A Novel Indium-Boron Amorphous Alloy Mediator for Barbier-Type Carbonyl Allylation in Aqueous Medium

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Abstract: A novel indium-boron (In–B) amorphous alloy was prepared by chemical reduction of indium(III) ions $[In^{3+}]$ with borohydride $[BH_4^-]$ in aqueous solution and was applied to the water-medium Barbier-type allylation reactions. A variety of allyl halides could be efficiently added to aldehydes or ketones in water. Additionally, the as-prepared In–B exhibits much higher activity than the commercial In powder and the crystallized In–B owing to the high surface area, the unique amorphous alloy structure,

Introduction

Homoallylic alcohols have been well known as important building blocks in many biological active molecules, such as macrolides, polyether and antibiotics,^[1] and can be achieved via Barbier-type reactions using organometallic reagents.^[2] Although highly active and selective, homogeneous organometallic catalysis suffers from numerous drawbacks, namely, high cost, non-reusability of catalyst, sensitivity toward moisture and air, as well as the environmental pollution from the presence of organic solvent.^[3] Recently, the use of water instead of organic solvents as reaction medium for organic synthesis has emerged as one of the most interesting fields for organic chemists because of substantial economical and ecological gains.^[4] In 1990, Li^[5] and Chan^[6] established the first utility of metallic indium powder to mediate Barbier-type carbonyl allylation in aqueous media. Although highly selective, such indium powder exhibits lower efficiency for allylation reactions in comparison with the homogeneous catalysts which limits its application.

and the high electron density on the In active sites resulting from the strong electronic interaction between the metal In and the alloying B. The yield of target product over the In–B amorphous alloy was similar to that obtained on the homogeneous Pd(II) organometallic catalyst, showing good potential in practical application.

Keywords: amorphous materials; Barbier reaction; cleaner organic synthesis; indium; water

Amorphous alloys represent a new class of environmentally friendly catalysts with higher activity, better selectivity and stronger sulfur resistance than the corresponding crystalline catalysts owing to their unique short-range ordering but long-range disordering structure.^[7] To date, a great number of amorphous alloys have been synthesized via chemical reduction of metallic ions with BH_4^- or/and $H_2PO_2^-$ and their catalytic performances have been thoroughly investigated.^[7d,e] To the best of our knowledge, however, indium-containing amorphous alloy has never been reported so far. We report here, with the aim to design powerful heterogeneous mediators for water-medium potentially cleaner organic reactions, the synthesis of a novel In-B amorphous alloy in the form of ultrafine nanoparticles, which exhibited much higher activity than either the commercial In powder or the crystallized In-B during Barbier-type allylation reactions of carbonyl compounds in aqueous medium. The correlation of the reactivity to the structural characteristics was tentatively established.

Results and Discussion

Structural Characteristics

The composition of the as-prepared In–B was determined as $In_{83}B_{17}$ (Table 1) by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

The X-ray diffraction (XRD) pattern [Figure 1, (a)] demonstrated that the fresh In-B sample was present in a typical amorphous structure indicated by a single broad peak around $2\theta = 32^{\circ}$.^[8] This amorphous structure could be further confirmed by a series of successive diffraction halos in an attached selective area electronic diffraction (SAED) image (inset in Figure 1).^[9] Heat treatment of the fresh In–B at 473 K in argon for 2 h resulted in the appearance of various crystalline diffraction peaks characteristic of metallic indium (PDF 85-1409) [Figure 1, (b)]. Meanwhile, the attached SAED image displayed diffraction dots indicative of the crystalline structure. These results demonstrated the transformation from an amorphous structure to the crystalline structure, together with the decomposition of In-B alloys. Using a low stirring speed (600 rpm), only crystalline metallic In diffraction peaks were observed from the XRD pattern (see Supporting Information, Figure S1). The formation of crystalline metallic In could be due to the crystallization during the preparation process, taking into account that the reaction between In³⁺ ions and BH₄⁻ was vigorous and strongly exothermic. Thus, the stirring speed is of central importance for the formation of In-B amorphous alloy.

The crystallization process was further investigated by differential scanning calorimetry (DSC) analysis. As shown in Figure 2, (a), the as-prepared In–B sample displayed an exothermic peak at around 658 K, implying the features of the typical thermody-



Figure 1. XRD patterns of (**a**) the as-prepared In–B and (**b**) the In–B treated at 473 K in an Ar flow for 2 h. The inset is the SAED images of the samples.

namically metastable structure.^[10] In addition, no significant endothermic peak corresponding to the melting point of metallic In had been detected at around 631 K as commercial metallic In powder [Figure 2, (**b**)], being attributed to the formation of In–B amorphous alloy.

The In 3*d* X-ray photoelectron spectroscopy (XPS) spectra [Figure 3, (**a**)] revealed that for all In species in the as-prepared In–B sample, the binding energy (BE) values of In $3d_{5/2}$ and In $3d_{3/2}$ were 443.8 and 451.4 eV, indicating that all In atoms were present in the metallic state.^[11] But the B species were present in both the elemental B and the oxidized B, with B 1*s* BE values of around 188.1 and 192.4 eV. The B 1*s* BE of the elemental B in In–B exceeded that of pure B (187.1 eV) by 1.0 eV,^[12] further indicating that the ele-

OH

Table 1. Structural parameters and performances of different mediators.^[a]

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	$H + Br \longrightarrow H$						
Mediator	Composition [atom%]	$S_{\rm BET} \left[m^2 g^{-1} \right]$	Conversion [%]	Selectivity [%]	$R^{S[b]} [\times 10^{-3} \mathrm{mmol}\mathrm{min}^{-1}\mathrm{m}^{-2}]$		
In–B Cryst. In–B ^[c] In powder $PdCl_2(PPh_3)_2^{[d]}$	In ₈₃ B ₁₇ In ₈₃ B ₁₇ In -	135 88 110	96 47 85 96	98 97 98 96	2.3 1.0 1.9		

[a] Reaction conditions: a mediator containing In (1.12 mmol), benzaldehyde (2.25 mmol), allyl bromide (4.50 mmol), Al (0.540 g), H₂O (10.0 mL), T=323 K, reaction time=120 min.

^[b] R^{s} is expressed as the amount of substance of benzaldehyde converted (at 10% conversion) per minute on per square meter In site.

^[c] After being treated at 473 K for 2 h in an Ar flow.

^[d] The amount of catalyst is 150 mg.

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Figure 2. DSC curves of (a) the In–B sample, and (b) the commercial metallic In powder.

mental B is alloyed with the metallic In. In the In–B alloys, some of the electrons may be transferred from B to In, as had been detected in other M–B (M=Ni, Co, Ru) samples.^[12,13] Thus, the combined results from XRD, SAED, DSC, and XPS characterizations clearly demonstrated the formation of In–B amorphous alloy through the reduction of In³⁺ by BH_4^- . According to the calculation based on XPS peak areas, the surface molar ratio of the alloying B to the metallic In in In–B was 7/93.

The representative transmission electronic microscopy (TEM) image (Figure 4) revealed that the asprepared In-B amorphous alloy was present in the form of uniformly ultrafine particles. The average particle size was about 8.5 nm (Figure 4). In contrast, the commercial In powder showed almost irregular shape with extremely broad particle size distribution, from <10 nm to > 100 nm (see Supporting Information, Figure S2). The relatively smaller size and narrow distribution for the as-prepared In-B nanoparticles could be attributed mainly to the rapid reduction of In^{3+} by BH_4^{-} . When the stirring speed was set to 600 rpm while keeping other experimental conditions as same as the typical preparation, large well-defined hexagonal crystallines (ca. 100–150 nm) would be formed (see Supporting Information, Figure S3). The corresponding SAED pattern showed periodic sharp diffraction points, indicated well-crystallized structure. The pattern could be indexed as $[0\bar{3}2]$ zone axis of In tetragonal phase (PDF 85-1409, I4/mmm). This is consistent with the aforementioned XRD characterization, which showed diffraction peaks corresponding to crystalline metallic In.

By an N_2 physisorption experiment, the Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) of all the In-containing samples were determined and are listed



Figure 3. XPS spectra of the In–B sample: (a) In 3*d*, and (b) B 1*s*.

in Table 1. The relatively higher S_{BET} of the as-prepared In–B amorphous alloy could be easily understood by considering its nanosized structure, which was consistent with the TEM observations.

Reactivity

The as-synthesized In–B amorphous alloy was subjected to Barbier-type carbonyl allylation reactions in aqueous medium. Figure 5 showed the reaction profiles of addition of allyl bromide to benzaldehyde over In–B and the commercial In powder, which revealed that both samples are highly selective towards 1-phenyl-3-buten-1-ol. The obtained ln(1-conversion)over In–B increased almost linearly with the reaction time (inset in Figure 5), indicating that the present reaction was first-order with respect to benzaldehyde.



Figure 4. TEM image (*left*) and its corresponding size distribution histogram (*right*) of an In–B sample.



Figure 5. Dependence of the benzaldehyde conversion and the 1-phenyl-3-buten-1-ol selectivity on reaction time over In–B amorphous alloy and In powder: (\blacksquare) conversion on In-B amorphous alloy; (\square) selectivity on In–B amorphous alloy; (\bigcirc) conversion on In powder; (\bigcirc) selectivity on In powder. Inset is the time *vs.* ln(1-conversion) curve over In–B amorphous alloy. Reaction conditions are listed in Table 1.

Along with the target product, the self-coupling product of the allyl bromide, 1,5-hexadiene was also identified in the reaction mixture. This suggested that this Barbier reaction followed a single-electron transfer (SET) mechanism as proposed by Li and Chan,^[3a,b] involving the formation of a radical anion intermediate. The role of Al powder is to regenerate In(0) species *in situ* during the reaction.

Table 1 summarizes the catalytic properties of different catalysts. All the In-containing samples exhibited high selectivity toward 1-phenyl-3-buten-1-ol. The as-prepared In–B amorphous alloy was more active

than the commercial In powder (Figure 5). Obviously, the higher reactivity may be attributed to both the higher S_{BET} and the enhanced intrinsic reactivity (see the R^{s} values in Table 1). This could be supported by the fact that an abrupt decrease in reactivity was observed for the In-B treated at 473 K for 2 h in an argon flow (Table 1), which was firstly due to the significant agglomeration of In-B nanoparticles at elevated temperature and, thus, decreasing S_{BET} and, secondly, the decrease in R^{S} resulted from the crystallization and decomposition of In-B amorphous alloy. The larger R^{S} of In–B amorphous alloy could be interpreted in terms of both the structural and electronic effects: (i) Structure effect: the unique short-range ordering but long-range disordering amorphous structure endowed In-B amorphous alloy with more highly unsaturated In active sites and stronger synergistic effect between these active sites, which may promote the adsorption of reactants and favor reactivity.^[14] (ii) *Electronic effect:* the aforementioned XPS spectra demonstrated the strong electronic interaction between In and B in the In-B amorphous alloy, making In electron-enriched while B is electron-deficient. The higher electron density on In active sites might benefit the formation of the radical anion intermediate through SET processes, which could promote the allylation reaction. The maximum yield of 1phenyl-3-buten-1-ol could reach 94% over the as-prepared In-B amorphous alloy, almost the same as that obtained by using the $PdCl_2(PPh_3)_2$ homogeneous catalyst (see Table 1).

Table 2 demonstrates that In–B was an active mediator for the Barbier-type allylation reactions of various aldehydes and allylic halides in water. The reactions of aldehydes with electron-withdrawing or electron-donating groups did not show obvious difference (entries 1–3 in Table 2). This means that the reaction is relatively insensitive to the electronic characteristics of the substituents under the present reaction condi-

Table 2. In-B mediated Barbier-type allylation of aldehyde.^[a]

R	Р	+	$x \xrightarrow{\text{In-B}} R$	OH
Entry	R	Х	Conversion [%]	Selectivity [%]
1	Н	Br	96	98
2	CH_3	Br	94	98
3	Cl	Br	97	97
4	Η	Cl	95	98

^[a] Reaction conditions: a mediator containing In (1.12 mmol), aldehyde (2.25 mmol), allyl halide (4.50 mmol), Al (0.540 g), H₂O (10.0 mL), T=323 K, reaction time = 120 min.

 Table 3. In-mediated Barbier-type allylation of acetophenone.^[a]



Entry	Catalyst	L	Time [h]	Conversion [%]	Selectivity [%]
1 ^[b]	In–B	B(pin)	12	90	93
2	In–B	Cl	12	58	98
3	In–B	Br	12	71	97
4	In–B	Br	24	90	94
5	In	Br	24	73	95
	powder				

^[a] Reaction conditions: a mediator containing In (1.12 mmol), acetophenone (2.00 mmol), allyl substance (3.00 mmol), Al (0.540 g), H₂O (10.0 mL), T=323 K.
^[b] T=303 K.

tions. Furthermore, In–B was even active for allylic chloride substrate, which could react with benzaldehyde to give the corresponding allylation product in high yield (entry 4 in Table 2).

To extend the scope of Barbier-type carbonyl allylation reaction, we examined the allylation of acetophenone in water (Table 3). The investigation started with the reaction of acetophenone and allylboronate (pin=pinacolyl) in water; the as-prepared In-B amorphous alloy gave a similarly high yield (84%) of 2phenyl-4-penten-2-ol (entry 1 in Table 3) to that reported by Kobayashi's group.^[15] Even if the desired product was obtained in high yield, the potential application is still limited due to the high cost of allylboronate. Clearly, with respect to cost concern, the use of simple allyl halides is appreciated. Further experiments showed that the as-prepared In-B amorphous alloy could mediate allylation of acetophenone with either allyl bromide or allyl chloride in moderate yields (entries 2 and 3 in Table 3). Most notably, by increasing the reaction time to 24 h, in the presence of In-B, allyl bromide reacted with acetophenone to yield the desired nucleophilic addition product in high yield (entry 4 in Table 3). Meanwhile, the as-prepared In-B amorphous alloy displayed enhanced reactivity over the commercial In powder (entry 5 in Table 3). Both the high dispersion of In active sites and the unique amorphous structure were likely responsible for the enhanced activity.

Conclusions

In summary, we have achieved the first synthesis of In–B amorphous alloy, which exhibited high activity and selectivity in water-medium Barbier-type carbon-

yl allylation reactions owing to the promotional effects from the high surface area, the unique amorphous alloy structure, as well as strong electronic interaction in the In–B alloy. This work might hold promise for new applications of amorphous alloys in catalysis besides hydrogenations and also offer opportunities to design efficient mediators for watermedium potentially cleaner organic synthesis.

Experimental Section

Catalyst Preparation

All of the chemicals used in this experiment were of analytical grade and used without further purification. In–B amorphous alloy was prepared by a chemical reduction method in the following procedure: a KBH₄ aqueous solution (2.5 mL, 2.0 M) was added dropwise into an InCl₃ aqueous solution (2.5 mL, 0.45 M) under vigorous stirring (> 800 rpm) at 283 K. After complete reaction, the black precipitate was washed free from Cl⁻ or K⁺ ions with deionized water until the pH reached 7, and finally soaked in water until the time of use.

Catalyst Characterization

The bulk composition was analyzed by means of ICP (Varian VISTA-MPX). The amorphous structure was determined by both XRD (Rigaku D/Max-RB with Cu Ka radiation) and SAED (JEOL JEM-2100). The crystallization process was followed by DSC (Shimadzu DSC-60) under an N2 atmosphere at the heating rate of 10 Kmin⁻¹. The surface morphology was observed by TEM (JEOL JEM-2100). The surface electronic states and surface composition were investigated by XPS (ULVAC-PHI PHI5000 VersaProbe using Al K α radiation), during which the In–B sample was dried and pretreated in situ in a pure Ar atmosphere to avoid oxidation. The BE values were calibrated by using C 1s =284.6 eV as a reference. N₂ adsorption-desorption isotherms were obtained at 77 K using a Quantachrome NOVA 4000e apparatus. S_{BET} was calculated by using the multiple-point BET method in the relative pressure range of $P/P_0 = 0.05$ -0.3.

Activity Tests

Allylation of aldehydes: In a typical experiment, aldehyde (2.25 mmol) and allyl halide (4.5 mmol) were added into water (10.0 mL). To this were added mediator (containing 1.12 mmol In) and Al powder (0.54 g), and the mixture was stirred vigorously at 323 K. Reaction samples were taken at regular intervals and monitored by GC (Agilent GC 1790 equipped with a HP-5 capillary column). After complete reaction, the mediator was recovered through centrifugation and subsequently washed thoroughly with ethyl acetate. After extraction with ethyl acetate, the product was analyzed by GC, from which the conversion of aldehyde and the selectivity to allylic alcohol were calculated.

Allylation of acetophenone: In a typical experiment, acetophenone (2.0 mmol) and allyl halide (3.0 mmol) were added into water (10.0 mL). To this were added mediator (containing 1.12 mmol In) and Al powder (0.54 g), and the mixture was stirred vigorously at 323 K. Reaction samples were taken at regular intervals and monitored by GC (Agilent GC 1790 equipped with a HP-5 capillary column). After complete reaction, the mediator was recovered through centrifugation and subsequently washed thoroughly with ethyl acetate. After extraction with ethyl acetate, the product was analyzed by GC, from which the conversion of acetophenone and the selectivity to allylic alcohol were calculated.

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References

- [1] W. R. Roush, in: *Comprehensive Organic Synthesis*, (Ed.: B. M. Trost), New York, Pergamon, **1991**, p 1.
- [2] A. Shuki, J. J. Shun, I. Yoshiyuki, Bull. Chem. Soc. Jpn. 1992, 65, 1736.
- [3] a) C. J. Li, *Chem. Rev.* 1993, *93*, 2023; b) T. H. Chan,
 C. J. Li, M. C. Lee, Z. Y. Wei, *Can. J. Chem.* 1994,72, 1181; c) C. J. Li, *Chem. Rev.* 2005, *105*, 3095.
- [4] a) F. Joh, Acc. Chem. Res. 2002, 35, 738; b) S. Narayan, J. Muldoon, M. G. Finn, V. V. Fokin, H. C. Kolb, K. B. Sharpless, Angew. Chem. 2005, 117, 3339; Angew. Chem. Int. Ed. 2005, 44, 3275; c) K. H. Shaughnessy, Eur. J. Org. Chem. 2006, 67, 1827; d) C. J. Li, L. Chen, Chem. Soc. Rev. 2006, 35, 68.
- [5] C. J. Li, T. H. Chan, Tetrahedron Lett. 1991, 32, 7017.
- [6] T. H. Chan, C. J. Li, J. Chem. Soc. Chem. Commun. 1992, 747.
- [7] a) J. Van Wonterghem, S. Mørup, C. J. W. Koch, S. W. Charles, S. Wells, *Nature* 1986, 322, 622; b) A. Molnar, G. V. Smith, M. Bartok, *Adv. Catal.* 1989, 36, 329; c) A. Baiker, *Faraday Discuss. Chem. Soc.* 1989, 87, 239; d) Y. Chen, *Catal. Today* 1998, 44, 3; e) J. F. Deng, H. X. Li, W. J. Wang, *Catal. Today* 1999, 51, 113.
- [8] A. Yokoyama, H. Komiyama, H. Inoue, T. Masumoto, H. M. Kimura, J. Catal. 1981, 68, 355.
- [9] S. Klein, J. A. Martens, R. Parton, K. Vercruysse, P. A. Jacobs, W. F. Maier, *Catal. Lett.* 1996, 38, 209.
- [10] F. Ye, K. Lu, J. Non-Cryst. Solids 2000, 262, 228.
- [11] P. Sen, M. S. Hegde, C. N. Rao, Appl. Surf. Sci. 1982, 10, 63.
- [12] H. Li, H. X. Li, W. L. Dai, W. J. Wang, Z. G. Fang, J. F. Deng, Appl. Surf. Sci. 1999, 152, 25.
- [13] a) H. Li, J. Liu, S. H. Xie, M. H. Qiao, W. L. Dai, H. X. Li, J. Catal. 2008, 259, 104; b) H. Li, Y. Wang, Q. F. Zhao, H. X. Li, Res. Chem. Intermed. 2009, 35, 779.
- [14] G. D. Angel, J. L. Benitez, J. Mol. Catal. 1994, 94, 409.
- [15] U. Schneider, M. Ueno, S. Kobayashi, J. Am. Chem. Soc. 2008, 130, 13824.