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Graphical Abstract

To create your abstract, type over the instructions in the template box below. Fonts or abstract dimensions should not be changed or altered.

Leave this area blank for abstract info. Acceptorless dehydrogenative synthesis of benzothiazoles and benzimidazoles from alcohols or aldehydes by heterogeneous Pt catalysts under neutral conditions Chandan Chaudhari, S. M. A. Hakim Siddiki, Ken-ichi Shimizu* Pt/Al₂O₃ (1 mol%) in N₂ 1.2 mmol NH₂ + OH or OH NH₂ + R H R H Pt/TiO₂ (1 mol%) in N_2 1 mmo 1.2 mmol

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dehydrogenative synthesis Acceptorless of benzothiazoles and benzimidazoles from alcohols or aldehydes by heterogeneous Pt catalysts under neutral conditions

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ABSTRACT

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Pt/Al₂O₃ and Pt/TiO₂ were effective catalysts for the synthesis of 2-substituted benzothiazoles

and benzimidazoles from 2-aminothiophenol and 1,2-phenylenediamine with alcohols or aldehydes under acceptor-free and additive-free conditions.

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Benzazoles such as benzothiazoles and benzimidazoles are considered as important class of chemicals in medicinal chemistry. In particular, 2-substituted benzothiazoles and benzimidazoles are of importance due to their pharmacological and biological activities.¹ The conventional synthetic method of 2-substituted benzothiazoles or 2-substituted benzimidazoles involves condensation of 2-aminothiophenols or 1,2phenelynediamines with carboxylic acids or their derivatives under acidic conditions or in the presence of dehydrating reagent. Although continuous efforts² have been focused on this method, it has serious drawbacks including low atom-efficiency and production of toxic salt wastes. The other important method is the condensation of aldehydes with 2-aminothiophenols or 1,2phenelynediamines, followed by oxidation by oxidants (H2acceptor) such as crotononitrile,^{3a} $(NH_4)_2S_2O_8$,^{3b} I_2/KI ,^{3c} H_2O_2/CAN ,^{3d} polymer supported hypervalent iodine,^{3e} or air.⁴ However, most of the methods suffer from the use of the stoichiometric oxidants,³ which results in low atom-efficiency. Use of alcohols as starting materials is also attractive because of wide availability of alcohols. There are reports on the synthesis of 2-substituted benzothiazoles or 2-substituted benzimidazoles from 2-aminothiophenols or 1,2-phenelydiamines with alcohols using stoichiometric amount of oxidants (MnO2, 5ª ®T3P/DMSO, 5b IBX⁵c) or H₂-acceptor^{3a} or air.⁶ Use of 2-nitroanilines^{7a} as a substrate and primary amines^{7b} as alkylating reagents are also reported. The most attractive method is the direct synthesis of benzazoles using alcohols (or aldehydes) in the absence of

Table 1 Synthesis of the benzothiazole by various catalysts.^a

SH 1 mmol	+ n-C ₇ H ₁₅ OH cataly 1.2 mmol reflux	st (1 mol%) ene (1.2 mL) K, N ₂ , 24 h	−N + 2H ₂ +H ₂ O `S ⊂ n-C ₇ H ₁₅
Entry	Catalysts	Conv.(%)	GC yield (%)
1	Pt/Al ₂ O ₃	99	97
2	Pd/Al ₂ O ₃	99	89
3	Ir/Al ₂ O ₃	99	57
4	Cu/Al ₂ O ₃	99	48
5	Re/Al ₂ O ₃	99	46
6	Rh/Al ₂ O ₃	99	44
7	Ru/Al ₂ O ₃	99	34
8	Ag/Al ₂ O ₃	99	13
9	Ni/Al ₂ O ₃	43	0
10	Al ₂ O ₃ (197 mg)	30	0
11	Pt/Nb ₂ O ₅	99	64
12	Pt/CeO ₂	99	19
13	Pt/SiO ₂ -Al ₂ O ₃	99	12
14	Pt/HBEA	99	10
15	Pt/La ₂ O ₃	99	5
16	Pt/MgO	99	0
17	Pt/ZrO ₂	99	0
18	Pt/TiO ₂	99	0
19	Pt/SiO ₂	99	0

^a Conversion and yield are based on 2-aminothiophenol.

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oxidants via acceptorless dehydrogenative coupling.⁸ Recently, homogeneous Ru,^{8a-c} Ir^{8d} and Fe^{8e} catalysts and a heterogeneous Ru catalyst^{8f} have been reported to be effective for the synthesis of benzazoles from alcohols under acceptor-free conditions. However, the homogeneous systems^{8a-e} require more than stoichiometric amount of basic additives or excess amount of alcohols, which results in low atom-efficiency. As a part of our studies on heterogeneous Pt catalysis for the acceptorless dehydrogenative coupling reactions of alcohols,⁹ we report herein the Pt catalyzed dehydrogenative synthesis of 2-substituted benzothiazoles and benzimidazoles directly from alcohols or aldehydes under acceptor-free and additive-free conditions.

Table 2 Synthesis of 2-substituted benzothiazoles from 2-
aminothiophenol with alcohols or aldehydes by Pt/Al ₂ O _{3.}



^b 3 h.

Initially, we investigated acceptorless synthesis of 2substituted benzothiazole from 2-aminothiophenol and 1-octanol as a model reaction for optimization of catalysts and conditions. Note that previous successful catalytic systems^{8b,e} for this reaction were not effective for the reaction with aliphatic alcohols probably because of low reactivity of them. Table 1 summarizes the results of the catalyst screening test under the same reaction conditions (reflux in mesitylene under N₂ for 24 h) using 1 mol% of transition metal (Pt, Pd, Ir, Cu, Re, Rh, Ru, Ag, Ni)-loaded Al₂O₃ pre-reduced under H₂ at 500 °C for 0.5 h. The Pt-loaded Al₂O₃ (Pt/Al₂O₃, entry 1) showed the highest yield (97%) of 2-substituted benzothiazole. Pd/Al₂O₃ (entry 2) gave good yield (89%), and the Ir, Cu, Re, Rh, Ru and Ag catalysts (entries 3-7) showed low to moderate yields (13%-57%) of the benzothiazole. Al₂O₃ (entry 10) and Ni/Al₂O₃ (entry 9) did not give the product. Then, we studied the support effect on the activity of Pt-loaded catalysts (entries 1, 11-19). Clearly, Al₂O₃ was the most effective support for this reaction, and Nb₂O₅, CeO₂, SiO₂-Al₂O₃, HBEA zeolite and La₂O₃ gave low to moderate yields (5-64%). The Pt catalysts loaded on MgO, ZrO₂, TiO₂ and SiO₂ showed did not give the benzothiazole. The Pt/Al₂O₃ catalyst with higher Pt loading (5 wt%) gave lower yield (40%)

than 1 wt% Pt/Al₂O₃. The reaction with 1 wt% Pt/Al₂O₃ in refluxing *o*-xylene gave lower yield (75%) that that in refluxing mesitylene. In summary, use of 1 wt% Pt/Al₂O₃ the refluxing mesitylene is the best conditions for the synthesis of the benzothiazole from 2-aminothiophenol and 1-octanol. This is the first successful example of acceptorless dehydrogenative synthesis of 2-substituted benzothiazole from 2-aminothiophenol and less reactive aliphatic alcohol. After the reaction of entry 1 in Table 1, Pt/Al₂O₃ was separated from the mixture by centrifugation, followed by drying at 90 °C for 12 h and by H₂-reduction at 500 °C for 0.5 h. The second cycle by the recovered catalyst showed lower yield (66%) than the first cycle.

Table 2 shows general applicability of the dehydrogenative from benzothiazoles synthesis of 2-substituted 2aminothiophenol and 1.2 equiv. of alcohols or aldehydes using Pt/Al2O3 containing 1 mol% of Pt with respect to 2aminothiophenol. After 24 h of the reaction, the linear aliphatic alcohols (entries 1 and 2) and benzyl alcohol (entry 3) were converted to the corresponding 2-substituted benzimidazoles in moderate to high yields. The method was also effective for the reaction with various aldehydes. After 3 h of the reaction, aliphatic aldehydes (entries 4,5), an aldehyde with C=C group (entry 6) and benzaldehydes (entries 7,8) reacted with 2aminothiophenol to give the corresponding 2-substituted benzimidazoles in moderate to high yields.

Table 3 Synthesis of the benzimidazole by various catalysts.^a

	+ n-C ₇ H ₁₅ OH me	alyst (1 mol%) sitylene (1.2 mL)	N + 2H ₂ +H ₂ O
1 mmol	יי 1.2 mmol	1 ₂ , renux, 24 fi	Н
Entry	Catalysts	Conv. (%)	GC yield (%)
1	Pt/TiO ₂	99	94
2	Ir/TiO ₂	99	80
3	Pd/TiO ₂	87	45
4	Rh/TiO ₂	59	34
5	Ru/TiO ₂	39	7
6	Re/TiO ₂	67	0
7	Ag/TiO ₂	70	0
8	Cu/TiO ₂	65	0
9	Ni/TiO ₂	57	0
10	TiO ₂ (197 mg)	21	0
11	Pt/ZrO ₂	99	60
12	Pt/La ₂ O ₃	99	46
13	Pt/Al ₂ O ₃	99	30
14	Pt/SiO ₂ -Al ₂ O ₃	99	20
15	Pt/MgO	99	0
16	Pt/HBEA	99	0
17	Pt/Nb ₂ O ₅	99	0
18	Pt/CeO ₂	99	0
19	Pt/SiO ₂	99	0

^a Conversion and yield are based on 1,2-phenylenediamine.

Next, we studied the direct synthesis of 2-substituted benzimidazoles from 1,2-phenylenediamine and alcohols or aldehydes. We adopted the reaction of 1,2-phenylenediamine (1 mmol) with 1-octanol (1.2 mmol) as a model reaction, because only one catalytic method was reported to be effective for the reaction with aliphatic alcohols.^{8d} Table 3 summarizes the results of the catalyst screening under the same conditions (reflux in mesitylene under N₂ for 24 h). The support screening tests for Pt catalysts showed that Pt/TiO₂ (entry 1) showed higher yield of the 2-substituted benzimidazole than the other Pt-loaded catalysts (entries 11-19). Then, we tested various transition metal-loaded TiO₂ catalysts. Ir/TiO₂ gave good yield of 80%, and other

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catalysts gave moderate to low yields (entries 3-9). TiO₂ itself was inert (entry 10). The Pt/TiO₂ catalyst with higher Pt loading (5 wt%) gave lower yield (83%) than 1 wt% Pt/TiO₂. The reaction with 1 wt% Pt/TiO₂ in refluxing *o*-xylene gave lower yield (65%) that that in refluxing mesitylene. In summary, use of 1 wt% Pt/Al₂O₃ the refluxing mesitylene is the best conditions, Pt/TiO₂ was found to be the most effective catalyst for the dehydrogenative synthesis of the 2-substituted benzimidazole from 1,2-phenylenediamine and 1-octanol. After the reaction of entry 1 in Table 3, Pt/TiO₂ was separated from the mixture by centrifugation, followed by drying at 90°C for 12 h and by H₂–reduction at 500 °C for 0.5 h. The second cycle by the recovered catalyst showed lower yield (89%) than the first cycle.

As shown in the eqn. (1), the reaction with 0.1 mol% of the Pt/TiO_2 catalyst for 52 h resulted in 97% yield, corresponding to the turnover number (TON) of 970 with respect to total Pt atoms in the catalyst. The TON of 970 is more than 2 times higher than the state-of-the-art system using a homogeneous Ir catalyst with KO'Bu reported by Kempe and co-workers.



With the most effective catalyst, Pt/TiO_2 , we investigated substrate scope of the dehydrogenative benzimidazoles synthesis. Table 4 shows the yields of the 2-substituted benzimidazoles from the reaction of 1,2-phenylenediamine with 1.2 equiv. of alcohols or aldehydes using 1 mol% of Pt/TiO_2 . Aliphatic alcohols (entries 1-3), an aliphatic aldehyde (entry 4), benzaldehydes (entries 4,5) and pyridine-3-carbaldehyde (entry 7) were converted to the desired 2-substituted benzimidazoles in good to high yields.

Table 4 Synthesis of 2-substituted benzimidazoles from 1,2-phenylenediamine and alcohols or aldehydes by Pt/TiO₂.

1 mmol	$\begin{array}{c} 2 \\ + \\ 2 \\ 2 \end{array} \begin{array}{c} 0 \\ + \\ - \\ - \\ 1.2 \\ - \\ 1.2 \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ $	Pt/TiO ₂ (1 mol%) mesitylene (1.2 mL) reflux, N ₂ , 24 h	
Entry	Alcohol Aldehyde	Product	Yield (%) ^a
1	n-C ₇ H ₁₅ OH	N N H n-C ₇ H ₁₅	87
2	n-C ₉ H ₁₉ OH	N n-C ₉ H ₁₉	82
3	ОН		60
4 ^b	n-C7H15-CHO	N n-C7H15	90
5 ^c	СНО	N N H	78
6 ^c	СНО		75
7°	CHO		54

^a Isolated yield based on 2-aminothiophenol.

^b 3 h.



Scheme 1 A plausible mechanism for the synthesis of benzimidazoles and benzothiazoles.

Considering the previous reports on acceptorless dehydrogenative synthesis of benzazole derivatives from alcohols⁸ and our reports on acceptorless dehydrogenative coupling reactions by heterogeneous Pt catalysts,⁹ the present system can proceed via a pathway shown in Scheme 1. The reaction begins with Pt-catalyzed dehydrogenation of alcohols to aldehydes, which undergoes condensation with 2aminothiophenol or 1,2-phenylenediamine to afford saturated intermediates 2 via imine 1. Finally, Pt-catalyzed dehydrogenation of 2 gives the unsaturated product 3. A kinetic study under the conditions in Table 4 (entries 1, 4) showed that the initial formation rate of the benzothiazole by the Pt/TiO₂catalyzed reaction of 1,2-phenylenediamine with n-octanal was 1.7 times higher than that with 1-octanol. This result is consistent with the proposed pathway assuming that the dehydrogenation of alcohols is a relatively slow step.

In summary, we have developed two heterogeneous catalytic systems for the acceptorless dehydrogenative synthesis of 2-substituted benzazoles under additive-free (neutral) conditions. Pt/Al_2O_3 is effective for synthesis of 2-substituted benzothiazoles from 2-aminothiophenol and alcohols/aldehydes, and Pt/TiO_2 is effective for synthesis of 2-substituted benzimidazoles from 2-phenylenediamine and alcohols/aldehydes.

Experimental

Commercially available organic compounds (from Tokyo Chemical Industry) were used without further purification. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA⁺-1 (Frontier Laboratories Ltd.) using nitrogen and helium as the carrier gas.

γ-Al₂O₃ was prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. TiO₂ (JRC-TIO-4), CeO₂ (JRC-CEO-3), MgO (JRC-MGO-3), H⁺-type BEA zeolite (HBEA, SiO₂/Al₂O₃ = 25±5, JRC-Z-HB25) and SiO₂- Al_2O_3 (JRC-SAL-2, $Al_2O_3 = 13.75$ wt%) were supplied from Catalysis Society of Japan. ZrO₂ and La₂O₃ were prepared by calcination (500 °C, 3 h) of hydroxide of Zr and La, which were prepared by hydrolysis of ZrO(NO₃)₂·2H₂O and La(NO₃)₃·6H₂O with aqueous NH_4OH solution (1.0 mol dm⁻³), followed by filtration of precipitate, washing with distilled water and drying at 100 °C for 12 h. Nb₂O₅ was prepared by calcination of niobic acid (CBMM) at 500 °C for 3 h. Precursor of 1 wt% Pt/Al₂O₃ or 1 wt% Pt/TiO₂ was prepared by impregnation method; a mixture of the support oxide and aqueous HNO₃ solution of Pt(NH₃)₂(NO₃)₂ (Furuya Metal Co, Ltd.) was evaporated at 50 °C, followed by drying at 90 °C for 12 h. Pre-reduced catalyst, named Pt/Al₂O₃ and Pt/TiO₂, were prepared by reduction of the precursors in a pyrex tube under a flow of H_2 (20 cm³ min⁻¹) at 500 °C for 0.5 h. By using various supports, several pre-reduced Pt catalysts (Pt = 1 wt%) were also prepared by the same method. Al₂O₃ or TiO₂-supported metal catalysts, M/Al₂O₃ or M/TiO₂ (M = Ni, Cu, Ru, Pd, Ag, Re, Ir) with metal loading of 1 wt% were prepared by impregnation method in a similar manner as Pt/Al₂O₃ or Pt/TiO₂ using aqueous solution of metal nitrates (Ni,

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Cu, Ag), RuCl₃, IrCl₃, NH₄ReO₄ or an aqueous HNO₃ solution of $Pd(NH_3)_2(NO_3)_2$ (Kojima Chemicals Co, Ltd.).

For the synthesis of 2-substituted benzothiazoles, Pt/Al_2O_3 (196 mg, 0.01 mmol of Pt) was used as the standard catalyst. After the pre-reduction at 500 °C, we carried out catalytic tests using a batch-type reactor without exposing the catalyst to air as follows. A mixture of 2-aminothiophenol (1 mmol) and aldehydes or alcohols (1.2 mmol) with *n*-tetradecane (0.2 mmol) in mesitylene (1.2 mL) was injected to the pre-reduced catalyst inside the reactor (cylindrical pyrex tube) through a septum inlet, followed by filling N₂. Then, the resulting mixture was magnetically stirred for 24 h for alcohols under reflux condition. The products was analyzed and confirmed by GC and GC-MS. The crude product was isolated by column chromatography using silica gel 60 (spherical, 63-210 µm, Kanto Chemical Co. Ltd.) with *n*-hexane/ethyl acetate as the eluting solvent, followed by analyses by GCMS and ¹H and ¹³C NMR.

For the synthesis of 2-substituted benzimidazoles, Pt/TiO_2 (196 mg, 0.01 mmol of Pt) was used as the standard catalyst. The reaction procedure is the same as that for the synthesis of 2-substituted benzothiazoles.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://

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