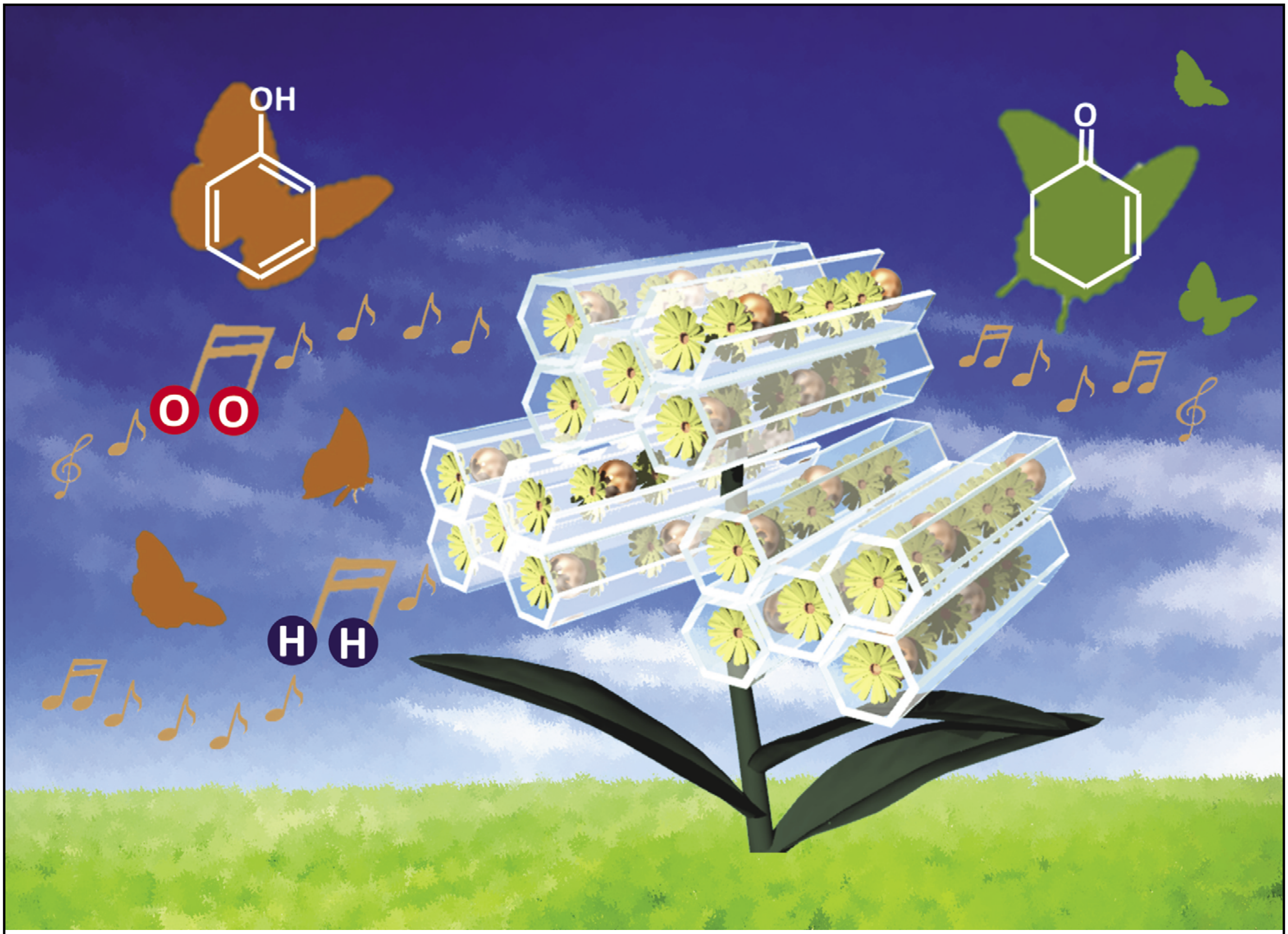


Showcasing research from the Laboratory of Profs. Hiromi Yamashita and Kohsuke Mori at the Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University

Unexpected Pd-catalyzed hydrogenation of phenol to 2-cyclohexene-1-one: enhanced activity and selectivity assisted by molecular oxygen

Addition of O_2 enables the liquid-phase hydrogenation of phenol using H_2 at low temperatures under atmospheric pressure with an unexpected selectivity towards 2-cyclohexene-1-one rather than cyclohexanone. As a catalyst, as-synthesized Pd/MCM-41 including the residual templates within the mesoporous channels exhibits a prominent positive effect on the catalytic performance.

As featured in:

See Hiromi Yamashita *et al.*, *Chem. Commun.*, 2012, **48**, 8886.

RSC Publishing

www.rsc.org/chemcomm

Registered Charity Number 207890

ChemComm

Dynamic Article Links

View Article Online

Cite this: *Chem. Commun.*, 2012, **48**, 8886–8888

www.rsc.org/chemcomm

COMMUNICATION

Unexpected Pd-catalyzed hydrogenation of phenol to 2-cyclohexene-1-one: enhanced activity and selectivity assisted by molecular oxygen†

Kohsuke Mori, Ken Furubayashi, Shusuke Okada and Hiromi Yamashita*

Received 19th March 2012, Accepted 17th April 2012
DOI: 10.1039/c2cc31995k

Addition of O_2 enables the liquid-phase hydrogenation of phenol using H_2 at low temperatures under atmospheric pressure with an unexpected selectivity towards 2-cyclohexene-1-one rather than cyclohexanone. As a catalyst, as-synthesized Pd/MCM-41 including the residual templates within the mesoporous channels exhibits a prominent positive effect on the catalytic performance.

Catalytic hydrogenation processes are employed in the chemical industry as a promising way to obtain several essential products and intermediates.[1] Among these processes, the hydrogenation of phenol to cyclohexanone is one of the most crucial reaction pathways for the manufacture of nylon-6 and nylon-66.[2] The process is performed in either gas or liquid phase with the use of supported Pd catalysts. The gas phase route can be carried out easily in a continuous reactor for higher throughput, but generally requires elevated temperatures (423–573 K).[3–6] The liquid phase route allows cost and energy savings because the reaction proceeds at relatively low temperatures. However, high hydrogen pressures (0.5–4 MPa) and Lewis acid additives ($AlCl_3$ and $SnCl_2$) are often required, thus the process sometimes suffers from subsequent hydrogenation to cyclohexanol.[7–11]

α,β-Unsaturated ketones are commonly known to be pharmacophores and versatile building blocks in organic synthesis, and numerous strategies have been documented for their production.[12] Unfortunately, most methods either involve several reaction steps or are often complicated by low yield and undesired by-products. For example, the production of 2-cyclohexene-1-one on a commercial scale is performed by selective hydrogenation of benzene to cyclohexene followed by allylic oxidation, which simultaneously produces the corresponding allylic alcohol, epoxide, and diol.[13]

In this communication, we present a new protocol for the one-step synthesis of 2-cyclohexene-1-one by the liquid-phase selective hydrogenation of phenol using a Pd-supported mesoporous silica (Pd/MCM-41) catalyst. The most important discovery here is that the addition of molecular oxygen (O_2) into the reaction mixture, together with molecular hydrogen (H_2) as a reducing reagent, substantially enhances the catalytic conversion of phenol as well as selectivity towards 2-cyclohexene-1-one. To the best of our knowledge, this is the first synthesis of 2-cyclohexene-1-one from the hydrogenation of phenol. It should also be noted that this paradoxical new reaction proceeds at low temperatures under atmospheric pressure without the need for co-catalysts.

The mesoporous silica material (MCM-41) was prepared *via* the sol–gel method according to a literature procedure, using cetyltrimethylammonium bromide (CTABr) as a structure-directing agent (SDA) and tetramethylorthosilicate (TMOS) as a Si source.[14] The incorporation of the Pd^{2+} precursor was done using the template ion exchange (TIE) method by the treatment of as-synthesized MCM-41 with an aqueous solution of $(NH_4)_2PdCl_4$.[15] Finally, reduction with an aqueous $NaBH_4$ solution in an Ar atmosphere afforded Pd/MCM-41 (Pd 0.5 wt%) as a pale gray powder. The residual SDA templates inside the mesoporous channel are generally removed by calcination or extraction prior to the catalytic reaction; however, this process was intentionally skipped. As discussed later, the residual SDA plays a significant role in enhancement of the catalytic activity during phenol hydrogenation. This new phenomenon is the other important issue we wish to report here.

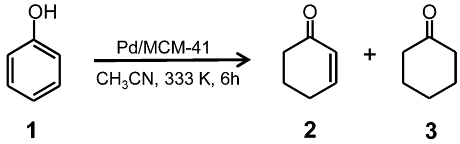
The low-angle X-ray diffraction (XRD) pattern of Pd/MCM-41 reveals a diffraction peak at around $2\theta = 2$–3° associated with the d_{100} spacing, which indicates a hexagonally-packed mesoporous structure. The amount of residual SDA template in the as-synthesized MCM-41 was determined to be 40 wt% by TG analysis. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}), pore volume (V_p), and pore diameter calculated from N_2 adsorption–desorption were 734 $m^2\ g^{-1}$, 0.63 $cm^3\ g^{-1}$, and 2.6 nm, respectively. The S_{BET} and V_p of the as-synthesized Pd/MCM-41 are lower than 974 $m^2\ g^{-1}$ and 0.87 $cm^3\ g^{-1}$ of the calcined Pd/MCM-41 as well as 886 $m^2\ g^{-1}$ and 0.81 $cm^3\ g^{-1}$ as synthesized Pd/MCM-41 before reduction. These results suggest that the SDA template and Pd nanoparticles are present within the mesoporous channel. The Pd K-edge Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) exhibited a single peak at approximately 2.5 Å due to the contiguous Pd–Pd bond in the metallic form with an interatomic distance and a coordination number of 2.76 Å and 9, respectively. These results are in good agreement with those of the transmission electron microscopy (TEM) analysis, where a

---

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: yamashita@mat.eng.osaka-u.ac.jp; Fax: +81-6-6879-7457; Tel: +81-6-6879-7457

† Electronic supplementary information (ESI) available: Experimental procedures, Pd K-edge XAFS spectra, and TEM analysis. See DOI: 10.1039/c2cc31995k

Table 1 Results of phenol hydrogenation using Pd/MCM-41 under different conditions[a]



Entry	H_2/mL	O_2/mL	Yield (%) (**2**)	Yield (%) (**3**)
1	20	0	0	0
2	20	5	47	42
3	20	10	63	36
4	20	20	72	21
5	10	20	42	3
6	5	20	28	1
7	0	20	0	0

[a] Catalytic tests were performed using catalyst (0.05 g, Pd: 2.3 × 10^{-3} mmol), phenol (1.0 mmol), and acetonitrile (20 mL) at 333 K for 6 h with magnetic stirring. Yields were determined using a gas chromatograph.

narrow size distribution of spherical Pd nanoparticles with a mean diameter (*d*) of 2.4 nm was observed, which is almost consistent with the pore diameter of MCM-41.

The hydrogenation of phenol (**1**) using Pd/MCM-41 was conducted by flowing several sets of gaseous H_2 and O_2 for 6 h at 333 K in the presence of CH_3CN solvent under atmospheric pressure (Table 1). No reaction occurred in the presence of either H_2 or O_2; however, both H_2 and O_2 flows were indispensable to achieve hydrogenation of phenol. 2-Cyclohexene-1-one (**2**) and cyclohexanone (**3**) were the only products detected over the entire range of conditions studied, and the highest yield (72%) with a high selectivity of **2** (77%) was achieved with H_2/O_2 = 20 (mL)/20 (mL). Excess O_2 flow relative to H_2 increased the selectivity toward **2** up to 94%, but the reaction rate was substantially decreased. Among the solvents examined, acetonitrile yielded favorable results, whereas ethanol, toluene, THF, and H_2O were completely ineffective.

The prominent effect of O_2 on the catalytic activity and selectivity can also be well demonstrated by switching the atmosphere during the course of the reaction. Fig. 1 shows that the initial stage of reaction under H_2 and O_2 flow proceeded smoothly with high selectivity towards **2**. After 2 h, conversion of phenol completely ceased by the removal of O_2 from the reaction mixture accompanied with a significant decrease in selectivity toward **2**, due to the formation of **3** through subsequent hydrogenation. Upon addition of O_2, the catalytic activity and selectivity returned to the same levels as those at the initial stage. When **2** was used as the substrate, hydrogenation using only H_2 proceeded rapidly to give **3**, whereas significant retardation was observed under an atmosphere of the H_2–O_2 mixture (Fig. 2).

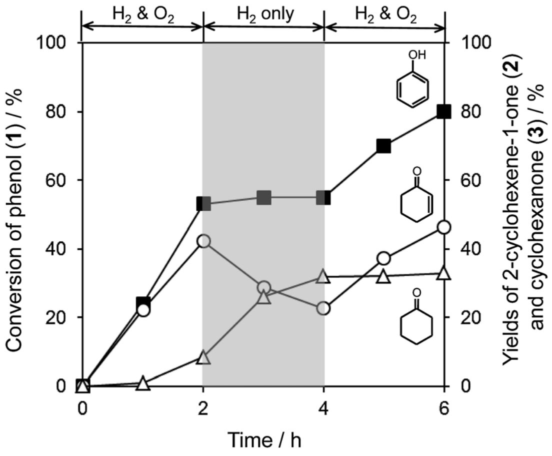


Fig. 1 Kinetic profile in the hydrogenation of phenol under a H_2–O_2 atmosphere (white zone) and H_2 atmosphere (gray zone).

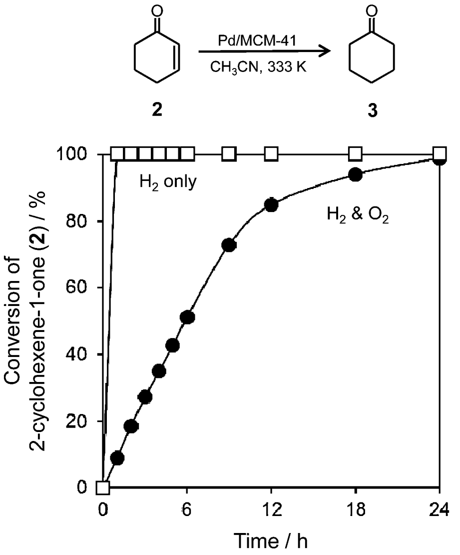
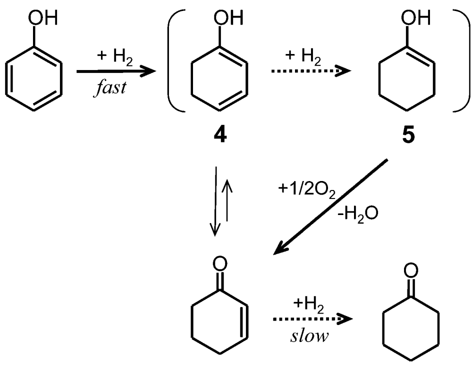


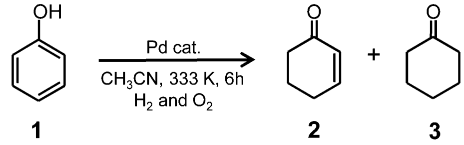
Fig. 2 Kinetic profile in the hydrogenation of 2-cyclohexene-1-one under a H_2–O_2 atmosphere (●) and H_2 atmosphere (□).

Treatment of as-synthesized Pd/MCM-41 with H_2 or a mixture of H_2 and O_2 had no significant effect on the mean diameter of the Pd nanoparticles, which indicates that the reaction did not involve structural change of the Pd nanoparticles. The addition of H_2O_2 had no significant influence on the hydrogenation rate of phenol and selectivity toward **2**, which suggests that the H_2O_2 produced *in situ* from H_2 and O_2 on Pd sites does not participate in the reaction mechanism. Although the detailed reaction mechanism is now under investigation in our laboratory, a possible reaction pathway is illustrated in Scheme 1. In the presence of H_2 and O_2, the



Scheme 1 A plausible reaction pathway for the Pd-catalyzed hydrogenation of phenol under a H_2–O_2 atmosphere.

Table 2 Results of phenol hydrogenation using various Pd catalysts under the H_2–O_2 mixture[a]



Entry	Sample	Template	Yield (%)	
			(2)	**(3)**
1	Pd/MCM-41	CTABr	72	21
2	Calcined Pd/MCM-41	—	18	8
3	Pd/MCM-41	CTACl	54	30
4	Pd/MCM-48	CTABr	71	16
5	Physical mixture of calcined Pd/MCM-41 and CTABr	—	0	0
6	Pd/Al_2O_3	—	33	46
7	Pd/SiO_2	—	9	1
8	Pd/TiO_2	—	0	0
9	Pd/CeO_2	—	0	0
10	Pd/Carbon	—	0	0
11	Pd/Na-Y zeolite	—	0	0

[a] Catalytic tests were performed using catalyst (0.05 g, Pd: 2.3×10^{-3} mmol), phenol (1.0 mmol), and acetonitrile (20 mL) at 333 K for 6 h with H_2/O_2 = 20 (mL)/20 (mL). Yields were determined using a gas chromatograph.

benzene ring of phenol may first be partially hydrogenated to dienol (**4**) and enol (**5**) as reaction intermediates, which are extremely unstable and transformed into **2** by isomerization or oxidative dehydrogenation, respectively.[16] In contrast, phenol is hydrogenated to **5** in one step and isomerized rapidly to form **3** under an only H_2 atmosphere.[10] The apparent activation energy (E_a) for the hydrogenation of **1** to **2** under the H_2–O_2 mixture was determined to be 39.5 kJ mol^{-1} by an Arrhenius plot, which is substantially lower than those reported for the hydrogenation of **1** to **3** using other Pd catalysts in the presence of only H_2, such as Pd/MgO (65.0 kJ mol^{-1})[7,17] and Pd/Al_2O_3 (56.8 kJ mol^{-1}).[18] This implies the involvement of another reaction pathway by the addition of O_2. Moreover, the relatively high E_a of 35 kJ mol^{-1} determined for the hydrogenation of **2** to **3** using the Pd/MCM-41 catalyst under the H_2–O_2 mixture compared to 11 kJ mol^{-1} under only H_2 clearly accounts for the high selectivity towards **2** over **3**.

The as-synthesized Pd/MCM-41 catalyst employed in the present reactions includes the residual SDA templates within the mesoporous channels, which exhibit a pronounced positive effect on the catalytic performance. Table 2 shows that as-synthesized uncalcined Pd/MCM-41 including SDA resulted in a yield that was three times higher than the conventionally calcined Pd/MCM-41 without SDA (entry 1 *vs.* 2). As SDA, CTACl exhibited slightly low selectivity, but achieved a role similar to CTABr (entry 3). MCM-48, which consists of a uniform array of 3D-connected tubular pores, exhibited a similar positive effect (entry 4). On the other hand, a negative effect was observed when a physical mixture of the calcined Pd/MCM-41 and CTABr was employed (entry 5), which suggests that the close proximity of the periphery of the active Pd nanoparticles to SDA within the mesoporous channels is an essential condition. The use of Al_2O_3, fumed SiO_2, TiO_2, CeO_2, carbon, and Na-Y–zeolite (SiO_2/Al_2O_3 = 5) gave poor results with respect to both conversion and selectivity (entries 6–11). This unique phenomenon can be explained by the weak basicity dispersed inside the mesoporous channel, which is in favor of interaction with the weak acidic phenol.[19] Preliminary investigation provided evidence that the as-synthesized Pd/MCM-41 exhibited high adsorption capacity for phenol (0.4 mmol g^{-1}) in CH_3CN solution over 6 h, while negligible adsorption ($< 4 \times 10^{-3}$ mmol g^{-1}) was observed for the calcined Pd/MCM-41.

In conclusion, the combination of H_2 and O_2 allows selective hydrogenation of phenol to 2-cyclohexene-1-one under mild reaction conditions. The use of as-synthesized uncalcined Pd/MCM-41 including the SDA template also plays a key role in achieving efficient hydrogenation that could potentially contribute to saving energy and time. The unprecedented catalytic performance demonstrated in this study holds a significant promise for the achievement of novel catalyst systems.

Notes and references

1 H. U. Blaser, C. Malan, B. Pugin, F. Spindler, H. Steiner and M. Studer, *Adv. Synth. Catal.*, 2003, **345**, 103–151.
2 I. Dodgson, K. Griffin, G. Barberis, F. Pignataro and G. Tauszik, *Chem. Ind.*, 1989, 830–833.
3 N. Mahata and V. Vishwanathan, *Catal. Today*, 1999, **49**, 65–69.
4 S. G. Shore, E. Ding, C. Park and M. A. Keane, *Catal. Commun.*, 2002, **3**, 77–84.
5 L. M. Sikhwivhilu, N. J. Coville, D. Naresh, K. V. R. Chary and V. Vishwanathan, *Appl. Catal., A*, 2007, **324**, 52–61.
6 M. Chatterjee, H. Kawanami, M. Sato, A. Chatterjee, T. Yokoyama and T. Suzuki, *Adv. Synth. Catal.*, 2009, **351**, 1912–1924.
7 N. Mahata, K. V. Raghavan, V. Vishwanatha, C. Park and M. A. Keane, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2712–2719.
8 H. Li, J. Liu, S. Xie, M. Qiao, W. Dai and Y. Lu, *Adv. Synth. Catal.*, 2008, **18**, 3235–3241.
9 P. Makowski, R. Demir Cakan, M. Antonietti, F. Goettmann and M. M. Titirici, *Chem. Commun.*, 2008, 999–1001.
10 H. Liu, T. Jiang, B. Han, S. Liang and Y. Zhou, *Science*, 2009, **326**, 1250–1252.
11 Y. Wang, J. Yao, H. Li, D. Su and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 2362–2365.
12 *Comprehensive Organic Synthesis*, ed. P. C. B. Page and T. McCarthy, Pargamon, Oxford, UK, 1991.
13 *Metal-catalyzed Oxidations of Organic Compounds*, ed. R. A. Sheldon and J. K. Kochi, Academic Press, New York, 1981.
14 K. Mori, K. Watanabe, M. Kawashima, M. Che and H. Yamashita, *J. Phys. Chem. C*, 2010, **115**, 1044–1050.
15 M. Yonemitsu, Y. Tanaka and M. Iwamoto, *Chem. Mater.*, 1997, **9**, 2679–2681.
16 G. D. Dzingeleski, G. Blotny and R. M. Pollack, *J. Org. Chem.*, 1990, **55**, 1019–1023.
17 N. Mahata and V. Vishwanathan, *J. Mol. Catal. A: Chem.*, 1997, **120**, 267–270.
18 J. R. Gonzalez-Velasco, M. P. Gonzalez-Marcos, S. Arnaiz, J. I. Gutierrez-Ortiz and M. A. Gutierrez-Ortiz, *Ind. Eng. Chem. Res.*, 1995, **34**, 1031–1036.
19 Y. Zhou, Y. F. Tao, J. Yang, W. G. Lin, M. M. Wan, Y. Wang and J. H. Zhu, *J. Hazard. Mater.*, 2011, **190**, 87–93.