-N_2-300, Co-B-N_2-500, Co-B-H_2-300) with those of fresh Co-B sample, and further made a relation with these characterization results to the reaction results. As shown in Figs. 1 and 2, it can be seen that the amorphous structures of Co-B-N_2-300 and Co-B-H_2-300 were still kept, and no clear crystallization was observed in the XRD profiles after treated at 300 °C in flowing N_2 or H_2. However, as above-mentioned, the self-aggregations of Co-B-N_2-300 and Co-B-H_2-300 were obvious from the results of TEM (Fig. 2b, d). Therefore, the microstructures of the thermal-treated Co-B-N_2-300 and Co-B-H_2-300 catalysts might be changed more or less, although the amorphous state of the catalysts was maintained, as testified by SAED. On the other hand, it is clear that S_{BET} of the thermal-treated Co-B samples (Co-B-N_2-300, Co-B-N_2-500, Co-B-H_2-300) decreased sharply with the increase of thermal-treating temperatures of fresh Co-B (Table 1). These aggregations and S_{BET} decrease of Co-B-N_2-300 and Co-B-H_2-300 would cause the decrease of active sites on the surface of the catalysts.

Furthermore, for Co-B-N_2-500 sample, the crystallization and aggregation were very obviously observed from the results of TEM and XRD (Figs. 1, 2c), and S_{BET} of Co-B-N_2-500 was only 2 $m^2 g^{-1}$ (Table 1). Therefore, it is suggested that self-aggregation, the decrease of S_{BET} and the crystallization of amorphous of Co-B were the reasons of the activity loss of Co-B-N_2-500.

On the other hand, when Co-B was supported on SiO_2, the specific activity of the catalyst increased remarkably (Table 2). This implies that the activity of the amorphous Co-B catalyst could be improved by dispersing it on a support with high surface area [16, 22]. Compared with Co-B/SiO_2 catalyst, the activity of the conventional supported Co/SiO_2 catalyst was much lower than Co-B/SiO_2 in present study.

Here we also compare the results of present study with the results reported in literatures [13, 16]. In the case of 10 wt% Co/C catalyzed 1-hexene hydroformylation (at 3 MPa and 130 °C for 4 h, 2-propanol as solvent), 80% conversion and 34.3% C_7-aldehyde yield (42.9% selectivity) were obtained, while in the hydroformylation of 1-octene catalyzed by the same catalyst, the conversion was 61.5% and C_9-aldehyde yield was 17.6% (28.6% selectivity) [13]. On the other hand, in the case of the hydroformylation of 1-hexene catalyzed by Co/SiO_2 (5 MPa, 130 °C and 2 h), 1-hexene conversions varied from 37.1 to 99.7% and C_7-aldehyde selectivities varied from 49.2 to 87.5% (C_7-aldehyde yields varied from 32.5 to 61.3%) with or without alcohol solvents (methanol, ethanol or 2-propanol) [16]. Under the reaction conditions of present study (120 °C, 5 MPa and 2.5 h), fresh Co-B showed 71.1% conversion and 70.2% C_9-aldehyde yield (98.7% C_9-aldehyde selectivity) and Co-B/SiO_2 showed 88.3% conversion and 86.1% C_9-aldehyde yield (97.5% C_9-aldehyde selectivity) in 1-octene hydroformylation. Evidently, amorphous Co-B catalyst shows not only fine activity but also higher selectivity to our goal product comparing the results reported in the literatures [13, 16]. Therefore, it is possible that Co-B and Co-B/SiO_2 could be potential catalysts for the hydroformylation of olefins.

3.2.2 Influence of Reaction Conditions on Catalytic Activity of Fresh Amorphous Co-B

The reaction conditions have a considerable influence on the formation of aldehydes in the hydroformylation of olefins [28]. We examined the influence of reaction temperatures, syngas pressures, reaction time and catalyst amounts (Co/Olefin ratio) on the hydroformylation of 1-octene over fresh amorphous Co-B catalyst.

The influence of reaction temperatures was examined in the range of 100–200 °C at the pressures of 5.0 MPa. As shown in Fig. 4, the effect of reaction temperatures on the catalytic activity of Co-B catalyst was remarkable. Firstly, the conversion of 1-octene increased with the increase of reaction temperatures from 100 to 120 °C, and then decreased with further increase in reaction temperatures from 120 to 200 °C. The optimum reaction temperature was 120 °C under the give reaction conditions in present

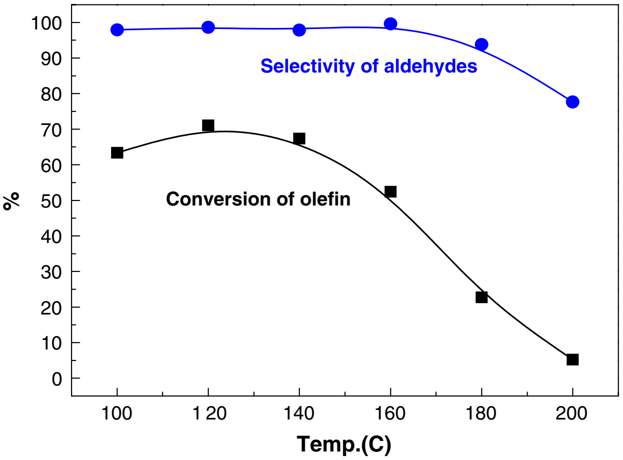

Fig. 4 Effect of reaction temperatures on hydroformylation of 1-octene catalyzed by Co-B catalyst. Catalyst: fresh Co-B (0.24 g); Co/Olefin = 0.096; 1-octene = 5 mL; solvent (*n*-butyl ether) = 15 mL; 5 MPa, 150 min

study. Although the conversion of 1-octene decreased when the reactions were carried out at high temperatures (160–200 °C) over Co-B catalyst, the amorphous structure of the catalyst was not changed after the reactions. It was confirmed by XRD characterization that no change in the amorphous structure was observed, both for the spent Co-B catalysts used at 120 and 160 °C (Fig. 5). Therefore, there might be other reasons that caused the decrease of the catalytic activity at high reaction temperatures. As above-mentioned, the heat-resistance ability could be one of the reasons, and the stability of the catalytic active species should be considered as another reason. High reaction temperatures (160–200 °C) might decrease the stability of the active species of the Co-B catalyst. It has been also reported that the catalytic active species might be unstable when the hydroformylation reactions were carried out at high temperatures [29].

As for the influence of reaction temperatures on the selectivity of C_9-aldehydes, the variety of the selectivity of aldehydes were not obvious with the change of temperatures, except for increasing temperature to 180–200 °C. The decrease of the aldehyde selectivity at the reaction temperatures of 180–200 °C was due to the formation of the dimmer of aldehydes (the condensation of C_9-aldehydes). It has been reported that the condensation products formed from aldehydes in hydroformylation would increase rapidly when the reactions were carried out at high temperatures [30]. The similar results of 1-hexene hydroformylation over Co/active carbon as a function of reaction temperature were also gained [13], and the optimum temperature reported in that literature was 130 °C. The yield of target oxygenates decreased when temperatures were higher than 130 °C [13].

The effect of initial reaction pressures on the hydroformylation of 1-octene over fresh Co-B catalyst was also investigated at 120 °C in the range of 3–8 MPa. As shown in Fig. 6, the conversion of 1-octene increased obviously with the increase of initial reaction pressures, while the change of aldehyde selectivity was not remarkably. This might be due to the CO molecular was easy to be adsorbed on the active sites of the catalysts at high reaction pressures, which benefits CO insert reaction, contributing to the formation of oxygenate products [15]. Another possible reason might be that the stability of active species could be influenced by reaction pressure, and too low CO/H_2 pressures might be disadvantaged to the steady existence of the active species. Generally, high pressures are favorable to the hydroformylation of olefins. For example, the conversion of 1-octene reached about 90% under the reaction condition of 120 °C and 8 MPa (Fig. 6).

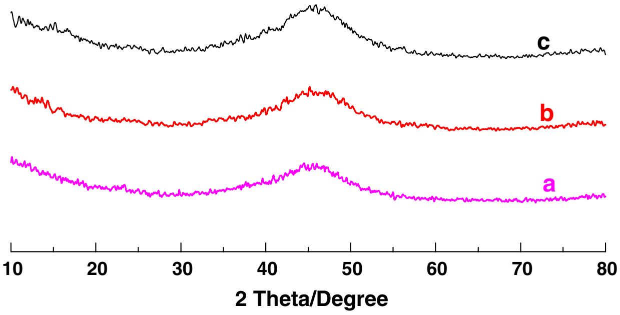

Fig. 5 Comparison of XRD patterns of fresh and spent Co-B samples. *a* Fresh Co-B (*b*) spent Co-B after reaction at 120 °C (*c*) spent Co-B after reaction at 160 °C

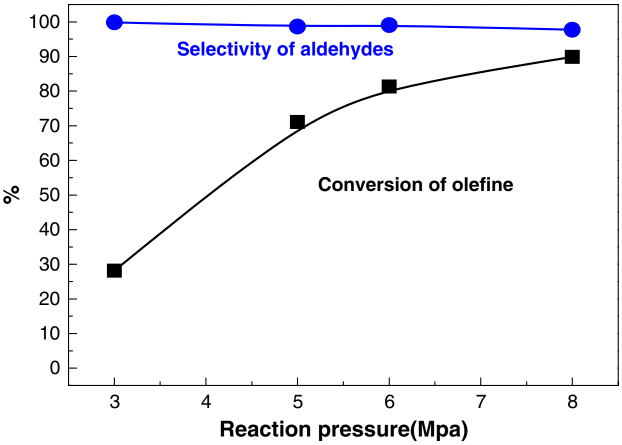

Fig. 6 Effect of reaction pressure on hydroformylation of 1-octene catalyzed by Co-B catalyst. Catalyst: fresh Co-B (0.24 g); Co/Olefin = 0.096; 1-octene = 5 mL; solvent (*n*-butyl ether) = 15 mL; 120 °C, 150 min

The results about the influence of reaction time are shown as Fig. 7. The conversion of 1-octene was increased sharply when reaction time increased from 60 to 150 min and increased slackly when reaction time exceeded 150 min. The selectivity of aldehydes was not influenced by the reaction time. The effect of Co/Olefin (molar ratio) on the hydroformylation of 1-octene was studied under the conditions of 120 °C, 5 MPa and 150 min, and the result is shown in Fig. 8. The conversion of 1-octene increased deeply when Co/Olefin ratio increased from 0.03 to 0.09 and increased weakly after Co/Olefin ratio beyond 0.09. However, the selectivity of nonyl-aldehyde was almost no change.

3.2.3 *Influence of Solvents on Catalytic Activity of Fresh Amorphous Co-B*

It has been reported that solvents had great influence on the conversion and selectivity in the Co catalyzed homogeneous hydroformylation of olefins [16]. In this study, several solvents, such as *n*-butyl ether, diethylene glycol dimethyl ether, 1,4-dioxane, toluene, cyclo-hexane and methanol were applied in the hydroformylation of 1-octene

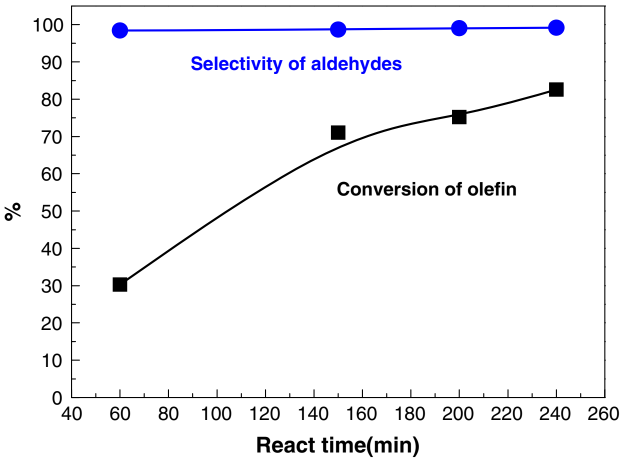

Fig. 7 Effect of reaction time on hydroformylation of 1-octene catalyzed by Co-B catalyst. Catalyst: fresh Co-B (0.24 g); Co/Olefin = 0.096; 1-octene = 5 mL; solvent (*n*-butyl ether) = 15 mL; 120 °C, 5 MPa

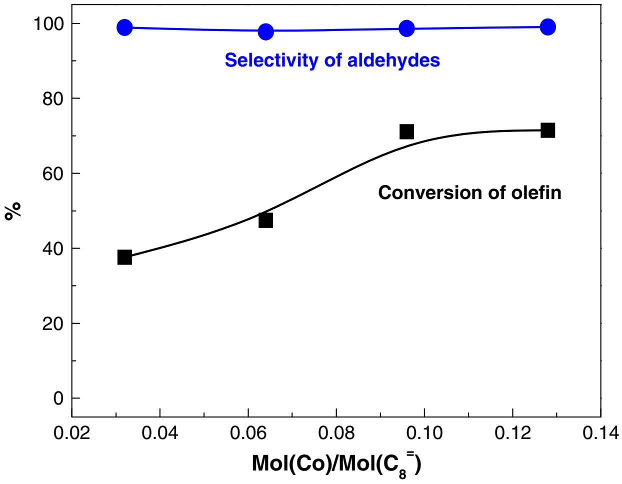

Fig. 8 Effect of Co/Olefin ratio on hydroformylation of 1-octene catalyzed by Co-B catalyst. Catalyst: 1-octene = 5 mL; solvent (*n*-butyl ether) = 15 mL; 120 °C, 5 MPa, 150 min

Table 3 Effect of solvents on hydroformylation of 1-octene catalyzed by Co-B catalyst

Solvent	1-Octene conv. (%)	C_9-aldehydes selectivity (%)
n-Butyl ether	71.1	98.7
Diethylene glycol dimethyl ether	68.6	96.2
1,4-Dioxane	75.1	99.2
Toluene	71.7	90.1
Cyclo hexane	42.9	94.8
Methanol	92.9	20.4

Catalyst: fresh Co-B (0.24 g); Co/Olefin = 0.096; 1-octene = 5 mL; solvent = 15 mL; 120 °C, 5 MPa, 150 min

catalyzed by fresh Co-B catalyst. The reaction results are presented in Table 3. When *n*-butyl ether or diethylene glycol dimethyl ether was used as a solvent, the conversion was relatively high (68.6–71.1%) and the selectivity to C_9-aldehydes could reach 96.2–98.7%. In addition, 1,4-dioxane also showed similar effect on the reaction as in the cases of using *n*-butyl ether as a solvent. When using toluene as a solvent, the conversion reached 71.7%, and the selectivity was 90.1%, which was somewhat lower than that when using *n*-butyl ether as a solvent. However, using cyclo-hexane as a solvent gave the result of low conversion of 1-octene. When methanol was used as a solvent, the conversion of 1-octene reached 92.9%, but the selectivity of nonyl-aldehyde was very low (20.4%), and large amount of acetal [$RCH(OCH_3)_2$], which was formed by the reaction of nonyl-aldehyde and methanol during the hydroformylation, was detected. Furthermore, certain amount of ester (RCH_2COOCH_3), which was formed by the reaction of 1-octene, CO and methanol was also detected. Therefore, methanol played not only as solvent but also as reactant in the hydroformylation. The analogous results in the hydroformylation of 1-hexene were also reported by Zhang et al. [16].

Solvents usually show some effects on reaction rates, chemical equilibrium as well as reaction mechanisms in organic reactions [31]. For cobalt catalyzed homogeneous hydroformylation, cobalt carbonyls, $HCo(CO)_x$, are usually considered as the active species [11, 32–37], and the reaction also obey Wilkinson's mechanism. For the hydroformylation catalyzed by supported Co solid catalysts, the active species were also cobalt carbonyls on the surface of the solid catalysts [11, 34, 36]. In present study, cobalt carbonyl species [$HCo(CO)_x$] would be in situ formed on the surface of Co-B catalysts under the present of CO/H_2 during the hydroformylation of 1-octene. The catalytic activity and selectivity would be related to the ease of formation of the catalytically active cobalt carbonyl species [11]. Solvents showed effects on formation of cobalt carbonyl species, and polar solvents showed excellent properties compared with nonpolar solvents in the formation of cobalt carbonyl active species [32, 37]. The polarity of solvents also affected the reaction rates of hydroformylation, and addition of polar solvents would be favorable the increase of alkene hydroformylation rates, which were catalyzed by phosphine-modified cobalt carbonyls [38]. Usually, the molecular dipole moment (μ) is used to quantify polarity of solvents [39, 40]. In present study, *n*-butyl ether, diethylene glycol dimethyl ether, 1,4-dioxane, toluene, methanol and cyclohexane were used as solvents in the hydroformylation of 1-octene. The molecular dipole moments of *n*-butyl ether, diethylene glycol dimethyl ether, 1,4-dioxane and toluene are 1.18, 1.92, 0.46 and 0.38 (in Debye units, measured in the gas phase), respectively [39]. These solvents show medium polarity, and they showed relatively high effect on the catalytic activity in the hydroformylation of 1-octene. Contrasting to this, the molecular dipole moments of cyclohexane is zero [39], and it showed low activity in the hydroformylation of 1-octene. On the other hand, methanol is a typical polar solvent with a high value of the molecular dipole moment [31], and it also showed high effect on the catalytic activity. However, as above-mentioned, the side-reaction of nonyl-aldehyde and methanol would occur during the hydroformylation when using methanol as the solvent.

3.2.4 *Recycle use of Amorphous Co-B in 1-Octene Hydroformylation*

The recycle use of amorphous Co-B catalyst proceeded in the hydroformylation of 1-octene under the conditions of 120 °C and 5 MPa. As it can be seen in Fig. 9, the Co-B catalyst exhibited relatively high stability (activity and selectivity) in the recycle of four times in the hydroformylation of 1-octene. Within four recycle reactions, no decrease in the conversion of 1-octene and selectivity of nonyl-aldehydes was observed, indicating the possibility of the recycle use for amorphous Co-B catalyst in the hydroformylation of 1-octene.

4 Conclusions

An amorphous Co-B catalyst showed relatively high activity (ca. 90% conversion) in the hydroformylation of 1-octene, and the selectivity to C_9-aldehydes reached to about 96% in a laboratory-scale stirred batch reactor with *n*-butyl ether as a solvent under the conditions of Co/Olefin molar ratio = 0.096, 120 °C, 8 MPa and 150 min. The activity of Co-B catalyst could be improved by dispersing it on SiO_2 support. The thermal-treatment of the Co-B catalyst in N_2 or H_2 atmosphere at the temperatures below 300 °C for 2 h had no influence on the amorphous structure of the catalyst, but decreased the specific surface area of the catalyst. The thermal-treatment temperatures of the Co-B catalyst and the reaction temperatures both had great influence on the activity of the catalyst. Increasing the thermal-treatment temperature would decrease the specific surface area and the activity of the Co-B catalyst evidently. The suitable reaction temperature was 120 °C for the hydroformylation of 1-octene over the Co-B catalyst under present study. The Co-B catalyst exhibited relatively high stability (activity and selectivity) in the recycle of four times in the hydroformylation of 1-octene under the conditions 120 °C, 5 MPa and 150 min.

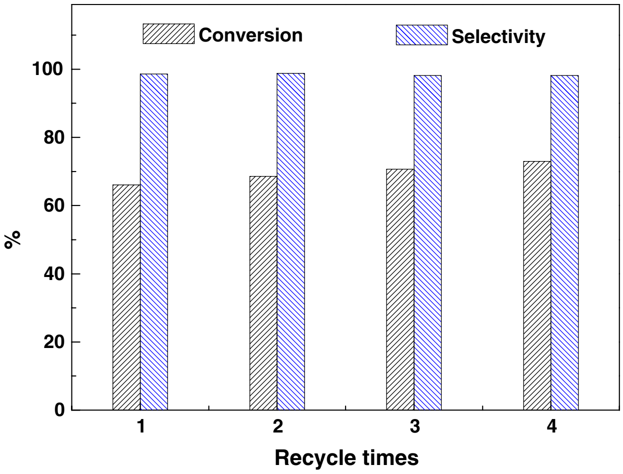

Fig. 9 Recycling use of Co-B in the hydroformylation of 1-octene. Catalyst: fresh Co-B (0.24 g); Co/Olefin = 0.096; 1-octene = 5 mL; solvent (*n*-butyl ether) = 15 mL; 120 °C, 5 MPa, 150 min

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