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Short Communication

Nanotubular TiO₂-supported amorphous Co–B catalysts and their catalytic performances for hydroformylation of cyclohexene



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1. Introduction

Nowadays, hydroformylation discovered by Roelen in 1938 is still an attractive reaction. Several million tons of aldehydes are produced annually by the reaction [1]. For decades, the Co-based [2,3], Ir-based [4,5] and Rh-based [6] catalysts for hydroformylation are widely investigated. Indeed, the Co-based catalysts are much less expensive than Rh-based and Ir-based catalysts, and are able to hydroformylate olefins selectively to aldehydes effectively. Though the soluble catalyst shows high catalytic activity and selectivity, it is very difficult to separate the catalyst from the products, especially in the case of high boiling aldehyde formation. Wiese and Obst have estimated the annual financial loss in a 400 kt plant when just 1 ppm Rh/kg product is lost at several million euros [7]. Therefore, exploring for a stable catalytic system incorporating the advantages of both homogeneous and heterogeneous catalysis should have been an interesting work. The conversion of homogeneous catalyst into heterogeneous system or sealing catalytically metal active species into supports may be more favorable, which prevents catalytically active species from loss [8,9]. Recently, several Co metal catalysts supported on inorganic supports have been investigated for the hydrogenation [10] and hydroformylation [11]. Nanotubes have large SSA, which has been widely used as supports for heterogeneous catalysts. Carbon nanotubes supported catalysts for the hydroformylation of olefine have been reported, and show high

ABSTRACT

TiO₂ nanotubes supported amorphous Co–B catalysts (Co–B/TNTs) were prepared via WI-CRP. The catalysts were characterized with TEM, XPS, TPD, nitrogen adsorption and so on. The catalytic performances and stabilities of Co–B/TNTs for hydroformylation of cyclohexene as well as the influence factors, such as reaction media and Co loading, were investigated. The Co–B/TNTs not only exhibited better catalytic performances in ether than in acetone and alcohol, but also showed higher activities and stabilities than TiO₂ powder supported amorphous Co–B under the same reaction conditions. The reuse of Co–B/TNTs was also tested, and the results showed that the used catalysts maintained high catalytic activity.

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catalytic activities [12]. Multiwall structured TiO_2 nanotubes (TNTs) prepared via simple hydrothermal treatment have many distinct properties [13,14]. It is well known that this kind of TNT is constructed by rolling up one (1 0 1) layer of the anatase structure along the [-101] direction and the (1 0 1) facet-constructed space between walls is about 0.76 nm [15]. In our previous works we have utilized such structure for preparing thermally stable TNTs and photocatalysts with good catalytic performances [16–18]. In the present contribution we report amorphous Co–B sealed in TNTs via WI-CRP and its catalytic activity for hydroformylation.

2. Experimental

 TiO_2 nanotubes were synthesized by the hydrothermal treatment as the previous report [19].

The Co–B/TNTs (X, T °C) were prepared via WI-CRP, where X is the mass fraction of Co and T is calcination temperature. The synthesis of Co–B/TNTs was performed as follows: 1.0 g TNTs were dispersed in 20 mL of aqueous Co(NO₃)₂ solutions (2 mol/L, 1 mol/L, 0.5 mol/L, respectively) and vigorously agitated for 24 h. After low-energy sonication for 2 h, the mixture was centrifuged and the obtained TNTs were transferred into 100 mL flask. Then 20 mL of aqueous KBH₄ solution (2 mol/L, 1 mol/L, 0.5 mol/L, respectively) was dropwise added, while vigorously stirred, in ice-water bath and under argon atmosphere. After addition of aqueous KBH₄ solution, the mixture was continually stirred for another 1 h at 0 °C and room temperature, respectively. The mixture was centrifuged and the black product was washed to neutral with distilled water repeatedly, and then washed





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three times with ethanol. The product was filtered, dried at 40 °C for 12 h in vacuum, and marked as Co–B/TNTs (X). Part of the product was calcinated in argon atmosphere at 300 °C for 2 h, which was marked as Co–B/TNTs (X, 300 °C). For comparison, the Co–B/TiO₂ was prepared under the same conditions except that commercial TiO₂ powder was substituted for TNTs, and a conventional amorphous Co–B sample marked as Co–B was also prepared by the same reduction processes. The detailed process of characterization is showed in the Supporting information S.1.

Hydroformylation with cobalt catalysts is usually carried out in the temperature range of 140–180 °C. Here 150 °C was chosen as the reaction temperature based on the DSC results and our previous work [2]. The hydroformylation of cyclohexene was carried out in a 250-mL stainless steel autoclave reactor with magnetic stirrer. In a typical experiment, the required amount of catalyst, substrate and solvent was charged into the reactor. The reactor was sealed, purged with nitrogen three times, heated to the reaction temperature and pressurized with gas $(CO + H_2)$ to the desired pressure while stirring. After the required reaction time, the stirring was stopped. Then the reactor was cooled to room temperature, and the pressure was carefully released. The reaction mixture was withdrawn and analyzed using GC-MS or GC (Beifen 3420A chromatograph equipped with a 50 m \times 0.53 mm SE-30 capillary column and a FID, cf. S.7-10). After reaction, the reaction system was centrifuged and the recovered solid catalyst was washed three times with ethanol, and then dried at 40 °C for 12 h in vacuum for the next reaction.

3. Results and discussion

The SSA of as-prepared Co–B/TNTs (12.96) and TNTs is 180 m^2/g and 235 m^2/g , respectively. The result can be ascribed to that amorphous Co–B deposits on the surface of TNTs or occupies the interspace

between walls of TNTs, which can be seen clearly by TEM. ICP-AES was used to determine the contents of Co and B in as-prepared Co-B/TNTs and Co-B. The atom ratio of Co to B is around 2 or 3 (Table 2), which means that the Co and B may exist as Co_2B or Co_3B in samples though there are other types of Co-B alloy [20].

Displayed in Fig. 1 are TEM images of conventional amorphous Co–B, as-prepared and calcinated Co–B/TNTs (12.96). As shown in Fig. 1, the conventional amorphous Co–B is an agglomeration of Co–B nanoparticles (Fig. 1A) and the multiwall structure of TNT is clear (Fig. 1B–D). For as-prepared Co–B/TNTs (12.96), amorphous Co–B not only deposited highly uniformly on the surface of TNTs, but also entered the interspace between layers (Fig. 1B–C). However, there were some black spots in the as-prepared Co–B/TNTs (12.96), which should be amorphous Co–B. After calcination at 300 °C, the Co–B/TNTs (12.96, 300 °C) (Fig. 1D) still kept its tubular structure, its multiwall structure became clearer in comparison with the as-prepared ones. The multiwall structure of TNTs may play an important role in preventing amorphous Co–B particles from aggregation or running off in the processes of hydroformylation.

XPS was used to analyze Co- $2p_{3/2}$ and B-1s in as-prepared Co-B/ TNTs (12.96). The binding energies of 778.8 eV and 780.8 eV arise from Co- $2p_{3/2}$ and 187.9 eV and 191.4 eV from B-1s (cf. Supporting information S.2). This means that the Co and B on the surface of asprepared Co-B/TNTs are present in both elemental and oxidized states. The binding energy peaks at 778.8 eV and 187.9 eV are assigned to the metallic Co species and elemental B, respectively. A small amount of oxidized cobalt (780.8 eV) is attributed to CoO that has been formed in the processes of preparation or measurement [21].

Fig. 2 is the magnetic hysteresis loop of as-prepared Co–B/TNTs (12.96) and Co(NO₃)₂/TNTs at room temperature, which shows that the as-prepared Co–B/TNTs (12.96) are of ferromagnetism. The saturation magnetization (Ms), residual magnetism (Br) and coercivity (Hc)

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B

Fig. 1. TEM images of as-prepared Co-B (A), Co-B/TNTs (12.96) (B, C) and Co-B/TNTs (12.96, 300 °C) (D).



Fig. 2. Magnetic hysteresis loop of as-prepared Co–B/TNTs (12.96) at room temperature. Inset: (A)–magnified view of Co–B/TNTs at smaller field; (B)–magnetic hysteresis loop of as-prepared $Co(NO_3)_2/TNTs$ at room temperature.

of as-prepared Co–B/TNTs (12.96) are 4.785 emu/g, 0.3976 emu/g and 34.04 Oe, respectively, which are all much larger than that of $Co(NO_3)_2$ /TNTs, implying formation of Co–B alloy, though the *Ms* of as-prepared Co–B/TNTs (12.96) is much smaller than that of the normal Co–B alloy (45.7 emu/g) [22]. It is well known that the *Ms* increases with the increase of particle size, so do the *Br* and *Hc*. Due to the nano-confinement effect of TNTs, the average size of amorphous Co–B particles that formed on the inner surfaces, especially in the interlayer space of TNTs, is certainly smaller than that of regular Co–B, and it is reasonable that the *Ms* of Co–B/TNTs (12.96) is smaller than that of the regular Co–B.

Fig. 3 is the XRD patterns of as-prepared Co–B/TNTs (12.96), Co–B/ TNTs (12.96) used at 150 °C for 3 h and Co–B/TNTs (12.96, 300 °C). The patterns of A, B and C all possess peaks of anatase TiO₂ (JCPDS21-1272), and the peaks at 25.24° and 48.1° are the diffractions of the (101) and (200) crystal planes, respectively. As shown in Fig. 3C, there is a very weak and broad diffraction peak at around $2\theta = 44.7°$, which is a characteristic peak of crystal Co–B particles. Fig. 3 indicates: 1) The Co–B in as-prepared Co–B/TNTs (12.96) (A) and Co–B/TNTs (12.96) used at 150 °C for 3 h (B) were amorphous. After being calcined at 300 °C for 2 h, the TNTs supported amorphous Co–B turned into crystal



Fig. 3. XRD patterns of as-prepared Co–B/TNTs (12.96) (A), Co–B/TNTs (12.96) used at 150 $^\circ C$ for 3 h (B) and Co–B/TNTs (12.96, 300 $^\circ C$) (C).

(C). 2) The amorphous structure of Co–B supported by TNTs did not change in the hydroformylation reaction at 150 $^{\circ}$ C for 3 h.

The DSC was used to characterize the thermally stability of asprepared Co–B/TNTs. The DSC thermogram of as-prepared Co–B/TNTs (12.96) can be roughly divided into three exothermic sections in the temperature range of 100–500 °C (cf. Supporting information S.3). A sharp exothermic peak at 213 °C in the first section (100–224 °C) might be relevance to the surface shrinkage of as-prepared Co–B/TNTs (12.96). A similar result has been reported [23]. The second (224– 406 °C) and third (above 406 °C) sections should be related to the phase transition of TNTs and agglomeration or crystallization of amorphous Co–B particles, which is confirmed by the XRD patterns of Co– B/TNTs (12.96, 300 °C) (Fig. 3C).

In order to investigate the adsorption capacities of samples for CO and H₂, the CO- and H₂-TPD were performed and the results are showed in Fig. 4. As shown in the Fig. 4A-a, two distinguished CO desorption peaks with maxima at 115 and 221 °C appear, which might be ascribed to the desorptions from the outer and inner surfaces of TNTs, respectively. Compared with TNTs, the as-prepared Co–B/TNTs (12.96) show three CO desorption peaks (Fig. 4A-b), and the peak at 338 °C should be assigned to the desorption from amorphous Co–B. In Fig. 4B, desorption peaks with maxima at 89 and 208 °C (Fig. 4B-c) should be the H₂ desorptions from the outer and inner surfaces of TNTs, respectively. For as-prepared Co–B/TNTs (12.96), four H₂ desorption peaks that appeared at around 89, 188, 329, and 369 °C (Fig. 4B-d) could be grouped to desorptions from TNTs (peaks at 89, 188 °C) and amorphous Co–B



Fig. 4. (A): CO-TPD profiles of TNTs (a) and Co-B/TNTs (12.96) (b). (B): H₂-TPD profiles of TNTs (c) and Co-B/TNTs (12.96) (d).

Table I		
Comparison of the catal	ytic activities of supported Co-	3 catalysts. ^a

Entry	Catalyst	Conversion of	Selectivity (%)		
		cyclohexene (%)	Aldehyde	Alcohols	
1	As-prepared Co-B/TNTs (12.96)	83.17	81.81	18.19	
2	Co–B/TNTs (12.96, 300 °C)	12.93	100	0	
3	As-prepared Co-B/TiO ₂ (11.99)	68.69	93.02	6.98	

 $^a~$ Reaction condition: 5 mL cyclohexene, 65 mL THF, 1 g as-prepared catalyst, 150 °C, t = 1 h, gas (CO:H_2 = 2:1): 6.0 MPa at 100 °C.

(peaks at 329, 369 °C), respectively. The peaks at 329 and 369 °C suggest that amorphous Co–B particles contained at least two kinds of Cobased active sites for H_2 [24].

Listed data in Table 1 are the catalytic activities of different forms of titania supported Co–B and Co–B/TNTs (12.96, 300 °C). The as-prepared Co–B/TNTs (12.96) are more active than both Co–B/TNTs (12.96, 300 °C) and as-prepared Co–B/TiO₂ (11.99), and the calcination affects the catalytic activity of Co–B/TNTs badly. As shown in DSC analysis, the as-prepared Co–B/TNTs underwent shrinkage at 213 °C, this resulted in the fact that the SSA and the amount of catalytically active species on the surface of Co–B/TNTs (12.96, 300 °C) were certainly smaller than that of as-prepared Co–B/TNTs (12.96), which were unfavorable for catalytic reaction. The SSA of TNTs is larger than that of the commercial titania powder; the large SSA is favorable not only for dispersion of amorphous Co–B, but also for the increase of absorption capacity of catalyst for CO and H₂. Thus, it is reasonable that the as-prepared Co–B/TNTs show higher catalytic activity than the Co–B/TO₂.

There would be four products, aldehyde (I), alcohol (II), acetal (III) and cyclohexane (IV), if all possible reactions took place equally in the hydroformylation processes of cyclohexene (cf. Supporting information S.4). The catalytic performances of various catalysts for hydroformylation of cyclohexene are listed in Table 2. The conversion of cyclohexene over Co-B/TNTs is related to the CO/H₂ ratio by comparison between Entries 1 and 2. The conversion of cyclohexene rises from 56.82% (Entry 1) to 99.15% (Entry 2) with the increase of CO/H₂ ratio from 1 to 2. The catalytic performances of as-prepared Co-B/TNTs (12.96) in tetrahydrofuran, dimethoxyethane, ethanol and acetone (Entry 2-5) imply that tetrahydrofuran is a more perfect solvent for the hydroformylation of cyclohexene. It is noteworthy that only in the case of ethanol used as solvent, the condensation product formed (Entry 4, cf. Supporting information S.6–7), which means that the condensation reaction between formed aldehyde and alcohol did not take place in the reaction processes. The reasonable interpretation for the results could be that the condensation molecule (III) was too large to form or nano-confinement effect of Co–B/TNTs prevented it from forming. Entries 2, 6 and 7 display the variation of catalytic activity of Co-B/TNTs with the Co loading under the same reaction conditions; the total conversion of cyclohexene and amount of alcohol increased with the increase of the Co content. However, as we concentrate on the cyclohexene conversion over per mole of Co, we can find that the catalytic activities of Co-B/TNT catalysts increase firstly and then decrease with the increase of Co loading. It is well known that there are some coordinative unsaturated oxygen atoms on the inner and outer surface of TNTs, which can be covered by Co^{2+} ions step by step (monolayer adsorption) along with the increase of amount of Co²⁺ ions in the processes of preparation. After monolayer adsorption, instead of raising the dispersion of Co²⁺ ions, the excess Co²⁺ ions may block tubes after reduction, which resulted in the decrease of catalytic activity per mole of Co. As a matter of fact, the TiO₂ nanotubes play an important role in enhancing the catalytic activity per mole of Co. which is confirmed by that the catalytic activity of Co-B/TNTs (7.53) (Entry 6) is higher than that of pristine Co–B (Entry 8) though the amounts of Co used in the reaction are almost identical.

Fig. 5 shows the variations of conversion and selectivity with reaction time. The conversion of cyclohexene increased steadily up to 2 h, and thereafter it remains constant. However, the selectivity to aldehyde increased steadily up to 1 h and decreased steadily. If the catalytic hydrogenation of (I) was faster than the hydroformylation of cyclohexene, the main product of the catalytic reaction should be alcohol (II), which was, however, not back up by the results showed in Table 2 and Fig. 5. The as-prepared Co–B/TNT catalyst has a good catalytic activity for both hydroformylation and hydrogenation, and its catalytic activity for hydroformylation is far higher than that for hydrogenation under the optimized reaction conditions. After 2 h, nearly all of cyclohexene turned into (I) and hydrogenation of (I) increased, which resulted in decrease in selectivity for (I).

In order to examine the difference in catalytic activity between fresh and used catalyst, the recycle uses of as-prepared Co–B/TNTs were carried out, and the results are showed in Fig. 6. The fresh Co– B/TNTs (12.96) showed the best catalytic performance, over which the conversion of cyclohexene was the highest (98.94%), but the selectivity for aldehyde was the lowest (aldehyde: 67.64%, alcohols: 32.36%). As it was used secondly, its catalytic performance changed slightly. The selectivity for aldehyde increased very much though the conversion of cyclohexene decreased a little (93%). Furthermore, the catalyst became stable onward, and the conversion as well as selectivity did not change evidently. After reaction, the contents of Co and B in the solution were detected by ICP, which are also showed in Fig. 6. The data exhibit that the Co and B leaching from Co–B/TNTs were very low and they decreased with recycle times. As discussed above, a small amount of oxidized cobalt existed on the as-prepared

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Catalytic performances of various Co-B/TNTs under different conditions.^a

Entry	Catalyst	Contents of Co (wt.%)	Atom ratio of Co to B	Solvent	Conver. of cyclohexene		Selectivity (%)		
					Total (%)	Moles ^b	Aldehyde	Alcohol	Acetal
1	Co-B/TNTs	12.96	3	THF ^c	56.82	12.67	99.97	0.03	0
2	Co-B/TNTs	12.96	3	THF	99.15	30.07	65.28	34.72	0
3	Co-B/TNTs	12.96	3	DME	92.28	24.08	84.13	15.87	0
4	Co-B/TNTs	12.96	3	Ethanol	77.19	17.19	6.62	0	93.38 ^d
5	Co-B/TNTs	12.96	3	Acetone	11.79	4.00	93.86	6.14	0
6	Co-B/TNTs	7.53	2	THF	91.88	43.53	78.17	21.83	0
7	Co-B/TNTs	4.75	3	THF	49.49	30.04	94.88	5.12	0
8 ^e	Co-B	68.27	2	THF	88.86	35.50	80.20	19.8	0

^a Reaction conditions: 5 mL cyclohexene, 65 mL solvent, 1 g as-prepared Co-B/TNTs, 150 °C, t = 3 h, gas (CO:H₂ = 2:1): 6.0 MPa at 100 °C.

^b Moles of cyclohexene conversion and aldehyde hydrogenation over one mole of Co.

 $^{\rm c}~$ Gas (CO:H_2 = 1:1): 6.0 MPa at 100 °C.

^d Acetal is the condensation product of aldehyde (II) and ethanol.

^e 0.128 g as-prepared Co-B catalyst.



Fig. 5. Variations of conversion/selectivity with reaction time. Reaction condition: 10 mL cyclohexene, 60 mL THF, 1 g as-prepared Co-B/TNTs (12.96), 150 °C, gas (CO:H₂ = 2:1): firstly, 6.0 MPa at 100 °C, and then charging gas (CO:H₂ = 1) to 6.5 MPa every 1 h at 150 °C.

Co–B/TNTs; the loss of oxidized cobalt took place during fresh catalyst catalyzing hydroformylation. The results showed in Fig. 6 indicate that the catalytically stability of Co–B/TNTs for hydroformylation is very good.

4. Conclusion

For the amorphous Co–B/TNT catalyst prepared by WI-CRP, Co–B particles were uniformly deposited on the outer and inner surface of TNTs. The nano-confinement effect of multiwall tubular TiO₂ plays an important role in fastening the amorphous Co–B. The amorphous Co–B/TNT catalyst shows high catalytic activity for the hydroformylation of cyclohexene and the optimal reaction media is THF. The asprepared Co–B/TNT catalyst not only shows good initial catalytic performance, but also keeps its catalytic activity in recycles.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2014.09.043. These data include MOL files and InChiKeys of the most important compounds described in this article.



Fig. 6. Influence of the cycling on the conversion, selectivity, and element leaching after reaction. Reaction condition: 5 mL cyclohexene, 65 mL THF, 1 g as-prepared Co–B/TNTs (12.96), 150 °C, t = 3 h, gas (CO:H₂ = 2:1): 6.0 MPa at 100 °C.

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