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Ti–Pd Alloys as Heterogeneous Catalysts for Hydrogen Autotransfer Reaction and Catalytic Improvement by Hydrogenation Effects

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Dedication ((optional))

Abstract: Ti–Pd alloys were investigated as heterogeneous catalysts for hydrogen autotransfer reactions. This is the first reported study of alloys as catalysts for hydrogen-borrowing reactions using alcohols. We improved the catalytic activities of alloys by increasing their specific surface areas via a hydrogenation–powdering process. The reactivities and selectivities of hydrogenated Ti–Pd alloys [Ti–Pd(Hy)] were higher than those of non-hydrogenated alloy catalysts in *N*-alkylation by hydrogen autotransfer using alcohols. A plausible catalytic cycle is proposed based on control studies and deuterium labelling experiments.

Novel catalyst identification is important for the development of modern society, in terms of efficient energy use to reduce costs.[1] In organic chemistry, catalysts with new characteristics enable the development of new routes for the synthesis of useful materials and functional groups and allow reactions to be performed under mild conditions.[2] Our groups have focused on investigating highly active catalysts such as nanoparticles and have reported their use in various organic reactions.[3]

We have reported bulk Ti–Pd alloys as novel heterogeneous Pd catalysts; these have high catalytic activity in Suzuki–Miyaura cross-coupling and Mizoroki–Heck reactions.[4,5] We used X-ray photoelectron spectroscopy (XPS) to examine the surfaces of Ti–Pd alloys and detected zero-valent Pd on/in a titanium oxide film. The surface characteristics of alloy catalysts differ from those of supported catalysts, which are commonly used as heterogeneous catalysts. Supported catalysts consist of metal particles and carriers such as inorganic oxides, carbon, and polymers.[6]

Ti-based alloys are well known as hydrogen-storage materials and have various applications, e.g. in hydrogen storage materials, biomaterials, aircraft materials, and marine facility structural materials.[7] Ti-based alloys containing Pd have improved hydrogen absorption abilities because of the catalytic effect of Pd, which accelerates hydrogen molecule dissociation, and promotes easy, rapid hydrogen absorption.[4] These findings suggest that Ti–Pd alloys could catalyse hydrogen autotransfer reactions.

We investigated Ti–Pd alloys as catalysts for *N*-alkylation of amines via hydrogen autotransfer reactions using alcohols. The C–N bond is an important building blocks and is present in medicines, pesticides, surfactants, and biological materials.[8] *N*-Alkylation is a useful reaction for forming C–N bonds. In particular, hydrogen autotransfer using alcohols has attracted much attention as a green reaction with high atom economy.[9]

Ti–*x*Pd alloy catalysts (*x* = 0.2, 1.0 mol%) were prepared by an arc melting method.[4] We also prepared hydrogenated Ti–Pd alloys, i.e. [Ti–Pd(Hy)], and compared their catalytic activities with those of non-hydrogenated Ti–Pd alloy catalysts. Hydrogenation decreases the alloy strength by hydrogen embrittlement. Ti–Pd(Hy) alloys can therefore be easily powderized, whereas this is difficult for bare Ti–Pd alloys (Figure 1). The Ti–Pd(Hy) alloys was prepared by Sievert's type apparatus with 3.0 MPa H_2 at 673 K. Then the alloys were powdered by stirring with magnetic stirrer for 5 min in toluene under Ar. Powdering gives a large specific surface area therefore it was thought that the catalytic activity of Ti–Pd(Hy) would be higher than that of Ti–Pd.

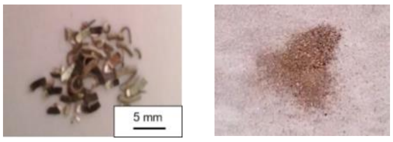

Figure 1. Photographs of Ti–Pd turnings (left) and Ti–Pd(Hy) powder (right).

First, we investigated the characteristics of the alloys before and after hydrogenation. Ti–Pd and Ti–Pd(Hy) were analysed in the form of turnings and a powder, respectively. X-ray diffraction showed that the crystal system changed from hexagonal close-packed to face-centred cubic, and the peaks in the Ti–Pd(Hy) pattern matched those in the $TiH_{1.924}$ pattern (Figure 2). These results suggest that the Ti–Pd(Hy) alloy consists of a hydride with a metal–hydrogen bond. XPS showed that the Pd valence in Ti–Pd(Hy) was higher than that in Ti–Pd, and zero-valent Ti was present (Figure 3). This is the result of electronic interactions between Pd and Ti. The surface and internal valence state of Ti and Ti hydride were reported as following; on the surface, these

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Ti and hydride were covered with Ti oxide and in the internal side, the valence state of Ti hydride was shift approximately 0.4 eV in high binding energy state comparing that of Ti.[12] Focused on alloyed Pd, the valence state was metallic state on the surface and in the internal Pd.[4] Therefore, the new face which was fabricated by powderizing on the Pd should be metallic state. We also determined the Brunauer–Emmett–Teller surface areas of the alloys. The specific surface area of Ti–Pd(Hy) was approximately ten times that of Ti–Pd [Ti–Pd(Hy): 0.283 m^2 g^{-1}, Ti–Pd: 0.0354 m^2 g^{-1}]. Scanning electron microscopy (SEM) showed that the Ti–Pd(Hy) particle size was 20–30 μm (Figure S1). The measurement of surface Pd atoms by CO-uptaking measurement can hardly be elucidated since the number of Pd atoms specific surface area of alloys were too small.

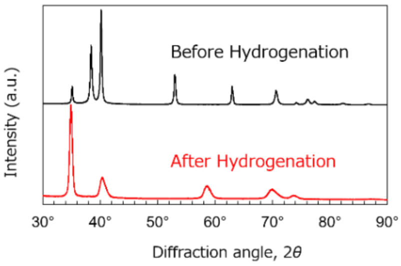


Figure 2. X-ray diffraction patterns of Ti–Pd (above) and Ti–Pd(Hy) (below).

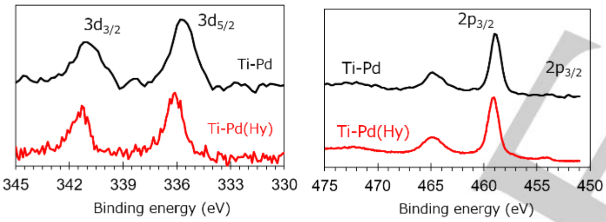
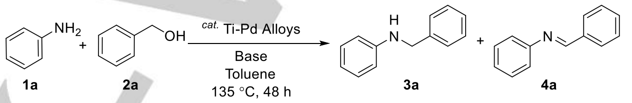


Figure 3. X-ray photoelectron spectra for (left) Pd 3d and (right) Ti 2p.

Ti–Pd-alloy-catalysed *N*-alkylation reactions of amines with alcohols via hydrogen autotransfer were investigated. Aniline (**1a**) and benzyl alcohol (**2a**) were selected as model reactants (Table 1). Ti–0.2Pd catalysed the reaction to give the desired alkylated amine, *N*-benzyl aniline (**3a**), in 64% yield and the imine intermediate, benzylideneaniline (**4a**), in 12% yield (entry 1). The yield of **3a** increased with increasing Pd content in the alloy, up to a maximum yield of 80% (entry 2). Ti–0.2Pd(Hy) was a more effective catalyst than Ti–0.2Pd and gave **3a** in 97% yield, with excellent selectivity, and in an isolated yield of 85% (entry 3). Strong bases were necessary for the reaction; reactions with weak bases or under base-free conditions were sluggish (entries 4–6 and Table S1). Excess alcohol accelerated the reaction smoothly; the optimum amount of **2a** was 1.5 mmol (3 molar equivalents with respect to **1a**) (entry 7). A reaction temperature of 135 °C and reaction time of 48 h were needed for good yields (entries 8 and 9). Polar solvents were not suitable for this reaction system (Table S2). Little reaction occurred without an alloy catalyst (entry 10).

The scope and limitation of this reaction were investigated by testing various amines and alcohols (Table 2). In these tests, imine intermediate **4** was hardly obtained. First, amines **3b**–**3g** were tested. Aniline derivatives bearing electron-donating groups, i.e. *p*-toluidine and *p*-anisidine, and an electron-withdrawing group, i.e. 4-chloroaniline, were tolerated and gave the corresponding alkylated amines in good yields. This catalyst was suitable for reactions using N-heterocyclic or sterically hindered amines. 2-Aminopyridine reacted with **2a** to give the desired product **3e** in 82% yield. The reactions using *o*-toluidine and 1-naptylamine gave the corresponding products **3f** and **3g** in 66% and 77% yields, respectively. However, the reactions of aliphatic amines were sluggish. No reaction occurred between secondary amines and **2a**.

Table 1. Optimization of alloy-catalysed *N*-alkylation of aniline (**1a**) with benzyl alcohol (**2a**).[a]

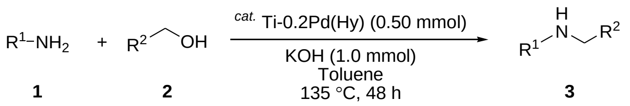


Entry	Alloy catalyst	Base	Conversion (%)[b]	Yield (%)[b]	
			1a	**3a**	**4a**
1	Ti–0.2Pd	KOH	80	64	12
2	Ti–1.0Pd	KOH	87	76	8
3	Ti–0.2Pd(Hy)	KOH	>99	97 (85)	<1
4	Ti–0.2Pd(Hy)	KO^{t}Bu	>99	>99	<1
5	Ti–0.2Pd(Hy)	K_3PO_4	19	<1	8
6	Ti–0.2Pd(Hy)	none	5	n.d.[c]	<1
7[d]	Ti–0.2Pd(Hy)	KOH	13	6	<1
8[e]	Ti–0.2Pd(Hy)	KOH	32	24	5
9[f]	Ti–0.2Pd(Hy)	KOH	71	68	<1
10	none	KOH	21	17	4

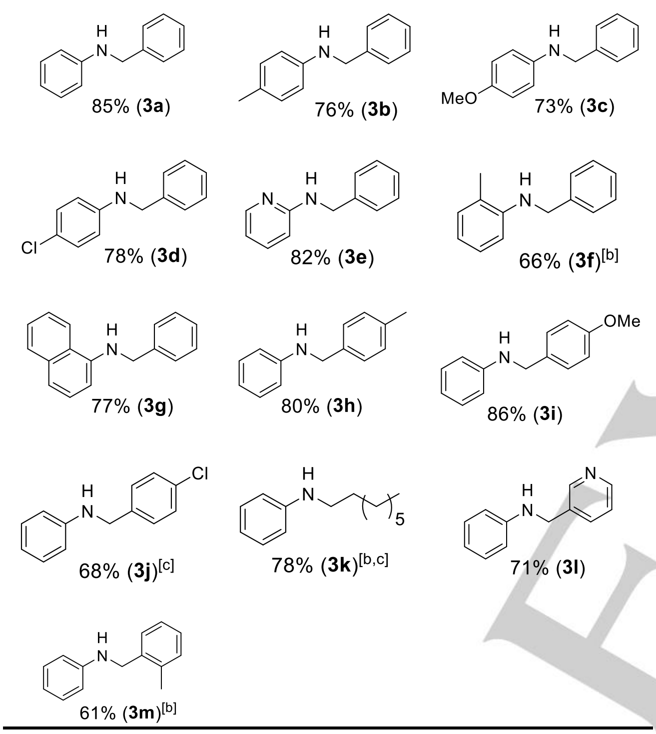
[a] Reaction conditions: **1a** (0.50 mmol), **2a** (1.5 mmol), alloy catalyst (0.50 mmol), and base (1.0 mmol) were stirred in toluene (2 mL) at 135 °C for 48 h under Ar. [b] Conversions and yields were determined by GC based on **1a** used. Numbers in parentheses showed isolated yields. [c] Not detected by GC. [d] **2a** (0.50 mmol) was used. [e] At 120 °C. [f] Reaction time was 16 h.

Next, the reactions of aniline (**1a**) with various alcohols were investigated. The reactions of 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol with **1a** gave the corresponding products **3h** and **3i** in excellent yields. When the substituent was an electron-withdrawing group, the reaction was slow; the reaction of 4-chlorobenzyl alcohol with **1a** for 72 h gave the desired product in moderate yield. Aliphatic alcohols reacted with **1a** to give *N*-alkylation products. N-heterocyclic alcohols were tolerated, and sterically hindered alcohols were also suitable. Secondary alcohols did not react with **1a**; the reaction with 1-phenylethyl alcohol gave styrene.

Table 2. *N*-alkylation of various amines with alcohols.[a]



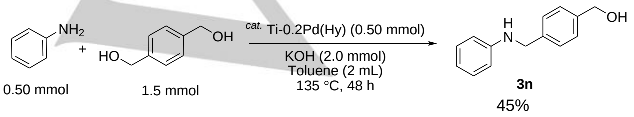
Isolated yield



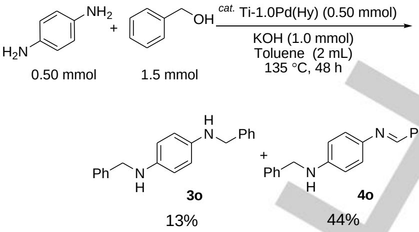
85% (**3a**)
76% (**3b**)
73% (**3c**)
78% (**3d**)
82% (**3e**)
66% (**3f**)[b]
77% (**3g**)
80% (**3h**)
86% (**3i**)
68% (**3j**)[c]
78% (**3k**)[b,c]
71% (**3l**)
61% (**3m**)[b]

[a] Conditions are the same as those for Table 1, entry 3, unless otherwise noted. [b] At 150 °C. [c] Reaction time was 72 h.

We further investigated the scope of the reaction by using diols or diamines. 1,4-Benzenedimethanol reacted with **1a** to produce the mono-alkylated compound **3n** in 45% yield and with high selectivity [Eq. (1)]. The reactions of diamines with alcohols gave dialkylation products. 1,4-Phenylenediamine reacted with **2a** to give three dialkylated compounds, namely the desired alkylation amine **3o**, the partial reduction product **4o**, and the non-reduced imine intermediate **5o**. These products were isolated in 13%, 44%, and 17% yields, respectively [Eq. (2)].



(1)



(2)

The reusability of the Ti–Pd(Hy) alloy catalysts was tested by performing multiple reactions under the optimum conditions (Table 1, entry 3). Similarly to recycling of the Ti–Pd alloy catalyst turnings,[5] recycling of the Ti–Pd(Hy) alloy catalysts was simple; preactivation was not needed, and only supernatant separation and catalyst washing were required. Figure 4 shows that the Ti–Pd(Hy) catalysts could be reused at least five times, and gave good product yields and excellent selectivities. The crystal structure of Ti–Pd(Hy) was unchanged by the reaction (Figure 5 and Figure S2). The alloy catalysts therefore retained their hydride structures and hydrogen in the alloys was not used for the reaction.

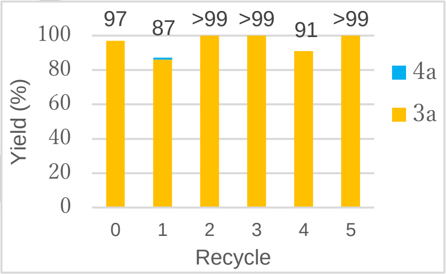


Figure 4. Recycling of Ti–Pd(Hy) alloy catalysts for *N*-alkylation of aniline (**1a**) with benzyl alcohol (**2a**).

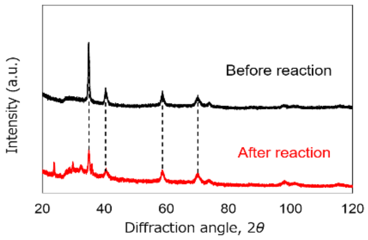


Figure 5. X-ray diffraction pattern of Ti–Pd(Hy) before (upper) after (bottom) reaction.

Next, we investigated the heterogeneous properties of the alloy catalysts by performing filter tests and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. Figure 6 shows the filter test results. When the alloy catalysts were removed after reaction for 8 h under the model conditions, the reaction stopped and the product yield did not increase further. If potassium hydroxide was added at the same time as the alloy catalyst was removed by filtration, the reaction degree was only that caused by the base effect. Additionally, ICP-AES analysis of the reaction mixture showed that the amount of leached Pd was

<0.08 ppm (less than the detection limit), i.e. little Pd leaching from the alloy catalysts occurred during the reaction (Table S3 and Figure S3).

Tests with Hg(0) (2.5 mmol) were conducted under the model conditions (Table 1, entry 3). In the presence of Hg, the catalytic activity of a metal-supported catalyst is lost because of amalgam formation.[10] The alloy catalysts retained their catalytic activities and the reaction proceeded to give the alkylated product in 37% yield.

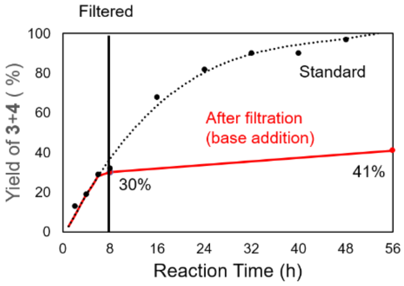
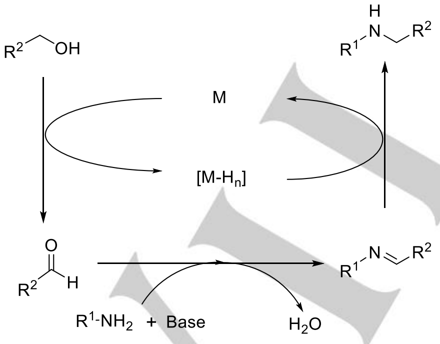


Figure 6. Filter tests on Ti–Pd(Hy) alloy catalysts for *N*-alkylation under the model conditions (entry3, Table 1).

Control experiments and deuterium labelling experiments were performed to explore possible reaction mechanisms. The proposed general process involved in hydrogen autotransfer for alkylation of amines using alcohols is shown in Scheme 1.[11] First, metal-catalysed dehydrogenation of an alcohol produces an aldehyde and a metal hydride. The aldehyde then undergoes condensation reaction with the amine to generate an imine intermediate. Finally, hydrogenation of the imine by the metal hydride gives the desired N-alkylamine, with regeneration of the metal catalyst.

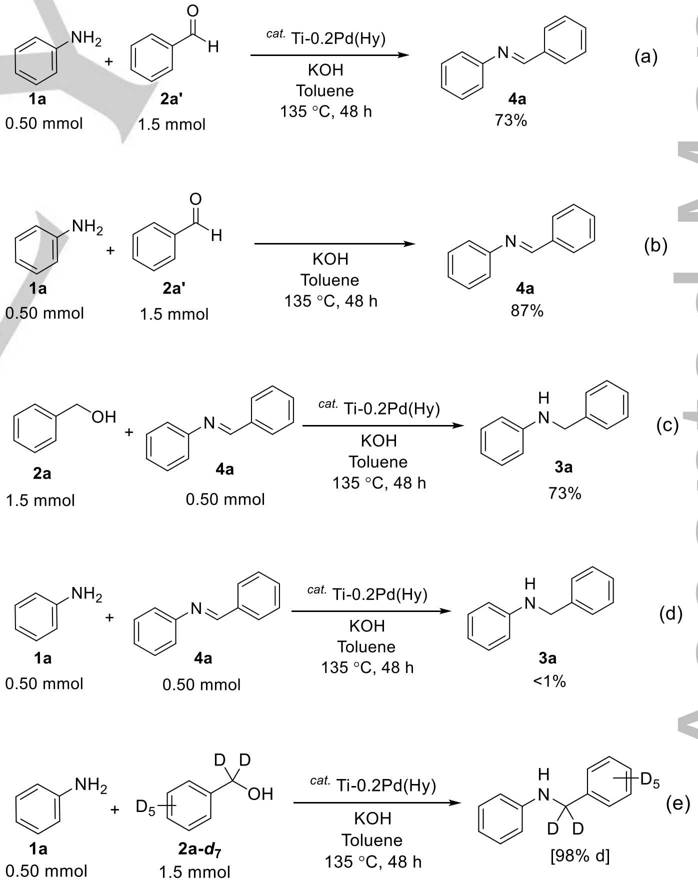


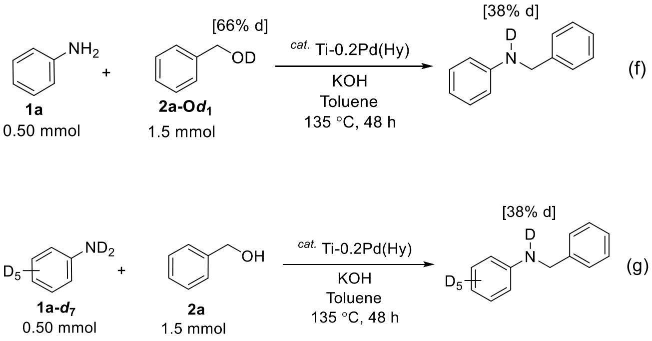
Scheme 1. Proposed general reaction mechanism for *N*-alkylation of amines using alcohols.

First, we checked the reaction intermediate. Aldehydes are often observed in hydrogen autotransfer reactions with alcohols,[11] and are thought to be formed by alcohol dehydrogenation. In our reaction system, a small amount of benzaldehyde was often detected by GC, which suggests that benzaldehyde was a reaction intermediate and transfer hydrogenation was achieved by the alloy catalysts. The reaction of benzaldehyde instead of benzyl alcohol with aniline under the optimum conditions gave **4a** in 73% yield (Scheme 2a). The reaction in the absence of an alloy catalyst also gave **4a** (Scheme 2b). These results indicate that benzaldehyde served as an intermediate and the alloy catalyst was not involved in this step.

Next, we investigated hydrogen sources. The reaction of benzylideneaniline (**4a**) with benzyl alcohol (**2a**) under the above conditions gave the hydrogenated amine **3a** in 73% yield (Scheme 2c). No reaction occurred between **4a** and aniline (**1a**) (Scheme 2d). These results show that the hydrogen source was the alcohol, not the alloy or amine.

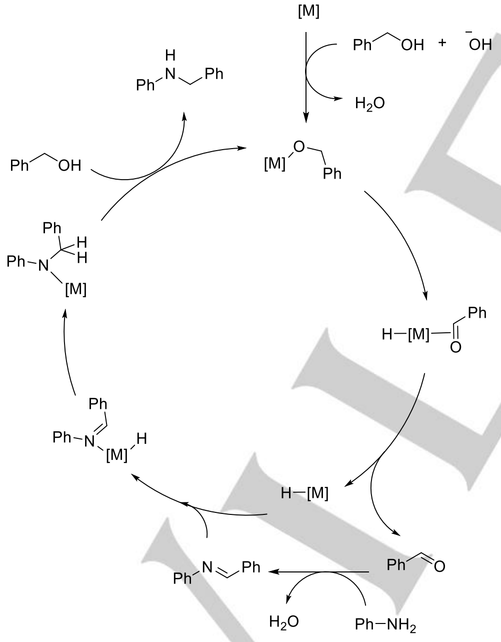
The proposed reaction mechanism was clarified by performing deuterium labelling experiments with α,α-dideuteriobenzyl alcohol (**2a-*d*$_7$**, $C_6D_5CD_2OH$), benzyl alcohol-OD (**2a-*Od*$_1$**, $C_6H_5CH_2OD$), and deuterated aniline (**1a-*d*$_7$**, $C_6D_5ND_2$). In the first test, deuteration occurred only at the methylene position of the product (Scheme 2e). However, in the second and third tests, the hydrogen on the imino group was replaced by deuterium but that on the methylene group was not (Scheme 2f and g).





Scheme 2. Mechanistic studies of *N*-alkylation reaction.

Based on the results of these control experiments and deuterium labelling experiments, we propose a plausible catalytic cycle (Scheme 3). Initially, benzyl alcohol (**2a**) coordinates with Ti–Pd(Hy). Abstraction of a methylene proton by Ti–Pd(Hy) forms benzaldehyde **2a’** with simultaneous generation of a [Ti–Pd(Hy)–H] species. Benzaldehyde then reacts with aniline (**1a**) to give imine intermediate **4a**. The imine is hydrogenated by [Ti–Pd(Hy)–H] and benzyl alcohol to generate the desired *N*-alkylamine product **3a**. Hydrogen source was from alcohols during the course of the reaction and hydrogen adsorption of alloys were not involved in the reaction.



Scheme 3. Plausible catalytic cycle for Ti–Pd(Hy)-catalysed *N*-alkylation of aniline (**1a**) with benzyl alcohol (**2a**).

In conclusion, Ti–Pd alloy catalysts were used as catalysts for hydrogen autotransfer. The Ti–Pd alloys were hydrogenated and powdered to give Ti–Pd(Hy), which had higher catalytic activity in the reaction than Ti–Pd flakes had. We investigated Ti–Pd(Hy)-catalysed *N*-alkylation of amines by alcohols via hydrogen autotransfer. The catalysts had high activities and good selectivities. The alloy catalysts were stable during the reaction and metal was not leached into the reaction solution. The catalysts were recycled without the need for complicated activation processes. We have proposed a reaction mechanism for this system on the basis of control experiments.

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Keywords: Alloy catalysts • Hydrogen transfer • Alkylation• Alcohols • Heterogeneous catalysis

[1] a) J. B. Goodenough, *Energy Environ. Sci.* **2014**, *7*, 14–18; b) M. Dinca, Y. Surendranath, D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 10337–10341; c) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757–3778. d) M. I. Hoffert, K. Caldeira, A. K. Jain, E. F. Haites, L. D. D. Harvey, S. D. Potter, M. E. Schlesinger, S. H. Schneider, R. G. Watts, T. M. L. Wigley, D. J. Wuebbles, *Nature* **1998**, *395*, 881–884.

[2] a) R. Sheldon, *Chem. Commun.* **2001**, *23*, 2399–2407; b) P. I. Dalko, L. Moisan, *Angew. Chem., Int. Ed.* **2004**, *43*, 5138–5175; *Angew. Chem.* **2004**, *116*, 5248–5286; c) A. T. Bell, *Science* **2003**, *299*, 1688–1691.

[3] a) K. Onishi, K. Oikawa, H. Yano, T. Suzuki, Y. Obora, *RSC Adv.* **2018**, *8*, 11324–11329; b) K. Oikawa, S. Itoh, H. Yano, H. Kawasaki, Y. Obora, *Chem. Commun.* **2017**, *53*, 1080–1083; c) H. Oka, K. Kitai, T. Suzuki, Y. Obora, *RSC Adv.* **2017**, *7*, 22869–22874; d) Y. Isomura, T. Narushima, H. Kawasaki, T. Yonezawa, Y. Obora, *Chem. Commun.* **2012**, *48*, 3784–3786; e) H. Yano, Y. Nakajima, Y. Obora, *J. Organomet. Chem.* **2013**, *745–746*, 258–261; f) M. Hyotanishi, Y. Isomura, H. Yamamoto, H. Kawasaki, Y. Obora, *Chem. Commun.* **2011**, *47*, 5750–5752; g) H. Yamamoto, H. Yano, H. Kouchi, Y. Obora, R. Arakawa, H. Kawasaki, *Nanoscale* **2012**, *4*, 4148–4154; h) R. Azuma, S. Nakamichi, J. Kimura, H. Yano, H. Kawasaki, T. Suzuki, R. Kondo, Y. Kanda, K. Shimizu, K. Kato, Y. Obora, *ChemCatChem* **2018**, *10*, 2378–2382.

[4] a) R. Kondo, S. Nakamichi, R. Azuma, Y. Takahashi, Y. Obora, H. T. Takeshita, *Mater. Trans.* **2018**, *59*, 1911–1914.

[5] a) R. Azuma. Y. Takahashi, R. Kondo, T. Suzuki, H. T. Takeshita, Y. Obora, *Bull. Chem. Soc. Jpn.* in press: DOI:10.1246/bcsj.20180363.

[6] a) N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199–217; b) W. Ai, R. Zhong, X. Liu, Q. Liu, *Chem. Rev.* in press: DOI:10.1021/acs.chemrev.8b00404; c) T. Shinoki, K. Ota, Y. Sono, Y. Okuhigashi, J. Funaki, K. Hirata, *Nippon Kikai Gakkai Ronbunshu, B-hen* **2012**, *78*, 1662–1670; d) D. Formenti, F. Frretti, F. K. Scharnagl, M. Beller, *Chem. Rev*. in press; DOI: 10.1021/acs.chemrev.8b00547; e) M. Pagliaro, V. Pandarus, R. Ciriminna, F. Beland, P. Demma Cara, *ChemCatChem* **2012**, *4*, 432–445; f) M. Bhadra, H. S. Sasmal, A. Basu, S. P. Midya, S. Kandambeth, P. Pachfule, E. Balaraman, R. Banerjee, *ACS Appl. Mater. Interfaces* **2017**, *9*, 13785–13792.

[7] a) C. Chen, Y. Cao, S. Liu, J. Chen, W. Jia, *Chin. J. Catal.* **2018**, *39*, 1347–1365; b) H. F. Li, Y. F. Zheng, *Acta Biomater.* **2016**, *36*, 1–20; c)

H. Hosoda, S. Hanada, K. Inoue, T. Fukui, Y. Mishima, T. Suzuki, *Intermetallics* **1998**, *6*, 291–301; d) I. V. Gorynin, *Mater. Sci. Eng., A* **1999**, *A263*, 112–116.

[8] a) P. F. Brasil, J. A. de Freitas, A. L. S. Barreto, C. M. Adade, L. F. Reis de Sá, P. Constantino-Teles, F. T. Toledo, B. A. de Sousa, A. C. Gonçalves, M. T. V. Romanos, J. V. Comasseto, A. A. dos Santos, A. C. Tessis, T. Souto-Padrón, R. M. A. Soares, A. Ferreira-Pereira, *Parasitol. Int.* **2017**, *66*, 47–55; b) T. C. Nugent, M. El-Shazly, *Adv. Synth. Catal.* **2010**, *352*, 753–819; c) M. D. Kärkäs, *Chem. Soc. Rev.* **2018**, *47*, 5786–5865; d) N. H. Park, G. Teverovskiy, S. L. Buchwald, *Org. Lett.* **2014**, *16*, 220–223; e) J. Wu, Y. Zhou, Y. Zhou, C. Chiang, A. Lei, *ACS Catal.* **2017**, *7*, 8320–8323; f) J. P. Wolfe, S. Wagaw, J.-F. Marcoux, S. L. Buchwald, *Acc. Chem. Res.* **1998**, *31*, 805–818; g) F. Paul, J. Patt, J. F. Hartwig, *J. Am. Chem. Soc.* **1994**, *116*, 5969–5979.

[9] a) K. Shimizu, *Catal. Sci. Technol.* **2015**, *5*, 1412–1427; b) Y. Obora, *ACS Catal.* **2014**, *4*, 3972–3981; c) Z. Liu, Z. Yang, X. Yu, H. Zhang, B. Yu, Y. Zhao, Z. Liu, *Adv. Synth. Catal.* **2017**, *359*, 4278–4283; d) G. Guillena, D. J. Ramón, M. Yus, *Angew. Chem., Int. Ed.* **2007**, *46*, 2358–2364; *Angew. Chem.* **2007**, *119*, 2410–2416; e) Y. Obora, Y. Anno, R. Okamoto, T. Matsu-ura, Y. Ishii, *Angew. Chem., Int. Ed.* **2011**, *50*, 8618–8622; *Angew. Chem.* **2011**, *123*, 8777–8781; f) Y. Iuchi, Y. Obora, Y. Ishii, *J. Am. Chem. Soc.* **2010**, 132, 2536–2537; g) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, *349*, 1555–1575; h) G. Guillena, D. J. Ramon, M. Yus, *Chem. Rev.* **2010**, *110*, 1611–1641.

[10] a) D. D. Tang, K. D. Collins, J. B. Ernst, F. Glorius, *Angew. Chem. Int. Ed.* **2014**, *53*, 1809–1813; *Angew. Chem.* **2014**, *126*, 1840–1844; b) T. Begum, M. Mondal, M. P. Borpuzari, R. Kar, P. K. Gogoi, U. Bora, *Eur. J. Org. Chem.* **2017**, *2017*, 3244–3248; c) G. M. Whitesides, M. Hackett, R. L. Brainard, J.-P. P. M. Lavalleye, A. F. Sowinski, A. N. Izumi, S. S. Moore, D. W. Brown, E. M. Staudt, *Organometallics* **1985**, *4*, 1819–1830.

[11] a) C. M. Wong, R. T. McBurney, S. C. Binding, M. B. Peterson, V. R. Gonçales, J. J. Gooding, B. A. Messerle, *Green Chem.* **2017**, *19*, 3142–3151; b) Y. Kayaki, H. Ikeda, J. Tsurumaki, I. Shimizu, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1053–1061; c) L. Zhao, H. An, X. Zhao, Y. Wang, *ACS Catal.* **2017**, *7*, 4451–4461.

[12] a) I. Paulin, D. Mandrino, C. Donik, M. Jenko, *Mater. Tehnol.*, **2010**, *44*, 73-76.

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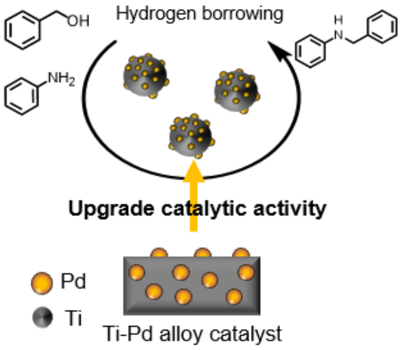
COMMUNICATION

Ti–Pd alloys were served as hydrogen borrowing catalysts. Their catalytic activity was improved by hydrogenation-powdering process to give desired alkylated product in excellent yield with high selectivity.



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