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ARTICLE

Improvement activity of palladium nanoparticles using a sulfur-containing metal–organic framework as an efficient catalyst for selective aerobic oxidation in water

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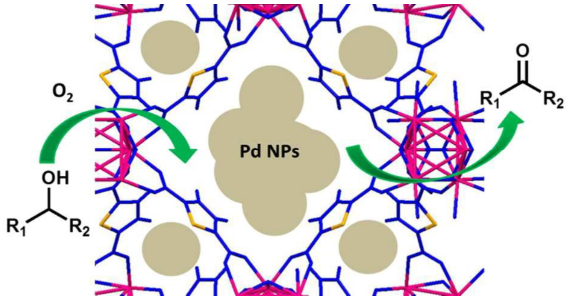
Simple and efficient nanostructured catalyst system comprising Pd nanoparticles stabilized by thiophene-groups of a metal-organic framework (MOF) was developed. The Pd species were deposited into the DUT-67(Zr) structure and reduced to nanoparticles that can be stabilized by the synergism effect of thiophene groups and confinement effect of the MOF pores. Increasing the interaction time of palladium entrance into the MOF cavities leads to more effective connecting them to the metal-organic framework and produced more efficient catalytic system. Reduction process was performed using $NaBH_4$ and N_2H_4. The catalysts were characterized by N_2 adsorption-desorption analysis, infrared spectroscopy (IR), powder X-ray diffraction (PXRD), scanning electronic microscopy (SEM) and transmission electron microscopy (TEM). Selective aerobic oxidation of alcohols in neat water under O_2 atmosphere was addressed with 0.5%Pd/DUT-67(Zr) including Pd nanoparticles created using $NaBH_4$. Furthermore, the catalyst could be easily separated from the reaction mixture by simple filtration and reused at least ten times without significant loss in catalytic efficiency under the investigated conditions.

Introduction

Although palladium catalyzed oxidation reaction of alcohols has a long and ancient history, but the capabilities and expertise of the metal and the importance of this type of reaction among chemical reactions, has led to continue efforts to perform more efficient oxidation reaction. Among the catalyst systems have been proposed to date, the design of heterogeneous systems to support the palladium nanoparticles have been notable successes in this field. During the past decade, great progress has been made in heterogeneous Pd catalysts for oxidation processes, for example, Pd/hydroxyapatite[1], Pd/mesoporous silicas[2, 3], polymer-supported Pd[4, 5], carbon nanotubesupported Pd [6, 7], Pd supported on metal oxide [8]. Recently applications of metal-organic frameworks (MOFs) in heterogeneous catalysis especially those as a support for metal nanoparticles (e.g., Pd, Au, Ru, and Pt) have attracted extensive attention owing to their high surface area, porosity, and chemical tunability.[9-20]

The most important challenge of these heterogeneous systems is to form palladium nanoparticle in the right active sizes and their stabilization during relatively harsh oxidation reaction conditions. Structural diversity of MOFs provides the opportunity of designing more improved base-free systems bearing amine functional organic linkers [21, 22]. Li and co-workers developed a heterogeneous Pd catalyst deposited on a zeolite-type MOF, MIL-101, using a simple colloid method.[22] The 0.35% Pd/MIL-101 has been shown to be highly efficient in the liquid-phase aerobic oxidation of a variety of alcohols in the absence of base in toluene at 80°C. This group also affirmed that the Co/C-N composite prepared by calcination of a triazine containing Co-MOF can be an efficient heterogeneous catalyst for base-free aerobic alcohol oxidation in water at 110°C. Moreover, using Zr-MOF containing thiolic group linkers, Xu and co-workers developed a heterogeneous system in which Pd (II) species anchor to the framework by poisoning effect of thiol groups dangling within the MOF pores.[23] The Suzuki-Miyaura couping reaction was performed with the catalyst in EtOH medium at 80°C. To create larger



Scheme 1. Entrapment of Pd NPs into the sulfur-containing pores of DUT-67(Zr) for aerobic oxidation reaction

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pore opening that causes less diffusion limitations, DMTA (dimercapthoterphenyldicaboxylate) was used as elongated building block. It has been proved that while Pd(0) atoms formed during the reaction, they combine to make less active Pd nanoparticles when the catalyst was placed in air. In another work by Wang and co-workers, Zr-MOF bearing thiophenedicarboxylic acid known as DUT-67, used for supporting Pd nanoparticles.[24] 0.5%Pd@DUT was introduced as the most suitable Pd loading for the Suzuki coupling reaction in the mixed water-ethanol solvents, at 70˚C, and Nitrobenzene hydrogenation at 60˚C. Pd NPs was formed before the catalytic reaction using $NaBH_4$, as reducing agent. The catalyst was recycled 4 times with slight decrease in its reactivity for coupling reaction, but there is no report of hot filtration or ICP analysis to clarify the exact fate of Pd NPs.

Principally, water is an environmentally benign medium especially for safety and scalable catalytic systems. It also can introduce many other benefits such as reaction and selectivity improvements, simplification of the work-up procedures and mild reaction conditions.[25] Generally, gold based catalysts are the ideal choice in water, since they do not suffer from deactivation in the presence of oxygen. Some oxidations of benzylic alcohols in water as solvent were also reported using copper-based catalysts.[26] Here, we try to investigate Pd NPs/DUT-67 as the catalyst for aerobic oxidation reaction of alcohols. Step by step survey of the conditions for Pd loading on the thiophene-containing MOF, led to develop a seldom heterogeneous Pd catalyst system for selective aerobic oxidation of alcohols in water. According to our studies, there is no report for water-tolerant oxidation catalyst of Pd NPs on MOF support for this reaction in water.

Experimental Section

Materials

2,5-thiophenedicarboxylic acid (H_2TDC, from Aldrich), Zirconium(IV) chloride ($ZrCl_4$ from Aldrich) and all alcohols (from Merck) N,N-dimethylformamide (DMF, from DAE JUNG Reagents Chemicals), CH_3CN (from Merck) were used without additional purification. Toluene (from Merck) was distilled, and dried by refluxing in the presence of sodium under the argon atmosphere and transferred into the reaction bottle through a syringe.

Instrumentation

Transmission electron microscopy (TEM) analyses were performed on a Philips CM 200FEG microscope. Powder X-ray diffraction (PXRD) data were acquired on a Philips X-Pert diffractometer using Cu Kα radiation. SEM images were captured on Philips XL-300 instrument. The nitrogen sorption isotherms were collected by Belsorb (BELMAX, Japan). The GC analyses were performed on Echrom A90 using a flame ionization detector (FID).

Catalyst preparation

Synthesis of DUT-67. DUT-67 was synthesized according to the references.[23, 24, 27] Typically, 230 mg solid powder of $ZrCl_4$ (1 mmol) was dissolved in a mixture of DMF (12.5 mL) and NMP (12.5 mL) and was sonicated for 10 min. Subsequently, 110 mg of 2,5-thiophenedicarboxylic acid (H_2TDC, 0.67 mmol) was added to the mixture and sonicated for another 5 min. Then, acetic acid (3.5 mL) was added to the solution and it was sonicated for a further 10 min and then transferred to a 100 mL Tefon-lined autoclave and heated at 120˚C for 4 h under autogenous pressure. The obtained powder was filtered off and washed several times with DMF and CH_3CN. The resultant product was dried at 80˚C under in air.

Synthesis of Pd/DUT-67 (1). Loading of Pd was performed according to previous report [24, 28] by some changes. Typically, for preparation of 0.5%Pd/DUT-$NaBH_4$ (1), 8.5 mg (0.05 mmol) $PdCl_2$ powder and 1.5 mg of NaCl was dispersed in 10 mL DMF through sonication for 10 min. Then, MeOH (1 ml) and H_2O (0.5 ml) was added and the mixture was further sonicated and stirred till a clear orang solution was obtained. In another container the as-prepared DUT-67 (0.5 g) was dispersed in 8 mL DMF and stirred for 20 min in a 25 mL beaker. Then, both solutions were mixed in a flask and stirred for a further 1h. Subsequently, NaBH4 (20 mg for 0.5% Pd/DUT-67) was added dropwise to the mixture. Immediately, the colour of the solution changed from orange to dark grey. The product was collected by filtration and washed with DMF several times and finally with CH_3CN. The resultant products were dried using a desiccator under vacuum for 3 days. The Pd content in the sample was ca. 0.47 wt% based on ICP analysis.

Identical procedures were followed to deposit Pd nanoparticles onto the DUT-67 for the synthesis of 2%Pd/DUT-$NaBH_4$ (1) unless 4 times amount of all materials was used. The Pd content in the sample was ca. 1.8 wt% based on ICP analysis.

0.7%Pd/DUT-N_2H_4 (1): All details were the same as above unless N_2H_4 (0.5 ml) was used as reducing agent instead of $NaBH_4$. The material produced in this way was denoted as 0.7%Pd/DUT-N_2H_4 (1), because the ICP analysis confirmed the 0.74 wt% of Pd content deposited onto the MOF structure.

Synthesis of Pd/DUT-67 (2). For preparation of 0.5%Pd/DUT-$NaBH_4$ (2), 8.5 mg (0.05 mmol) $PdCl_2$ powder and 1.5 mg of NaCl were dispersed in 10 mL DMF through sonication for 10 min. Then, MeOH (1 ml) and H_2O (0.5 ml) was added and the mixture was further sonicated and stirred till a clear orang solution was obtained. In another container the as-prepared DUT-67 (0.5 g) was dispersed in 8 mL DMF and stirred for 20 min in a 25 mL beaker. Then, both solutions were mixed in a flask and stirred for a further 1h. The argon gas was purged into the solution and the beaker was sealed and stirred for another 24 h. Subsequently, $NaBH_4$ (20 mg for 0.5% Pd/DUT-67) was added dropwise to the mixture. The dark grey mixture was stirred for 1h. The product was collected by filtration and washed with DMF several times and finally with CH_3CN. The resultant products were dried using a desiccator under vacuum for 3 days. The Pd content in the sample was ca. 0.51 wt% based on ICP analysis.

Aerobic oxidation reaction using Pd/DUT-67 catalysts

A mixture of alcohol (0.5 mmol), base (0.5 mmol) and catalyst (0.04 g, ca. 0.3 mol% of Pd for 0.5%Pd/DUT-$NaBH_4$ (1) and 0.4 mol% of Pd for 0.5%Pd/DUT-$NaBH_4$ (2)) in dry toluene (or other solvents, 4 ml) was prepared in a two-necked Schlenk flask. The flask was then evacuated, refilled with pure oxygen. The resulting mixture was stirred at 80˚C under an oxygen atmosphere. Before analysing with

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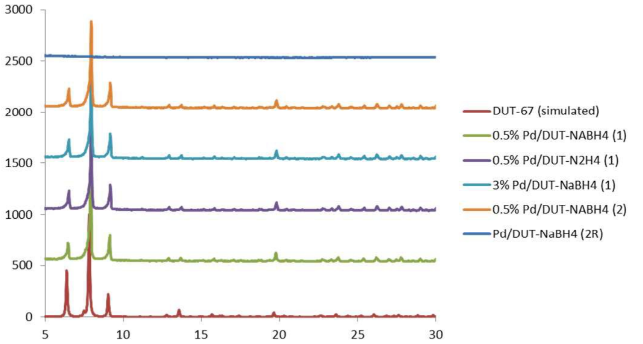

Fig. 1 PXRD pattern of the prepared DUT-67 after Pd loading

GC, 100 ml of cyclohexane as the internal standard was added. Then, the organic layer was extracted with ethyl acetate, subsequently subjected to GC analysis.

Results and discussion

DUT-67 (Zr) was prepared based on Kaskel report and its structure confirmed by powder X-ray diffraction, PXRD, and scanning electron microscope, SEM analyses.[27] The powder XRD of the prepared sample has been shown in Figure 1, accordingly indicated the high agreement of the planes in as-synthesized MOF with the simulated pattern of DUT-67. SEM images, Figure 2a, provided the both hexagon and square shape planes of the polyhedral microcrystals that are characteristics of DUT-67 (Zr). Two previous methods mixed together and changed a little to use for Pd deposition onto the MOF structure.[24, 28] As described in details in experimental section, $PdCl_2$ powder was used as precursor of Pd in a mixture of DMF, H_2O and MeOH solvents. In protocol (1), after addition of Pd source into the mixture of MOF stirring in DMF, reducing agent, $NaBH_4$ was added one hour later. Two types of Pd-supported MOF were prepared at the ratio of 0.5% and 2% for Pd loading which was measured by ICP analysis, denoted as 0.5%Pd/DUT-$NaBH_4$ (1) and 2%Pd/DUT-$NaBH_4$ (1). To investigate the effect of reducing agent, one another catalyst was prepared with 0.5% of Pd ratio (which known as the best loading of Pd on DUt-67 for coupling reaction), while N_2H_4 was used as reducing agent instead of $NaBH_4$. It was named as 0.5%Pd/DUT-N_2H_4 (1). Finally, we prepared 0.5%Pd/DUT-$NaBH_4$ (2) by considering the results of aerobic oxidation reaction which will explain later. In this case, addition of the reducing agent, $NaBH_4$, was performed 24 h after the mixing of Pd source with the MOF support under the inert atmosphere. All these four material were identified completely. Figure S1 (Electronic Supplementary Information) showed the IR spectrum of the original DUT-67 and the prepared materials after Pd loading. As it is clear, no remarkable changes was determined after Pd loading in the whole samples. PXRD patterns of the materials compared in Figure 1, confirmed that the crystallinity of the MOF remains intact after Pd loading using both procedures and both reducing agents. SEM images were also averred these analyses, Figure 2. The polyhedral microcrystals of the MOF support stayed stable during the Pd loading even in the case of 0.5%Pd/DUT-$NaBH_4$ (2) that changed a little more, Figure 2e.

Table 1. Lattice parameters of the catalyst structures prepared in the absence or presence of different amounts of Pd species on DUT-67.

Sample	S_{BET} (m^2g^{-1})[a]	D_{micro} (nm)[b]	D_{meso} (nm)[c]	V_{meso} (cm^3g^{-1})[c]
DUT-67	642(748)	0.34	1.5 (2.5)	0.27
0.5% Pd/DUT-$NaBH_4$ (1)	593(701)	0.34	1.5 (2.7)	0.27
2% Pd/DUT-$NaBH_4$ (1)	702(842)	0.35	1.5 (2.8)	0.33
0.5% Pd/DUT-$NaBH_4$ (2)	650 (762)	0.32	1.8 (2.9)	0.29
0.5% Pd/DUT-$NaBH_4$ (2R)	187 (236)	0.36	1.6 (2.7)	0.09
0.5% Pd/DUT-N_2H_4 (1)	736(865)	0.34	1.5 (2.6)	0.31

(a) The Brunauer-Emmett-Teller (BET) surface area. (b) The misopore size distributions were calculated using MP plot. (c) The mesopore pore volume and the mesopore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) method of adsorbtion branch; data in parentheses are calculated from desorption branch.

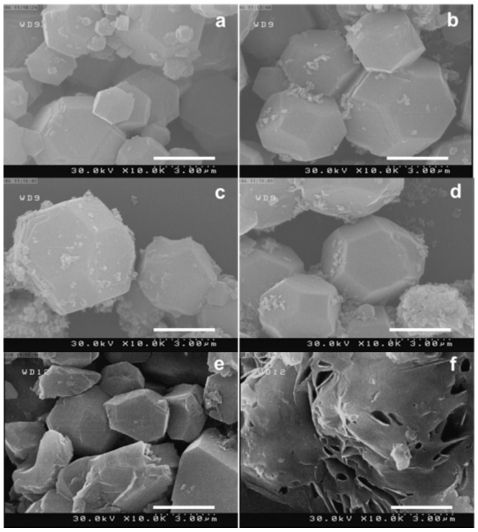

Fig. 2 Scanning electron microscope (SEM) images of a) DUT-67 (Zr); b) 0.5% Pd/DUT-$NaBH_4$ (1); c) 0.5% Pd/DUT-N_2H_4 (1); d) 2% Pd/DUT-$NaBH_4$ (1); e) 0.5% Pd/DUT-$NaBH_4$ (2); f) 0.5% Pd/DUT-$NaBH_4$ (2R).

The lattice parameters of the materials was examined by N_2 adsorption-desorption analysis. As summarized in Table 1, the as-prepared DUT-67 has a BET surface area of 642 m^2g^{-1}, which has been changed randomly for the prepared catalysts when Pd loaded onto the net. In the case of 0.5%Pd/DUT-$NaBH_4$ (1), insertion of the Pd species led to reducing the specific surface area to 592 m^2g^{-1}. Increasing the amount of Pd component to four times unexpectedly augmented the average surface area in 2%Pd/DUT-$NaBH_4$ (1). Comparison of SEM images of these two materials with bare MOF represented in Figure 2, demonstrated this discrepancy. As it shown, when Pd content increased, some Pd species have been integrated with each other and a new separated cluster phase of Pd was formed besides the MOF structure. The construction of this new phase of Pd caused the augmentation of surface area for 2%Pd/DUT-$NaBH_4$ (1) and actually indicated low efficient deposition of Pd species in this case. Increasing the amount of palladium content only creates larger particles that accumulate during the reaction and inactive clusters are obtained. Moreover, reducing the

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catalytic activity of 2%Pd/DUT-$NaBH_4$ (1) points to the crucial role of palladium nanoparticles in the catalyst system. Change the method and further timing of the loading process of palladium ions onto the support, resulting in better dispersion of Pd particles into the MOF and their more effective interaction with sulfur atoms. As it is clear in SEM images of 0.5%Pd/DUT-$NaBH_4$ (2), no Pd nanoparticles was accordingly observed on microcrystal surfaces of DUT-67, while more palladium content was detected by ICP analysis, 4 mmol/g Pd for 0.5%Pd/DUT-$NaBH_4$ (2) instead of 3 mmol/g for 0.5%Pd/DUT-$NaBH_4$ (1). Meanwhile, TEM image of the sample interestingly displayed that Pd NPs significantly penetrated into the cavities and deposited within the MOF interfaces, Figure 3b. A little increasing the surface area of the MOF after the Pd loading confirmed that these most likely sources of catalytic activity entered into polyhedral cages of DUT-67. It will be showed that this small amount of Pd NPs do not separate from the bed even after several reaction runs causing the possibility of repeating the reaction in several stages. An important point is that the average size of Pd NPs deposited in these two samples is not different, 12-17 nm. Meanwhile, comparison of TEM images of these samples clearly indicated more uniformity for nanoparticles in the case of 0.5%Pd/DUT-$NaBH_4$ (2), Figure 3a and 3b.

The type of reducing agent is also very important. 0.5%Pd/DUT-N_2H_4 (1) was just prepared in a similar procedure to 0.5%Pd/DUT-$NaBH_4$ (1). The lower catalytic reactivity of the former is may be due to different kinetics of the reduction process by these two reagents $NaBH_4$ Vs N_2H_4. In general, the type of reducing agent affected the final properties of the nanoparticles. The two reducing agents have different reduction potentials in solution, i.e. 1.24 V for $NaBH_4$ Vs 1.15 V for N_2H_4.[29-32] Higher reduction power of NaBH4 than hydrazine probably increases the formation of smaller catalytically active Pd nanoparticles versus larger inactive Pd clusters using the former reagent.

Aerobic oxidation reaction with these Pd supported DUT-67 catalysts was performed using benzyl alcohol as substrate. The results of experimental reactions summarized in Table 2. As it shows surprisingly, no detectable oxidation product was formed using 2%Pd/DUT-$NaBH_4$ (1) that confirmed the obtained observation based on the construction of deactivated Pd clusters (Table 2, entry 2). Moreover, 0.7%Pd/DUT-N_2H_4 (1) also indicated a very weak catalytic performance. While about 57% of benzaldehyde produced using 0.5%Pd/DUT-$NaBH_4$ (1), only 3% of this product was formed using 0.7%Pd/DUT-N_2H_4 (1) in the same reaction conditions (Table 2, entries 1 and 3). This data actually introduced the former as the best catalyst among three samples synthesized via protocol (1). Therefore, we tried to optimize the reaction conditions using 0.5%Pd/DUT-$NaBH_4$ (1). However, no remarkable improvement was happened using Et_3N and NaOH as base or replacing the solvent, with CH_3CN, DMF or NMP (Table 2, entries 4-8). Using the mixture of solvents, $PhCH_3$/PEG, 1:1, did not also improve the catalyst performance of the heterogeneous system (Table 2, entry 9).

Subsequently, we decided to produce some changes in deposition stage of Pd NPs onto DUT-67. So, as indicated before, using the optimum amount of Pd precursor, 0.5%Pd/DUT-$NaBH_4$ (2) was synthesized via timing the mixture of MOF and Pd source to be stirred for 24 h in DMF. After that, reducing agent, $NaBH_4$ was added and the same procedure was followed to get the final catalyst. Interestingly, oxidation reaction of benzylalcohol using this catalyst led to producing 75% of benzaldehyde in the best reaction conditions that resulted 57% aldehyde yield in the presence of 0.5%Pd/DUT-$NaBH_4$ (1). This notable improvement encouraged us to examine the more reaction conditions in the presence of the new prepared catalyst. As displayed in Table 2, replacing K_2CO_3 with Na_2CO_3 and/or Et_3N greatly diminished the yield of aldehyde (entries 11 and 12). Using the solvent mixture of $PhCH_3$/PEG did not also develop the catalytic system (13% yield, not shown in the Table 2).

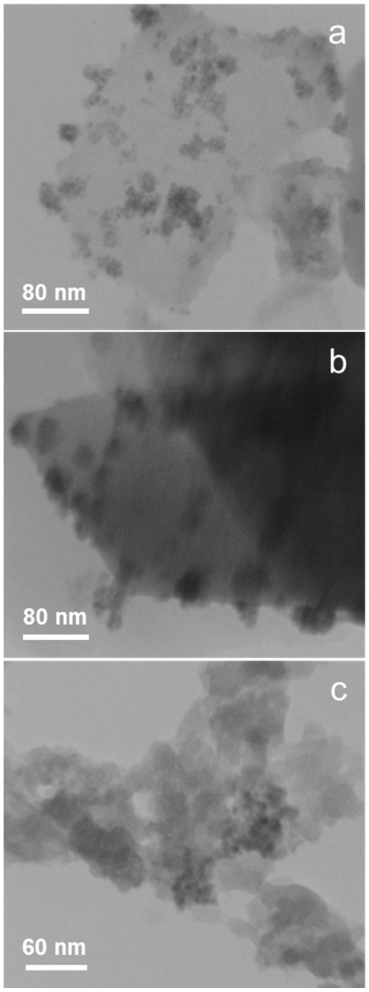

Fig. 3 Transmission electron microscope (TEM) images of a) 0.5%Pd/DUT-$NaBH_4$(1), b) 0.5%Pd/DUT-$NaBH_4$(2) and c) the recovered catalyst, 0.5%Pd/DUT-$NaBH_4$(2R).

Surprisingly, in the presence of water as solvent 82% of benzaldehyde was formed without any detectable benzoic acid (more than 99% selectivity, entry 15). This significant result in the greenest solvent, H_2O, has not been yet observed for heterogeneous oxidation of alcohols with Pd nanoparticles under the O_2 atmosphere with this kind of MOF catalysts. Substrate scope of the reaction was indicated in Table 2 and demonstrated the reactivity of the other substrates according to their electronic and/or hindrance character. The substrates bearing electron

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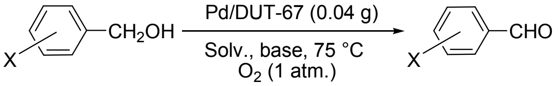
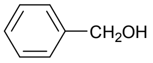
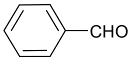
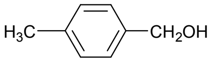
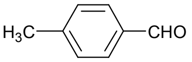
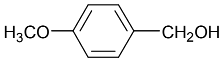
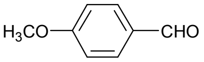
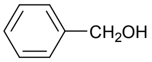
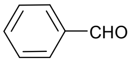
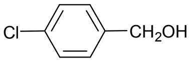
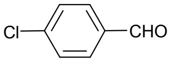
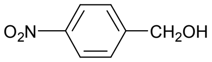
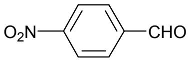
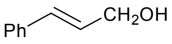
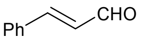
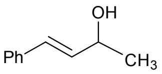
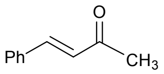
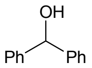
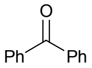
Table 2. aerobic oxidation reaction using the prepared Pd/DUT-67(Zr) samples in different conditions



Entry	Cat.	Substrate	Solvent	Product	Time: Yield (%)[a]
1	0.5%Pd/DUT-NaBH$_4$(1)		PhCH$_3$		6h: 23 24h: 57
2	2%Pd/DUT-NaBH$_4$(1)		PhCH$_3$		24h: ---
3	0.7%Pd/DUT-N$_2$H$_4$(1)		PhCH$_3$		24h: 3
4	0.5%Pd/DUT-NaBH$_4$(1)		PhCH$_3$		23h: 38[b]
5	0.5%Pd/DUT-NaBH$_4$(1)		PhCH$_3$		23h: 53[c]
6	0.5%Pd/DUT-NaBH$_4$(1)		CH$_3$CN		24h: 9.8
7	0.5%Pd/DUT-NaBH$_4$(1)		DMF		24h: 21
8	0.5%Pd/DUT-NaBH$_4$(1)		NMP		24h: 12
9	0.5%Pd/DUT-NaBH$_4$(1)		PhCH$_3$-PEG		24h: 6[d]
10	0.5%Pd/DUT-NaBH$_4$(2)		PhCH$_3$		22h: 75
11	0.5%Pd/DUT-NaBH$_4$(2)		PhCH$_3$		24: 53[e]
12	0.5%Pd/DUT-NaBH$_4$(2)		PhCH$_3$		24h: 8.2[f]
13	0.5%Pd/DUT-NaBH$_4$(1)-PEG		PhCH$_3$		24h: 2.5
14	0.5%Pd/DUT-67(Zr)		PhCH$_3$		24h: 8.3
15	0.5%Pd/DUT-NaBH$_4$(2)		H$_2$O		24h: 82
16	0.5%Pd/DUT-NaBH$_4$ (1)-PEG		H$_2$O		24h: 4
17	2%Pd/DUT-NaBH$_4$(1)		H$_2$O		24h: 2.5
18	0.5%Pd/DUT-NaBH$_4$(2)		H$_2$O		10h: 100
19	0.5%Pd/DUT-NaBH$_4$(2)		H$_2$O		8h: 100
20	0.5%Pd/DUT-N$_2$H$_4$ (1)		H$_2$O		24h: 3.5
21	0.5%Pd/DUT-NaBH$_4$(2)		H$_2$O		15h: 74
22	0.5%Pd/DUT-NaBH$_4$(2)		H$_2$O		15h: 7
23	0.5%Pd/DUT-NaBH$_4$(2)		H$_2$O		10h: 73
24	0.5%Pd/DUT-NaBH$_4$(2)		H$_2$O		10h: 54
25	0.5%Pd/DUT-NaBH$_4$(2)		H$_2$O		24h: 15

[a] GC Yield. 0.5 mmol K$_2$CO$_3$ as base.[b] Using 0.5 mmol Et$_3$N as base. [c] Using 0.5 mmol NaOH as base. [d] PhCH$_3$/ PGE (200), 1:1. [e] Using 0.5 mmol Na$_2$CO$_3$ as base. [f] Using 0.5 mmol Et$_3$N as base; 3% of benzoic acid was also detected.

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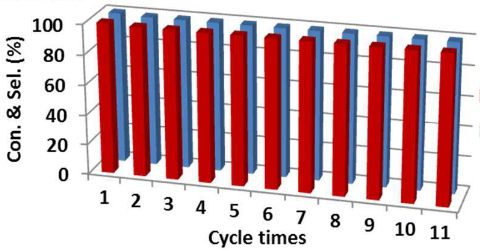

Fig. 4 The catalyst, 0.5%Pd/DUT-NaBH$_4$ (2) was recycled and reused in ten frequent aerobic oxidation of p-methylbenzyl alcohol in water with high conversion and selectivity.

donating group react more efficiently than their containing electron-withdrawing group.

What makes this catalyst as a specific MOF-base Pd heterogeneous catalyst is its capability to proceed the partial oxidation reaction of alcohols in water with high selectivity. As discussed above, comparing the SEM and TEM images of this catalyst showed that the Pd species could permeate into the cavities of MOF and Pd NPs were formed within the interfaces of polyhedral microcrystals of MOF. Furthermore, the light brown colour of the reaction solution in the presence of 0.5%Pd/DUT-NaBH$_4$ (1) compared with 0.5%Pd/DUT-NaBH$_4$ (2) is obviously evidence for the more effective anchoring of Pd species into thiophene groups of the MOF framework in the later, Figure S2 (Electronic Supplementary Information).

For more investigation about the catalyst system, hot filtration test was performed, consequently. The reaction of p-methylbenzyl alcohol was run in the optimum conditions described in Table 2 using 0.5%Pd/DUT-NaBH$_4$ (2). After 4 h of the reaction (47% yield), the solid phase of the reaction mixture was hot-filtered off. Then the reaction was run again to continue without catalyst. Further reaction took place after another 10 h and progressed only 6% more (total conversion: 53%). Analysing the reaction solution by ICP indicated that less than 0.02% of the Pd species had leached into the reaction mixture. Hence, the contribution of local leaching[45] induced homogeneous catalysis[33, 34] and heterogeneous character of the catalyst both play for the catalyst reactivity.[46]

Disclosing the recyclability of 0.5%Pd/DUT-NaBH$_4$ (2) were then served using of p-methylbenzyl alcohol in the presence of twice amount of the catalyst (The reaction time dropped to 6 h) in the same reaction conditions indicated in Table 2. After each run, the reaction mixture was let to settle down and the supernatant was sintered off. The flask was charged by substrate, base and solvent and the reaction let to run again. Surprisingly, the recovered catalyst was successfully used in 10 subsequent reactions without loss of catalytic activity and selectivity. Quantitative amount of the corresponding aldehyde was produced with more than 99% selectivity in all recycling runs, determined by GC analysis, Figure 4.

Figure 3c is a typical TEM image of the recovered 0.5%Pd/DUT-NaBH$_4$ (2) catalyst after the tenth reaction cycle. The image showed that the polyhedral microcrystals structure of the pristine DUT-6 was mostly destructed, though the catalyst reactivity remained intact after 10 recycle runs. Pd nanoparticles as well distributed throughout the regular channels. These clearly demonstrate the porous thiophene-containing support provides the means for distributing and stabilizing the Pd nanoparticles inside the micro/mesochannels of the catalyst system during the reaction even after reducing the MOF crystallinity indicated by PXRD pattern, Figure 1 and SEM image, Figure 2f.

The appealing point in this investigation is that no over oxidation to acid formation was observed even after prolonged reaction time. In addition, aerobic oxidation of alcohols using heterogeneous systems comprising transition metal nanoparticles such as cobalt [35] platinum [36-38] and gold [39-41] nanoparticles in neat water solvent has been developed. Heterogeneous catalyst based on palladium nanoparticles for aerobic oxidation of alcohols in neat water and O$_2$ atmosphere has been also developed using inorganic and organic supports such as mesoporous carbon [42] and functionalized polymers. [43, 44] However, there is no report of this worth reaction in water using MOF structures.

Conclusions

Pd-catalyzed aerobic oxidation of alcohols has been addressed using Pd nanoparticles entrapped into the thiophene-containing MOF structure. DUT-67 (Zr) was loaded with different amounts of Pd sources. Utilizing NaBH$_4$ and N$_2$H$_4$ as reducing agent indicated that the best results were obtained in the presence of 0.04 g of the catalysts (ca 0.4 mol% of the Pd) prepared by the former. In addition, increasing the time of Pd deposition into MOF structure afforded an efficient and recoverable heterogeneous Pd catalyst which developed selective aerobic oxidation in water.

Acknowledgements

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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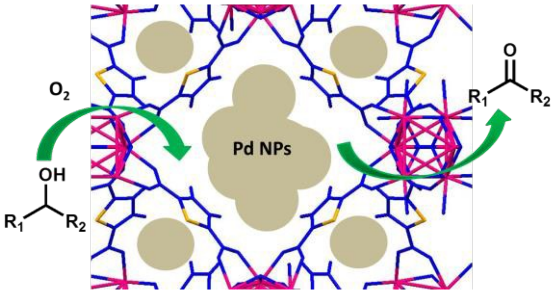

Highlight

Synergism of thiophene and confinement of MOF with time of Pd entrance leads an efficient catalyst for oxidation in water.