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Author(s)	Siddiki, S. M. A. H.; Touchy, Abeda S.; Chaudhari, Chandan; Kon, Kenichi; Toyao, Takashi; Shimizu, Ken-ichi
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Synthesis of 2,5-disubstituted pyrroles via dehydrogenative condensation of secondary alcohols and 1,2-amino alcohols by supported platinum catalysts

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S. M. A. H. Siddiki,^a Abeda S. Touchy,^a Chandan Chaudhari,^a Kenichi Kon,^a Takashi Toyao,^{a,b} Ken-ichi Shimizu^{*a,b}

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Direct synthesis of 2,5-disubstituted pyrroles has been achieved via acceptorless dehydrogenative heterocyclization of 1,2-aminoalcohols and secondary alcohols by utilizing a heterogeneous carbon-supported Pt catalyst (Pt/C). The optimized method gave 92 % yield of 2-ethyl-5-phenyl-1*H*-pyrrole as a desired product from 2-amino-1-butanol and 1-phenylethanol in the presence of 0.1 mol% of Pt/C and 1.1 equiv. of KO^tBu. It has been revealed that Pt/C demonstrates superior catalytic activity to a number of catalysts tested in this study including other transition metal-loaded carbon and various metal-oxide-supported Pt catalysts. In addition, turnover number (TON) obtained in the present system was found to be higher than those obtained in previously-reported catalytic systems. It is significant that the Pt/C catalyst could be recycled as a heterogeneous catalyst without significant loss in the activity and showed wide substrate scope for the 2,5-disubstituted pyrrole forming process.

Introduction

Pyrroles are key compounds in organic synthesis¹ and industrial production of pharmaceutical compounds with various biological activities¹ as well as functional materials used for solar cells and batteries.² Classical synthetic methods of pyrroles such as Hantzsch and Paal–Knorr reactions¹ and recent catalytic methods^{1,3a–h} suffer from several problems including multistep procedure or difficult availability of the starting compounds. Following the pioneering works,^{3i,j} several groups^{4–8} have recently reported new synthetic protocols to get pyrroles from easily available starting materials. The protocols employ acceptorless dehydrogenative coupling methodology.⁹ Three groups (Kempe,⁴ Saito,⁵ Milstein⁶) discovered new catalytic methods for direct synthesis of pyrroles through dehydrogenative condensation of 1,2-amino alcohols with secondary alcohols (or ketones) using homogeneous Ir or Ru catalysts with a basic additive (KO^tBu). Beller et al.⁷ also developed the direct dehydrogenative

synthesis of pyrroles from benzylic ketones, vicinal diols, and amines by utilizing a homogeneous Ru catalyst. However, these systems require elaborate homogeneous catalysts and have difficulties in catalyst recycling. From the viewpoint of sustainable chemistry and for industrial applications, these processes should be carried out by a recyclable heterogeneous catalyst which is advantageous for easy product separation and recycling of the catalysts. In this sense, Kempe's group developed a new heterogeneous catalyst, Ir@SiCN, that was effective for acceptorless dehydrogenative synthesis of pyrroles from 1,2-amino alcohols and secondary alcohols with KO^tBu.⁸ Although the heterogeneous system was successfully developed, the catalyst preparation could be complicated since they made a precursor by themselves and the preparation procedure requires several steps. Therefore, development of versatile heterogeneous catalytic systems is desired for easy access to this organic synthesis and its practical applications. We have previously reported a series of studies on acceptorless dehydrogenation of alcohols^{10a} and acceptorless dehydrogenative coupling reactions of alcohols^{10b–e} promoted by heterogeneous Pt catalysts. The Pt catalysts are synthesized by a facile impregnation method by employing commercially-available Pt precursors and carbon supports. In addition, these catalytic systems show high versatility toward various dehydrogenation reactions with wide substrate scopes, and thus, it is expected that our Pt/C-catalyzed system could be utilized for acceptorless

^a Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan
E-mail: kshimizu@cat.hokudai.ac.jp

^b Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520, Japan

† Footnotes relating to the title and/or authors should appear here.

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dehydrogenative synthesis of pyrroles. The observations made in this effort show that this expectation is correct. Specifically, we report herein the first example of Pt-catalyzed acceptorless dehydrogenative synthesis of 2,5-substituted pyrroles from 1,2-amino alcohols and secondary alcohols. This new method shows a good catalyst reusability and higher turnover number (TON) than previously-reported catalysts.^{4,6,8}

Results and discussion

The catalysts were screened by employing the reaction of 2-amino-1-butanol (**1a**) and 1.5 equiv. of 1-phenylethanol (**2a**) with 1.1 equiv. of KOtBu in diglyme at 125 °C for 4 h under N₂ as a model system. Table 1 shows conversion of **1a** and the yield of 2-ethyl-5-phenyl-1H-pyrrole (**3a**) based on **1a**. Under the present condition, no reaction took place without catalysts (entry 1). Active carbon itself (entry 2) and platinum oxides-loaded carbon (PtO_x/C in entry 3) were also inactive for the reaction. In contrast, metallic Pt-loaded carbon (Pt/C), pre-reduced in H₂ at 300 °C, gave 92% yield (entry 5). Once the

pre-reduced Pt/C was exposed to air at room temperature, the air-exposed Pt/C (Pt/C-air in entry 4) showed lower yield (60%) than Pt/C. Entries 5–13 compare the results for various transition metal-loaded carbon catalysts, pre-reduced in H₂ at 300 °C, containing 0.01 mmol of metals (1 mol% with respect to **1a**). Among the catalysts tested (Pt, Re, Ir, Rh, Pd, Ru, Ni, Co, Cu), Pt-loaded carbon (Pt/C) showed the highest yield of the desired product **3a**. Other precious metals (Re, Ir, Rh, Pd, Ru) gave moderate to low yields of 48–18%, and base metals (Ni, Co, Cu) gave only 1% yields. Next, the catalytic property of Pt/C was compared with various metal oxides-supported Pt catalysts (entries 14–23). Pt/C showed the higher yield (92%) than the other Pt catalysts. For example, Pt-loaded Al₂O₃, CeO₂, TiO₂, HBEA zeolite, Nb₂O₅, ZrO₂ and SiO₂ gave moderate to low yields of 61–20%. Entries 5 and 24–26 compare the results for different Pt-loaded carbon catalysts. The Pt-loaded different carbon materials (Ketjenblack EC-600JD in entry 24; Vulcan-XC72 in entry 25) and a commercial Pt catalyst from Sigma-Aldrich (Pt/C_{SA}, entry 26) showed slightly lower yields (83–90%)

Table 1 Catalyst screening.

Entry	Catalysts	1a conv. (%) ^a	3a yield (%) ^a
1	blank	0	0
2	C ^b	3	0
3	PtO _x /C	4	0
4	Pt/C-air ^c	72	60
5	Pt/C	100	92
6	Re/C	56	48
7	Ir/C	44	35
8	Rh/C	33	26
9	Pd/C	29	21
10	Ru/C	25	18
11	Ni/C	4	1
12	Co/C	3	1
13	Cu/C	3	1
14	Pt/Al ₂ O ₃	72	61
15	Pt/CeO ₂	59	51
16	Pt/TiO ₂	43	35
17	Pt/HBEA	40	34
18	Pt/Nb ₂ O ₅	28	22
19	Pt/ZrO ₂	27	20
20	Pt/SiO ₂	29	20
21	Pt/SiO ₂ -Al ₂ O ₃	19	14
22	Pt/MgO	11	6
23	Pt/SnO ₂	3	1
24	Pt/C _{KB}	100	83
25	Pt/C _{VX}	100	90
26	Pt/C _{SA}	100	85

^aGC yields. ^b 0.039 g. ^cPre-reduced Pt/C was exposed to air at room temperature for 0.5 h.

Table 2 Optimization of reaction conditions.

Entry	1a (mmol)	2a (mmol)	base (x mmol)	Solvent	3a yield (%) ^a
1	1.0	1.0	-	diglyme	0
2	1.0	1.0	KOtBu (0.5)	diglyme	41
3	1.0	1.0	KOtBu (1.0)	diglyme	67
4	1.0	1.0	KOtBu (1.1)	diglyme	75
5	1.0	1.0	KOtBu (1.5)	diglyme	71
6	1.0	0.5	KOtBu (1.1)	diglyme	39
7	1.0	1.25	KOtBu (1.1)	diglyme	83
8	1.0	1.5	KOtBu (1.1)	diglyme	92
9	1.0	2.0	KOtBu (1.1)	diglyme	84
10 ^b	1.0	1.5	KOtBu (1.1)	toluene	81
11 ^b	1.0	1.5	KOtBu (1.1)	1,4-dioxane	73
12	1.0	1.5	KOtBu (1.1)	<i>o</i> -xylene	78
13	1.0	1.5	KOtBu (1.1)	mesitylene	75
14	1.0	1.5	K ₂ CO ₃ (1.1)	diglyme	13
15	1.0	1.5	Cs ₂ CO ₃ (1.1)	diglyme	21
16	1.0	1.5	NaOH (1.1)	diglyme	47
17	1.0	1.5	NaOMe (1.1)	diglyme	39
18	1.0	1.5	KOH (1.1)	diglyme	51

^a GC yields. ^b reflux conditions.

than the Pt/C catalyst developed in this study (entry 5; the carbon support was supplied by Kishida Chemical). This result indicates that the activity of Pt-loaded carbon catalysts does not markedly depend on the type of the carbon and preparation methods. Hereafter the Pt/C catalyst in entry 5 is used as the standard Pt/C catalyst. Recently, we have reported detailed study on the structure of the Pt/C.^{10e} The results demonstrated that Pt nanoparticles in the Pt/C catalyst exist in the metallic state and have average particle size of 4.4 nm.

In order to optimize the reaction conditions such as amount of reactants, effects of bases and solvents for the pyrrole synthesis, various reactions were carried out over Pt/C for 4 h. The results are given in Table 2. We tested the reaction of 1 mmol of **1a** with 1 mmol of **2a** in diglyme at 125 °C with different amount of KOtBu (entries 1-5). The product **3a** was not obtained in the absence of KOtBu (entry 1). This indicates that the base is indispensable for the reaction. The addition of 1.1 equiv. of KOtBu gave the highest yield (entry 4). The reaction at different temperatures (results not shown) showed that the lower (105 °C) and higher (162 °C) temperatures gave lower yields (49% and 64%) than the standard temperature (75% yield at 125 °C). In the presence of the optimal amount (1.1 mmol) of KOtBu, the reactions with different amount (0.5–2.0 equiv.) of 1-phenylethanol (**2a**) were compared in entries 4 and 6–9. It was found that 1.5 equiv. of **2a** (entry 8) gave the highest yield of **3a** based on **1a**. For the reaction of 1 mmol of **1a** and 1.5 equiv. of **2a** in the presence of 1.1 equiv. of KOtBu, we tested the solvent effect (entries 8 and 10–13). The result shows that diglyme (entry 8) would serve as the best solvent. The reaction with various basic additives (entries 8, 14–18) showed that KOtBu (entry 8) was more effective than other bases such as K₂CO₃, Cs₂CO₃, NaOH, NaOMe and KOH.

Detailed catalytic properties of the Pt/C-catalyzed system were further investigated with the optimized conditions. Fig. 1 shows the results of catalyst recycling experiments. After completion of the first run, 2-propanol (3 mL) was added to the reaction mixture and the catalyst was separated by centrifugation, followed by washing the catalyst with water (1 × 3 mL) and acetone (3 × 3 mL), drying at 100 °C for 3 h and by

H₂-reduction at 300 °C for 0.5 h. The recovered Pt/C catalyst showed high yield (88–92%) for the next three cycles. ICP-AES analysis of the filtrate after the first cycle showed that the content of Pt in the solution was below the detection limit. These results demonstrate that the present catalytic system is able to be recycled and offer advantages as a heterogeneous catalytic process even under the basic reaction condition. Furthermore, TON of this system was investigated in a gram scale synthesis of **3a**. The reaction of 10 mmol of **1a** and 15 mmol of **2a** was carried out using small amount of the Pt/C catalyst in this attempt. As shown in eqn. (1), the reactions with 0.03 mol% of Pt/C for 96 h resulted in 83% yield, corresponding to TON of 2767. This TON is larger than those for previous homogeneous Ir (TON=1860)⁴ and Ru (TON=150)⁶ catalysts and a heterogeneous Ir catalyst (TON=260)⁸ for the same reaction.

Table 3 demonstrates substrate scope of the dehydrogenative synthesis of 2,5-disubstituted pyrroles from 1,2-amino alcohols (**1**) and 1.5 equiv. of secondary alcohols (**2**) using Pt/C containing 0.1 mol% of Pt with respect to 1,2-amino alcohols. Entries 1–10 summarize the results for the reaction of 2-amino-1-butanol (**1a**) with various secondary alcohols. 1-Phenylethanol (entry 1) and its derivatives with electron-donating and withdrawing groups (methyl, methoxy, chloro) at *p*-positions (entries 2–4) were converted to the corresponding pyrroles with good to high yields (78–92%). 1-(2-Naphthyl)ethanol (entry 5) and a cyclic aliphatic alcohol (entry 6) were also transformed to the corresponding pyrroles with moderate to high yields (64, 92%). An alcohol with C=C double bond, 6-methyl-5-hepten-2-ol (entry 7), was converted to the corresponding pyrrole with the C=C group in 76% yield. The reaction of different aminoalcohols such as 2-amino-3-methyl-1-butanol (**1b**, entries 8–12), (*R*)-2-amino-3-methyl-1-butanol (**1c**, entries 13, 14) and (*R*)-(-)-2-amino-2-phenyl-ethanol (**1d**, entries 15–18) with various secondary alcohols resulted in formation of the corresponding pyrroles with moderate to high yields (63–91%).

Fig. 1. Catalyst reuse for synthesis of **3** from **1** and **2** by Pt/C under the conditions for entry 8 in Table 2.

Table 3. Synthesis of 2,5-disubstituted pyrroles by supported Pt catalysts.^a

Entry	1	2	Product	Yield (%) ^b
1	1a			92
2	1a			90
3	1a			86
4	1a			78
5	1a			92
6 ^c	1a			64
7	1a			76
8	1b			79
9	1b			81
10	1b			84
11 ^c	1b			91

12	1b			67
13	1c			88
14	1c			84
15	1d			65
16	1d			74
17	1d			63
18	1d			78

^a Conditions: A mixture of 1 mmol 1,2-amino alcohols (**1**), 1.5 mmol secondary alcohol (**2**), 1.1 mmol KOtBu and 0.1 mol% Pt/C in 1.5 mL diglyme was heated at 125 °C for 18 h under N₂. ^b GC yields. ^c 24 h

Time course of the reaction of **1a** and **2a** (result not shown) showed a profile characteristic to a consecutive reaction mechanism via acetophenone; acetophenone formed at an initial induction period was gradually consumed to give the product **3a**. Actually, the model reaction of **1a** and acetophenone in the presence of Pt/C and KOtBu under N₂ for 4 h resulted in the formation of **3a** in 70% yield as shown in eqn. (2). As shown in eqn. (3), the same reaction in the absence of Pt/C and KOtBu did not give the pyrrole **3a** but gave 2-(1-phenyl-ethylideneamino)-1-butanol (**4a**) in 55% GC yield. Also, the reaction of **1a** and **2a** by Pt/C in the absence of KOtBu, shown in eqn. (4), did not give the pyrrole **3a**; the reaction resulted in 25% yield of acetophenone and 16% yield of **4a**.

Scheme 1 A possible reaction pathway.

Taking account of the results obtained above and the previous mechanistic proposals for the acceptorless dehydrogenative synthesis of pyrroles from 1,2-amino alcohols and secondary alcohols,^{4,6,8} we propose a possible reaction pathway of the present catalytic reaction in Scheme 1 adopting the reaction of **1a** and **2a** as an example. The reaction begins with Pt-catalyzed dehydrogenation of secondary alcohol (**2a**) to ketone, which then undergoes condensation with 1,2-amino alcohol (**1a**) to afford 2-(1-phenylethylideneamino)-1-butanol (**4a**) as an intermediate. The intermediate **4a** undergoes Pt-catalyzed dehydrogenation followed by base-catalyzed condensation to give the 2,5-disubstituted pyrrole **3a**. The dehydrogenation steps may be also accelerated by the basic co-catalyst, KOtBu, via activation of OH groups in **2a** and **4a**.

Conclusions

Pt/C-based heterogeneous catalytic system has been found to be effective for direct synthesis of 2,5-disubstituted pyrroles from 1,2-amino alcohols and secondary alcohols in the presence of KOtBu as a base. The catalytic system involves acceptorless dehydrogenation of alcohols and condensation reactions. Observations made in studies of the substrate scope demonstrate that Pt/C is capable of synthesizing a wide range of pyrroles from 1,2-amino alcohols and secondary alcohols. In addition, the developed system would provide advantages that the catalyst is prepared by a simple impregnation method and can be reused as a heterogeneous catalyst without significant loss in the catalytic activity. Furthermore, the system showed higher TON than previously-reported systems. These findings will offer a simple and sustainable synthetic method for the pyrroles.

Experimental

Commercially available organic compounds (from Tokyo Chemical Industry, Sigma-Aldrich, Kishida Chemical) 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.

The standard carbon support (296 m² g⁻¹, Kishida Chemical) and other carbon materials (C_{KB} = Ketjenblack EC-600JD, Lion, 1310 m² g⁻¹; C_{VX} = carbon black, Vulcan XC72, 210 m² g⁻¹) were commercially supplied. γ-Al₂O₃ was prepared by calcination of γ-AlOOH (Catapal B from Sasol) at 900 °C for 3 h. CeO₂ (JRC-

CEO3, 81 m² g⁻¹), TiO₂ (JRC-TiO-4) and H⁺-type BEA zeolite (HBEA, SiO₂/Al₂O₃ = 25±5, JRC-Z-HB25), MgO (JRC-MGO-3), SiO₂-Al₂O₃ (JRC-SAL-2) were supplied by Catalysis Society of Japan. Nb₂O₅ was prepared by calcination of niobic acid (supplied from CBMM) at 500 °C for 3 h. ZrO₂ was prepared by hydrolysis of zirconium oxynitrate 2-hydrate by an aqueous NH₄OH solution, followed by filtration, washing with distilled water, drying at 100 °C for 12 h, and by calcination at 500 °C for 3 h. SiO₂ (Q-10, 300 m² g⁻¹) was supplied from Fuji Silysia Chemical Ltd. SnO₂ was prepared by calcination of H₂SnO₃ (Kojundo Chemical Laboratory Co., Ltd.) at 500 °C for 3 h.

The precursor of Pt/C was prepared by impregnation method; a mixture of carbon and an aqueous HNO₃ solution of Pt(NH₃)₂(NO₃)₂ was evaporated at 50 °C, followed by drying at 90 °C for 12 h. Before each catalytic experiment, the Pt/C catalyst with Pt loading of 5 wt% was prepared by pre-reduction of the precursor in a Pyrex tube under H₂ flow (20 mL min⁻¹) at 300 °C for 0.5 h. Other supported Pt catalysts with Pt loading of 5 wt% were prepared by the same method. M/C (M= Re, Ir, Rh, Pd, Ru, Ni, Co, Cu) catalysts with metal loading of 5 wt% were prepared by the similar manner as for Pt/C using aqueous solution of NH₄ReO₄, IrCl₃·nH₂O, RuCl₃ or metal nitrates (for Ni, Cu, Co) or aqueous HNO₃ solution of Rh(NO₃)₃ or Pd(NH₃)₂(NO₃)₂. A commercial Pt-loaded carbon catalyst with Pt loading of 5 wt%, named Pt/C_{SA}, was purchased from Sigma-Aldrich.

Typical procedure of catalytic reactions is as follows. After the pre-reduction, Pt/C (39 mg; 1 mol% Pt with respect to **1a**) in the closed glass tube sealed with a septum inlet was cooled to room temperature under N₂. Then, 1 mmol of 2-amino-1-butanol (**1a**), 1.5 mmol of 1-phenylethanol (**2a**) and *n*-dodecane (0.2 mmol) in 1.5 mL diglyme were injected to the glass tube through the septum inlet. The septum was removed, and KOtBu (1.1 mmol) and a magnetic stirrer bar were put in the tube followed by filling N₂ through the septum inlet. Then, the resulting mixture was heated at 125 °C under stirring. The conversion of **1a** and yields of the products (based on **1a**) were determined by GC using *n*-dodecane as an internal standard adopting the GC sensitivity estimated using the isolated products or commercial products. After the reactions in Table 3, substrates, solvent and byproducts were removed by column chromatography with silica gel 60 (spherical, 63-210 μm, Kanto Chemical Co. Ltd.) using hexane/ethylacetate (20:1) as eluting solvent, and the products were identified by ¹H and ¹³C NMR analyses as well as GC-MS equipped with the same column as GC analyses.

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Notes and references

- (a) V. Estévez, M. Villacampa and J. C. Menéndez, *Chem. Soc. Rev.*, 2014, **43**, 4633; (b) V. Bhardwaj, D. Gumber, V. Abbot, S. Dhiman and P. Sharma, *RSC Adv.*, 2015, **5**, 15233.
- (a) M. C. De Jesus, Y. Fu and R. A. Weiss, *Polym. Eng. Sci.*, 1997, **37**, 1936; (b) J. R. Reynolds, P. A. Poropatic and R. L. Toyooka, *Macromolecules*, 1987, **20**, 958; (c) S. Qu and H. Tian, *Chem. Commun.*, 2012, **48**, 3039; (d) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595; (e) H. Nishide and K. Oyaizu, *Science*, 2008, **319**, 737.
- (a) C. M. Park and Y. Jiang, *Chem. Sci.*, 2014, **5**, 2347; (b) Y.-H. Xu, T. He, Q.-C. Zhang and T.-P. Loh, *Chem. Commun.*, 2014, **50**, 2784; (c) M.-N. Zhao, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Chem. Eur. J.*, 2014, **20**, 1839; (d) M.-N. Zhao, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Org. Lett.*, 2014, **16**, 608; (e) L. Ran, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Green Chem.*, 2014, **16**, 112; (f) Z. Shi, M. Suri and F. Glorius, *Angew. Chem., Int. Ed.*, 2013, **52**, 4892; (g) J. Liu, Z. Fang, Q. Zhang, Q. Liu and X. Bi, *Angew. Chem., Int. Ed.*, 2013, **52**, 6953; (h) T. Miura, K. Hiraga, T. Biyajima, T. Nakamuro and M. Murakami, *Org. Lett.*, 2013, **15**, 3298; (i) K. Taguchi, S. Sakaguchi and Y. Ishii, *Tetrahedron Lett.*, 2005, **46**, 4539; (j) N. Schley, G. Dobereiner and R. H. Crabtree, *Organometallics*, 2011, **30**, 4174.
- S. Michlik and R. Kempe, *Nat. Chem.*, 2013, **5**, 140.
- K. Iida, T. Miura, J. Ando and S. Saito, *Org. Lett.*, 2013, **15**, 1436.
- D. Srimani, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2013, **52**, 4012.
- M. Zhang, X. Fang, H. Neumann and M. Beller, *J. Am. Chem. Soc.*, 2013, **135**, 11384.
- D. Forberg, J. Obenau, M. Friedrich, S. Hühne, W. Mader, G. Motz and R. Kempe, *Catal. Sci. Technol.*, 2014, **4**, 4188.
- C. Gunanathan and D. Milstein, *Science*, 2013, **341**, 249.
- (a) K. Kon, S. M. A. H. Siddiki and K. Shimizu, *J. Catal.*, 2013, **304**, 63; (b) S. M. A. H. Siddiki, K. Kon, A. S. Touchy and K. Shimizu, *Catal. Sci. Technol.*, 2014, **4**, 1716; (c) S. K. Moromi, S. M. A. H. Siddiki, Md. A. Ali, K. Kon and K. Shimizu, *Catal. Sci. Technol.*, 2014, **4**, 3631; (d) C. Chaudhari, S. M. A. H. Siddiki, M. Tamura and K. Shimizu, *RSC Adv.*, 2014, **4**, 53374; (e) S. M. A. H. Siddiki, A. S. Touchy, K. Kon and K. Shimizu, *Chem. Eur. J.*, 2016, **22**, 6111.