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12-Tungstophosphoric acid supported on nano silica from rice husk ash as an efficient catalyst for direct benzylation of 1,3-dicarbonyl compounds in solvent-free condition

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ABSTRACT

Nano silica has been prepared from rice husk, which is an agricultural waste, with high surface area and in amorphous form. 12-Tungstophosphoric acid, $H_3PW_{12}O_{40}$ (PW) has been supported on this silica to produce nano silica supported PW (NPW/SiO₂) as a nano catalyst. Characterization of this catalyst has been investigated by TEM, FTIR, and ICP, also, acidic properties have been studied by potentiometric titration method. 40% NPW/SiO₂ has been used as a high effective catalyst for benzylation of 1,3-dicarbonyl compounds with benzylic alcohols. The present methodology offers a clean, practical, simple, mild, environmentally friendly, green and time-saving method under solvent free condition. Also, the catalyst is a good candidate for large-scale in direct benzylation of 1,3-dicarbonyl compounds.

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1. Introduction

The recent emergence of nano catalysis has received a lot of attention because it opens new perspectives for the mild catalysis of important reactions with lower environmental impact. The development of an ultra high strength concrete was made possible by the application of densified system containing homogeneously arranged ultra fine particles [1–3]. Heteropoly acids (HPAs) such as PW have been extensively studied as acid catalysts for many reactions and found industrial applications in several processes [4–8]. Heterogeneous HPAs are advantageous over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture thereby eliminating the need for separation through distillation or extraction. Supported HPA catalysts are important for applications due to environmental and economic considerations. They also have excellent activity and present a greater number of surface acid sites than their bulk components and have been pointed lately as versatile green catalysts for a variety of organic reactions [9–11]. Acidic or neutral substances, such as SiO₂, active carbon, and acidic ion-exchange resins are all suitable supports, but SiO₂, which is relatively inert towards HPAs, is the one most often used [12]. The support can either play only a mechanical role or modify the catalytic properties by dispersion of acidic sites of HPAs as catalysts. This interaction takes place during the catalyst preparation and is strongly dependent on the support characteristics, the preparation method and some of the operating variables. Also, the support can modify the properties of the precursor deposited on the surface by favoring growth of certain structures or by inducing different types of interaction. Rice husks (RHs) are the natural sheaths that are formed on rice grains during their growth and removed as waste during the processing of rice in the mills. Having no commercial value itself, and normally, RH usually ends up being burned openly, thus causing environmental pollution and disposal problems. Recently, efforts are being made not only to overcome the pollution but also to find value addition to these wastes by using them as secondary source materials. Dry husk contains 70-85% organic matter and the inorganic remainder consists of silica. The rice husk ash (RHA) containing over 90% silica by mass with a small proportion of metallic elements is considered to be the most economical source of silica. At present, nano scale silica materials are prepared using several methods, including vapor-phase reaction, sol-gel, and thermal decomposition technique [13–15]. However, their high cost of preparation has limited their wide applications. Very fine particle size silica powder with very high purity and surface area can be prepared under controlled conditions [16-24]. The large amount of silica freely obtained from RHA provides an abundant and cheap alternative source of silica

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which is applicable particularly as a support for heterogeneous catalysis. If the HPAs are supported on the silica nano particles, it can exhibit quite different characteristics from the bulk HPAs.

Nowadays, supported PW are introduced to heterogeneous catalytic researches [25-28]. Among these fine chemical reactions, alkylation of 1,3-dicarbonyl compounds is a useful transformation involving C-C bond formation. In principle, direct nucleophilic substitution of the hydroxy group in alcohols with nucleophiles generally requires preactivation of the alcohol functionality because of its poor leaving ability [29,30]. Recently, acid catalysts such as BF₃-OEt₂, InCl₃, Bi(OTf)₃, Yb(OTf)₃, FeCl₃ and H-montmorillonite have been employed to perform nucleophilic substitution of benzylic alcohols with active methylene compounds [31-36]. However, most of these methods have problems including drastic reaction conditions, long reaction times and use of expensive, toxic and moisture sensitive reagents. Hence, the development of new catalysts with more efficiency is of interest. Solvent-free reactions have been paid more and more attentions recently, often providing clean, efficient, and high-yielding organic processes in modern synthetic chemistry. The present work, deals with the preparation of nano silica supported PW (NPW/SiO₂). Then, reactivity of the produced catalyst was investigated in benzylation of a wide variety of 1,3-dicarbonyl compounds under solvent-free condition. To the best of our knowledge this is the first attempt on using of silica from RH as a support for PW.

2. Experimental

2.1. General remarks

All organic materials were purchased commercially from Fluka and Merck companies that were used without further purification. PW from Aldrich and Aerosil 300 silica from Degussa was used. The raw material was supplied from a rice mill of the north of Iran. FTIR spectra were recorded with KBr pellets using a WOF-510 FTIR Rayleigh. NMR spectra were recorded on a Bruker Avance 200 MHz NMR spectrometer with CDCl₃ as the solvent and TMS as the internal standard. CHN compositions were measured by Hekatech elemental analysis model Euro EA 3000. Tungsten content of the catalyst was measured by inductively coupled plasma (ICP atomic emission spectroscopy) on a Spectro Ciros CCD spectrometer. Surface area was calculated from the linear part of the BET plot. Low temperature nitrogen adsorption experiments were performed using a Quantachrome instrument, model Nova 2000, USA system for measuring surface area. Transmission electron microscopy (TEM) examination was performed with a TEM microscope Philips CM 120 KV Netherland.

2.2. Preparation of silica from rice husk

RH was washed thoroughly with water to remove the soluble particles, dust and other contaminants. The heavy impurities like sand are also removed. It was then dried in an air oven at about 110 °C for 24 h. The dried RH was refluxed with an acidic solution (0.1 M HCl) for nearly 90 min with frequent stirring. It was cooled and kept intact for about 20 h. Then it was decanted, thoroughly washed with warm distilled water until the rinse became free from acid. The wet solid was subsequently dried in an oven at 110 °C for 24 h. The obtained white powder was burned inside a programmable furnace (Model Nobertherm controller B 170) at 700 °C with rate of 10 °C/min and 2 h as soaking time. We designated this as RHA.

20 g RHA sample was stirred in 160 mL of 2.5 M sodium hydroxide solution. The solution was heated in a covered beaker for 3 h with constant stirring. It was filtered and the residue was washed with 40 mL boiling distilled water. The obtained viscous, transparent and colourless solution was allowed to cool down to room temperature. Then, $2.5 \text{ M } \text{H}_2\text{SO}_4$ was added under constant stirring at controlled condition until pH = 2 and pH readjusted to 8.5 by NH₄OH addition. It was allowed to cool down to room temperature for 3 h. Silica was prepared by refluxing of extracted silica with 6.0 M HCl for 4 h and then washed repeatedly using deionised water to make it acid free. It was then dissolved in 2.5 M sodium hydroxide stirring. H₂SO₄ was added until pH 8. The precipitate silica was washed repeatedly with warm deionised water to make it alkali free, dried at 50 °C for 48 h in the oven.

2.3. Preparation of NPW/SiO₂ and PW/SiO₂

For the preparation of $40 \text{ wt.\% NPW/SiO}_2$ catalyst, firstly, solution of 3.0 g silica was sonicated for 2 h. Then 2.0 g of PW was dissolved in 40 mL of water and added to solution of silica. The mixture was stirred overnight at room temperature. The solvent was removed by filtration and catalyst was calcinated at 150 °C for 2 h.

PW/SiO₂, was prepared by impregnating Aerosil 300 silica (S_{BET} , 300 m²/g) with an aqueous solution of PW as describe above. The mixture was stirred overnight at room temperature, followed by filtration and drying at 150 °C for 2 h.

2.4. Acidity measurement

For the potentiometric titration, 0.05 g of solid was suspended in acetonitrile (90 mL) and stirred for 3 h. The suspension was titrated with a 0.05 mol/L solution of *n*-butylamine in acetonitrile. The potential variation was measured with a Hanna 302 pH meter using a double junction electrode.

2.5. General procedure for benzylation of 1,3-dicarbonyl compound

The solid acid catalyst (0.4 g), was added to a mixture of alcohol (1 mmol) and 1,3-dicarbonyl compound (1 mmol) at 80 °C. The reaction mixture was stirred for the short period of time listed in Table 1. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was washed with acetonitrile then the catalyst was removed by a repeated centrifugation (4000–6000 rpm, 30 min) and decantation. The catalyst was washed with acetonitrile again, followed by calcination at 150 °C for 2 h for reusing. The filtrate was concentrated and product was purified by column chromatography on silica-gel using EtOAc/hexane as eluent. All products were identified by comparing their spectral data with those of the authentic samples except for new compounds (**3cd, 3ad**). Analytical data for these compounds are presented below:

3-(3-Methoxybenzyl)pentane-2,4-dione (compound **3ad**): Pale yellow, M.p. 84–85 °C, ¹H NMR (200 MHz, CDCl₃) δ 6.41–7.15 (m, 4H), 3.71 (s, 3H), 3.00–3.55 (m, 3H), 2.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 202.1, 157.8, 140.5, 130.9, 118.1, 109.4, 102.6, 68.7, 54.8, 25.9, 19.7; Anal. Calcd for C₁₃H₁₆O₃: C, 70.89; H, 7.32; found: C, 70.86; H, 7.35; HRMs calcd for C₁₃H₁₆O₃: M, 220.26434; found: 220.2643.

Ethyl 2-(3-*methoxybenzyl*)-3-*oxobutanoate* (*compound* **3cd**): Pale yellow, M.p. 65–67 °C, ¹H NMR (200 MHz, CDCl₃) δ 6.51–7.15 (m, 4H), 4.01 (q, 2H, *J* = 7.1 Hz), 3.75 (s, 3H), 3.08–3.65 (m, 3H), 2.06 (s, 3H), 1.27 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 203.1, 169.1, 158.2, 139.4, 130.2, 1180.9, 110.3, 108.5, 58.9, 57.1, 53.6, 30.9, 20.4, 110.3; Anal. Calcd for C₁₄H₁₈O₄: C, 67.18, H, 7.25; found: C, 67.20; H, 7.23; HRMs calcd for C₁₄H₁₈O₄: M, 250.29032; found: 250.2903. Table 1

+ R'-OH
$$\xrightarrow{NPW/SiO_2(0.4 \text{ g})}$$
 H₃C \xrightarrow{O} R'
Solvent free, 80 °C 3

1a: R= CH₃ **1b:** R= OCH₃ **1c:** R= OCH₂CH₃ **2a:** R'= (Ph)₂CH **2b:** R'= PhCH₂ **2c:** R'= 2-OH-PhCH₂ **2a:** R'= 3-OCH₃-PhCH₂

Benzylation of different 1,3-dicarbonyl compounds catalyzed by 40% NPW/SiO₂...

Entry	Diketone	Alcohol	Product	Time (min)	Yield (%) ^a	TON ^b
1	1a	2a	O O H ₃ C CH ₃ Ph Ph 3aa	6	95	21
2	1b	2a	$\begin{array}{c} H_{3}C & OCH_{3} \\ Ph & Ph & 3ba \\ O & O \\ O & $	4	94	20
3	1c	2a	H ₃ C Y OCH ₂ CH ₃ Ph Ph 3ca O O	5	96	21
4	1a	2b	$H_3C' CH_3$ Ph 3ab O O	5 (10)	98 (90)	21
5	1b	2b	$H_3C \xrightarrow{OCH_3} 3bb$	3 (10)	98 (92)	21
6	1c	2b	$H_{3}C \neq OCH_{2}CH_{3}$ 3CD Ph O O	5 (10)	97 (88)	21
7	1b	2c	$H_{3}C$ OCH_{3} $3bc$ OH $H_{3}C$ $OCH_{2}CH_{3}$ $3cd$	5	95	21
8	1c	2d		2	99	22
9	1b	2d	3bd OCH ₃ OO H ₃ C CH ₃ 3ad	2	97	21
10	1a	2d	ОСН3	2	98	21

^a Isolated yield, results in parentheses refer to large scale syntheses.

^b Turn over number.

2.6. Large scale synthesis

3. Results and discussion

Three entries in Table 1 (entries 4–6) were selected for largescale synthesis. The reactions of **1a**, **1b** and **1c** (20.0 mmol) with **2b** (20.0 mmol), in the presence of 40% NPW/SiO₂ (8.0 g) were done at 80 °C in solvent free condition. As can be seen, 40% NPW/SiO₂ is a good candidate for large-scale and yields of the reactions were in the range of 88–92% in larger reaction times compared to small scale. The average size of 40% NPW/SiO₂ particles was estimated to be about 7 nm by TEM (Fig. 1). By processing BET results, the surface area of nano silica particles and 40% NPW/SiO₂ were determined 623 and 270 m²/g, respectively. Impregnation of PW on silica support caused a remarkable decrease in the surface area, but still showed a very high value. The reduction in the surface area of the supported catalyst may be due to the blockage of smaller pores by



Fig. 1. TEM image of 40% NPW/SiO₂.

active species. Elemental analysis from ICP showed that PW content of 40% NPW/SiO₂ was 33.2 wt.% of PW to silica. Typically, the PW content from ICP was slightly less than the amount of expected from the preparation stoichiometry.

The FTIR spectrum of 40% NPW/SiO₂ catalyst is shown in Fig. 2. For comparative purposes, the FTIR spectrum of bulk PW is also included. Characteristic bands of the bulk PW appeared at 1080 (P–O), 985 (W=O), 890 and 814 cm⁻¹ (W–O–W). In 40% NPW/SiO₂, the PW band placed at the 1080 cm⁻¹ zone is masked by the Si–O–Si absorption band. Anyway, information can still be obtained from the less affected regions, which showed an intensity increase of the band placed at 814 cm⁻¹ and non-overlapped bands at 890 and 985 cm⁻¹ that confirm the PW on support exists in Keggin structure.

The acidity measurements of the catalyst by means of potentiometric titration with *n*-butylamine were used to estimate its relative acid strength according to the two values (a) E_i as initial potential and (b) number of acid sites (Fig. 3). The initial electrode potential (E_i) indicates the maximum strength of the acid sites and the value from which the plateau is reached (mmol amine/g solid) indicates the total number of acid sites that are present in the titrated solids [28]. The acidic strength of the solids can



Fig. 2. FTIR of: (a) bulk PW and (b) 40% NPW/SiO₂.



Fig. 3. Potentiometric titration curves of nano silica, 40% NPW/SiO₂ and bulk PW.



Scheme 1. Model reaction.

be classified according to the following range: $E_i > 100 \text{ mV}$ (very strong sites), $0 < E_i < 100 \text{ mV}$ (strong sites), $-100 < E_i < 0 \text{ mV}$ (weak sites) and $E_i < -100 \text{ mV}$ (very weak sites). According to potentiometric titration curves (Fig. 3), PW presented very strong acidic sites ($E_i = 650 \text{ mV}$). Also, the total number of acid sites increased compared to the silica and bulk PW. With these results, it seems that this nano catalyst is active in organic reactions. Benzylation of 1,3-dicarbonyl compounds was employed for assessment of the catalytic activity.

The reaction of benzyl alcohol (1 mmol) and ethylacetoacetate (1 mmol) under solvent free condition was carried out as a model system for studying the effects of catalyst loading and reaction temperature on the product yield (Scheme 1). Initially, the quantity of the catalyst used in this reaction was optimized (Fig. 4). Improvement in time of the reaction was observed as the catalyst quantity increased from 0.3 to 0.4 g. Further increase in the catalyst quantity showed no improvement in the yield or reaction time. It should be noted that the reaction did not proceed in the absence



Fig. 4. Efficiency of the catalyst loading on the yield of the model reaction.



Fig. 5. Efficiency of support only, bulk PW, $40\%\,\text{PW}/\text{SiO}_2$ and NPW/SiO_2 in the model reaction.

of NPW/SiO₂. The effect of temperature was also studied. It was observed that with increase in the reaction temperature from 25 to 80°C, the yield of the product was increased from 10 to 98% after 5 min. To understand the effect of support on catalytic activity nano silica (support only), bulk PW and 40 wt.% of PW/SiO₂ (PW support on Aerosil silica as a commercial support) were checked as catalysts in model reaction (Fig. 5). NPW/SiO₂ showed higher catalytic activity in comparison with PW/SiO₂ due to its higher surface area and higher dispersion of acidic protons. Encouraged by these results; we turned our attention to various 1,3-diketones and benzylic alcohols (Table 1). The experimental results showed that benzyl alcohols or dicarbonyl compounds both with electron withdrawing or donating substitution performed to afford the products without the formation of any side products, in excellent yield. To our surprise, all reactions proceeded efficiently and completed within 2-6 min. By action of 40% NPW/SiO₂ the alcohol was protonated to generate a stable benzyl cation after dehydration. This carbocation could be quickly combined with the employed 1,3dicarbonyl compound to produce, after the release of H⁺, the final alkylated product (Scheme 2).

The stability of the active species in solution has been of concern for solid acids, especially for supported materials. The reusability of the catalyst was studied by employing it in a model reaction. In the present cases, the quantity of the catalyst used was too less



Scheme 2. Proposed mechanism for catalytic addition of diketones to alcohols.

Table 2

nvestigation of	the reusability	of the	catalyst.
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Run	Time (min)/yield (%)			
	Without calcinations	With calcinations		
1	5/97	5/97		
2	30/10	20/91		
3	_	20/87		
4	-	20/85		

to recollect and can be reused after the first run. Hence, higher quantity of the catalyst was taken to investigate its reusability. The model reaction was carried out by using 1 g of the catalyst and the experiments were properly scaled up. After each run, the catalyst was washed with EtOAc/hexane (1:3) as solvent and dried as described in Section 2. As shown in Table 2, only 12% reduction in product yield was observed after four times reuse. It should be noted that the reusability of the catalyst without calcinations was found unfavorable. In this case, when the supernatant portion of the NPW/SiO₂ catalyzed reaction mixture was subjected to UV spectrum, it exhibits the presence of absorption band at 265 nm assigned to Keggin type of $PW_{12}O_{40}^{3-}$. It was due to the leaching of PW from the support into the liquid phase. This catalyst could be recovered and subsequently reused several times in a solventless system just after calcinations at 150 °C for 2 h.

The applicability of this method for the large-scale operations was investigated in the reactions of **1a**, **1b** and **1c** (20.0 mmol) with **2b** (20.0 mmol) under the optimized conditions (Table 1, entries 4–6). Corresponding products were obtained with approximately similar yields but in longer reaction times. As can be seen, 40% NPW/SiO₂ is a good candidate for large-scale in direct benzylation of 1,3-dicarbonyl compounds.

4. Conclusion

The silica support was successfully prepared from rice husk as an agriculture waste in nano sized particles with high surface area. PW was supported on the silica to make an effective catalyst with very strong acidic property. An efficient methodology for solvent-free direct benzylation reactions of 1,3-dicarbonyl compounds catalyzed by 40% NPW/SiO₂ was demonstrated. The catalytic reactions proceeded in excellent yields in very short times without toxic organic solvent. 40% NPW/SiO₂ was found as an efficient, environmentally friendly, cheap and non toxic nano catalyst. The catalyst can be a good candidate for large-scale in direct benzylation of 1,3-dicarbonyl compounds.

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References

- [1] L. Hui, X. Hui-Gang, Y. Jie, O. Jinping, Composites Part B: Eng. 35 (2003) 185–189.
- [2] Y. Qing, Z. Zhang, D. Kong, R. Chen, Constr. Build. Mater. 21 (2007) 539–545.
- [3] P.K. Jal, M. Sudarshan, A. Saha, P. Sabita, B.K. Mishra, Colloids Surf. 240 (2004) 173-178.
- [4] S.Y. Oh, T. Yoshida, G. Kawamura, H. Muto, M. Sakai, A. Matsuda, J. Power Sources 195 (2010) 5822–5828.
- [5] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113-252.
- [6] M. Misono, Chem. Commun. (2001) 1141–1152.
- [7] E.F. Kozhevnikova, J. Quartararo, I.V. Kozhevnikov, Appl. Catal. A: Gen. 245 (2003) 69–78.
- [8] J.R. Ferrell III, M.C. Kuo, M. Herring Andrew, J. Power Sources 195 (2010) 39-45.
- [9] I.V. Kozhevnikov, Catalysis by Polyoxometalates, 2, Wiley, Chichester, 2002.
- 0] I.V. Kozhevinkov, Chem. Rev. 98 (1998) 171–198.
- [11] E. Rafiee, F. Shahbazi, M. Joshaghani, F. Tork, J. Mol. Catal. A: Chem. 242 (2005) 129–134.

- [12] I.V. Kozhevinkov, Catal. Rev. Sci. Eng. 37 (1995) 311-352.
- [13] M. Tomozawa, D.L. Kim, V. Lou, J. Non-Cryst. Solids 296 (2001) 102-106.
- [14] P.A. Tanner, B. Yan, H. Zhang, J. Mater. Sci. 35 (2000) 4325-4328.
- [15] G. Wu, J. Wang, J. Shen, T. Yang, Q. Zhang, B. Zhou, Z. Deng, F. Bin, D. Zhou, F. Zhang, J. Non-Cryst. Solids 275 (2000) 169–174.
- [16] D. Li, D. Chen, X. Zhu, Bioresour. Technol. 102 (2011) 7001-7003.
- [17] D. Li, X. Zhu, Mater. Lett. 65 (2011) 1528-1530.
- [18] T.H. Liou, Ch. Yang, Mater. Sci. Eng. B 176 (2011) 521-529.
- [19] D. An, Y. Guo, B. Zou, Y. Zhu, Z. Wang, Biomass Bioenergy 35 (2011) 1227-1234.
- [20] Y. Liu, Y. Guo, Y. Zhu, D. An, W. Gao, Z. Wang, Y. Ma, Z. Wang, J. Hazard. Mater. 186 (2010) 1314–1319.
- [21] S.P.B. Lima, R.P. Vansconcelos, O.A. Paiva, G.C. Cordeiro, M.R.M. Chaves, R.D.T. Filho, E.M.R. Fairbairn, Quim. Nova 34 (2011) 71-78.
- [22] J. Umeda, K. Kondoh, Ind. Crops Prod. 32 (2010) 539-544.
- [23] D. An, Y. Guo, Y. Zhu, Z. Wang, Chem. Eng. J. 162 (2010) 509-514.
- [24] N. Thuadaij, A. Nuntiya, C. Mai, J. Sci. 35 (2008) 206-211.

- [25] E. Rafiee, M. Joshaghani, F. Tork, A. Fakhri, S. Eavani, J. Mol. Catal. A: Chem. 283 (2008) 1–4.
- [26] E. Rafiee, H. Mahdavi, M. Joshaghani, Mol. Divers. 15 (2011) 125-134.
- [27] E. Rafiee, H. Mahdavi, S. Eavani, M. Joshaghani, F. Shiri, Appl. Catal. A: Gen. 352 (2009) 202-207.
- [28] E. Rafiee, M. Joshaghani, S. Eavani, S. Rashidzadeh, Green Chem. 10 (2008) 982–989.
- [29] B.M. Trost, M.L. Crawley, Chem. Rev. 103 (2003) 2921–2943.
- [30] S. Ma, S. Yu, Z. Peng, H. Guo, J. Org. Chem. 71 (2006) 9865-9868.
- [31] F. Bisaro, G. Pretat, M. Vitale, G. Poli, Synlett (2002) 1823-1826.
- [32] M. Yasuda, T. Somyo, A. Baba, Angew. Chem. 45 (2006) 793-796.
- [33] M. Rueping, B.J. Nachtsheim, A. Kuenkel, Org. Lett. 9 (2007) 825-828.
- [34] W. Huang, J. Wang, Q. Shen, X. Zhou, Tetrahedron Lett. 48 (2007) 3969-3973.
- [35] U. Jana, S. Biswas, S. Maiti, Tetrahedron Lett. 48 (2007) 4065-4071.
- [36] K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, Angew. Chem. 45 (2006) 2605–2609.