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MOFs as catalysts: Activity, reusability and shape-selectivity of a Pd-containing MOF

Françesc X. Llabrés i Xamena, Alberto Abad, Avelino Corma *, Hermenegildo Garcia *

Instituto de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, Avda. de los Naranjos, s/n, 46022 Valencia, Spain

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Abstract

A palladium-containing metal–organic framework (Pd-MOF) was found to be an active catalyst for alcohol oxidation, Suzuki C–C coupling, and olefin hydrogenation. The MOF structure is preserved throughout catalysis, and the material is reusable. The Pd-MOF demonstrates remarkable shape-selectivity for olefin conversion.

Keywords: Metal–organic framework; Pd catalysts; Shape-selectivity; Alcohol oxidation; Suzuki C–C coupling; Olefin hydrogenation

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1. Introduction

Metal–organic frameworks (MOFs) are crystalline porous solids composed of a three-dimensional (3D) network of metal ions held in place by multidentate organic molecules [1,2]. The spatial organization of these structural units leads to a system of channels and cavities in the nanometer length scale, analogous to that found in zeolites. Correct selection of the structural subunits and the way in which they are connected allows systematic modification of the pore structure of MOFs. Over the last decade, the elevated surface area and pore volume and the flexibility of pore design characteristic of MOFs have sparked research aimed mainly at preparing new MOF structures and studying their applications in gas storage and separation [3,4].

Based on the similarity to zeolites, a logical application of MOFs could be as solid catalysts. However, despite the elevated metal content of MOFs, their use in catalysis is largely hampered by the relatively low stability to thermal treatments, chemical agents, and moisture, due to the presence of the organic component. Moreover, in most known MOF structures, the coordination sphere of the metal ions is totally blocked by the organic linkers, so that the metal centers are not accessible to reactants. However, there are some precedents in the literature reporting some MOFs with accessible metal sites, opening the possibility of their use in catalysis [5–8]. Consequently, despite the limited number of catalytic studies using MOFs as the active materials in catalysis [9–14] and photocatalysis [15,16] in the literature, their number can be anticipated to grow considerably in the near future.

In the search for suitable MOF candidates for use in catalysis, we anticipated that the recently reported Pd-containing material, with the molecular formula $[\mathrm{Pd(2\text{-}pymo)_2}]_n$ (2-pymo = 2-hydroxypyrimidinolate) [17], should exhibit interesting catalytic activity derived from tetracoordinated palladium ions. This material (designated Pd-MOF) is structurally related to 3D sodalite-type frameworks, with two different hexagonal windows with free openings of 4.8 and 8.8 Å and with a fraction of 42% of the crystal volume available to adsorbed guests, as shown in Fig. 1. Expansion of Pd coordination sphere could allow it to participate in catalysis without disrupting the structure of Pd-MOF.

Another remarkable property of Pd-MOF with regard to its possible application in catalysis is that, in sharp contrast with many other MOFs, the material is insensitive to moisture, because this material is actually synthesized in aqueous medium. Although a 3D coordination palladium–phosphine complex [12] is a related precedent to our work, that solid is amorphous, so that it cannot be strictly considered a metal–organic frame-

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* Corresponding authors. Fax: +34 96 387 7809.
E-mail addresses: acorma@itq.upv.es (A. Corma), hgarcia@qim.upv.es (H. Garcia).

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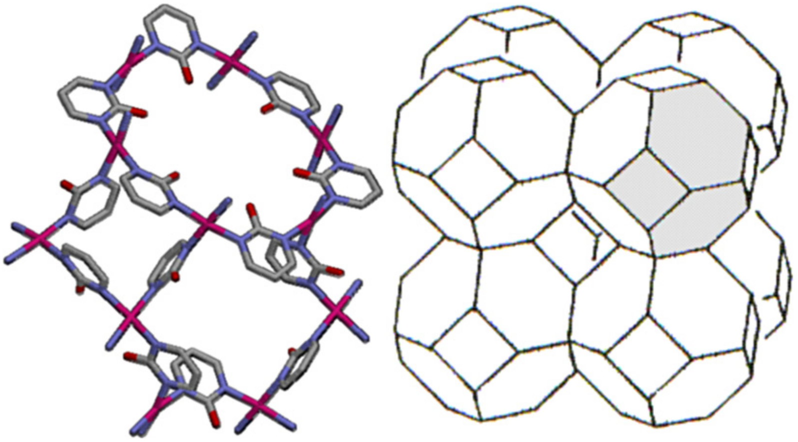


Fig. 1. (Right) Detail of Pd-MOF, showing the 4-membered and the two 6-membered rings. Atom colors: C = gray, N = blue, O = red and Pd = pink. (Left) 3D arrangement of the sodalite cages in sodalite-type frameworks. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

work [18]. Moreover, the lack of a regular pore system in this coordination palladium–phoshine complex precludes the occurrence of shape selectivity. Finally, the Pd-MOF considered in the present work comprises phosphine-free ligands.

To test the catalytic performance of this Pd-MOF, we selected three typical palladium-catalyzed reactions: aerobic alcohol oxidations, Suzuki C–C couplings, and olefin hydrogenation. We also studied the possible shape-selective properties of the material, because Pd^{II} ions are located in well-defined framework positions and they are accessible through a channel system of regular size and shape. Herein we report the results to show the activity and potential of this porous palladium-containing solid as a reusable heterogeneous catalyst. We demonstrate that (i) the material is active in all the aforementioned reactions; (ii) the reaction conditions do not alter the crystal structure of the MOF, so that the material remains intact, and it can be readily reused without significant loss of activity; and (iii) shape-selectivity properties of the material are demonstrated for hydrogenation of olefins with different steric hindrances.

To give a fair overview of the catalytic activity of Pd-MOF relative to the state-of-the-art palladium catalysis, three different tests covering a range of palladium catalyzed reactions were selected. Table 1 compiles the main results obtained.

2. Experimental

Pd-MOF was synthesized as described previously [17], and its structure was confirmed by X-ray diffraction using a Phillips X'Pert diffractometer. The synthesis involved condensation of the palladium complex [Pd(2-hydroxypyrimidine)$_2$Cl$_2$] by refluxing a suspension of this complex in an aqueous solution adjusted with NaOH 1 M to pH 6.0 for 5 days. The starting palladium complex was prepared by reacting an aqueous solution of K_2PdCl_4 with two equivalents of 2-hydroxypyrimidine until a yellow microcrystalline powder was obtained. The final Pd-MOF was a stoichiometric material with a molecular formula $[Pd(2\text{-pymo})_2]_n \cdot 3H_2O$, which results in a Pd content of 32 wt%. According to the original work reporting the synthesis of Pd-MOF [17], the material shows a type I N_2 adsorption isotherm, as expected for a material containing micropores and in agreement with the crystallographic structure of the material (with main pores 8.8 Å in diameter). The calculated BET surface area for the material was found to be 600 $m^2\,g^{-1}$.

Table 1
Summary of the catalytic tests

Substrate	Product	%Conversion[a]	%Selectivity[a]
p-Bromoanisole[b]	*p*-Methoxybiphenyl	85 (5 h, 150 °C)	99
p-Bromoanisole[c]	*p*-Methoxybiphenyl	74 (5 h, 150 °C)	99
p-Bromoanisole[d]	*p*-Methoxybiphenyl	87 (48 h, 25 °C)	96
p-Bromoanisole[e]	*p*-Methoxybiphenyl	90 (48 h, 25 °C)	98
Cinnamylalcohol[f]	Cinnamylaldehyde	99 (20 h, 90 °C)	74
1-Octene[g]	*n*-Octane	99 (40 min, 35 °C)	59[h]
Cyclododecene[g]	Cyclododecane	0 (5 h, 35 °C)	–

[a] Determined by GC using hexadecane as external standard.

[b] Substrate (1.3 mmol), 11 mg of Pd-MOF (2.50 mol% Pd), phenylboronic acid (1.95 mmol), 575 mg K_2CO_3, *o*-xylene (35 ml).

[c] As in [b], second use of Pd-MOF.

[d] As in [b], at 25 °C, EtOH as solvent.

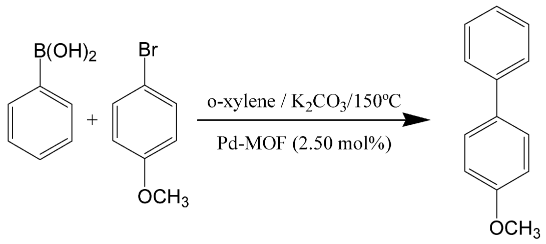
[e] As in [d], second use of Pd-MOF.

[f] Substrate (1 mmol) in toluene (5 ml), 5.5 mg of Pd-MOF (1.75 mol% Pd). Atmospheric air as oxidant.

[g] Substrate 0.4 mmol of alkene, 5.2 mg of Pd-MOF (4 mol% Pd), hexane (5 ml), $P(H_2) = 2$ atm.

[h] See text for an explanation.

For all of the catalytic reactions, reagent-grade products were purchased form Aldrich and used as received. The specific conditions for each catalytic test are included in the footnotes of Table 1. As a way of example, we describe in detail the procedure for the Suzuki–Miyaura C–C reactions. *p*-Bromoanisole (1.3 mmol) and a slight excess of phenylboronic acid (1.95 mmol) were dissolved in *o*-xylene (35 ml) containing 575 mg K_2CO_3 (ca. 6 mmol) as a base. The solution was heated at 150 °C in a thermostatted silicone oil bath, and the Pd-MOF (11 mg, 2.50 mol% Pd) was then added. The course of the reaction was followed by gas chromatography using hexadecane as external standard. At the end of the reaction, the solid catalyst was recovered by filtration at reduced pres-



Scheme 1. Suzuki–Miyaura cross coupling.

sure. The solid was thoroughly washed with CH_3CN and water (to eliminate K_2CO_3). Fresh and used samples were characterized by X-ray diffraction and DRUV–vis spectroscopy, and the results were compared.

3. Results and discussion

3.1. Suzuki–Miyaura cross coupling

The first reaction tested was the C–C cross coupling between aryl halides and arylboronic acids (Suzuki–Miyaura coupling). As substrates for this reaction forming biphenyls, phenylboronic acid and 4-bromoanisole were chosen (Scheme 1) because this coupling has been proposed as a benchmark reaction to compare highly active palladium catalysts [19]. Although aryl iodides react readily, aryl bromides and chlorides are considerably less reactive due to the stronger C–halogen bond. In addition, the presence of strong electron-donating substituents in the aromatic ring (4-methoxy in our case) disfavors the coupling, making highly active palladium sites necessary.

As is shown in Table 1, high values of conversion (85%) and selectivity toward the cross-coupling product (99%) are obtained after 5 h using Pd-MOF at 150 °C. It has been reported that leaching of Pd occurs during C–C coupling reactions with Pd-supported catalysts in polar solvents, particularly in DMF, which has an affect on the final catalytic results observed [20–22]. On the other hand, when xylenes or toluene were used as solvents, leaching was not detected, at least during a few runs [21–24]. Based on previous work, we used *o*-xylene as solvent. Then, under these experimental conditions, Pd-MOF was recovered intact together with K_2CO_3 after the coupling. Preliminary controls showed that Pd-MOF did not dissolve and remained unaltered when this solid was stirred in *o*-xylene at 150 °C for prolonged periods. After the reaction, the solid was collected and washed. The X-ray diffractograms of used Pd-MOF were almost identical to those of fresh samples and completely analogous to that reported for this material, with no appreciable loss of crystallinity. This result indicates that the structural integrity of the catalyst was maintained during the reaction. Moreover, reduction of Pd^{II} ions with formation of Pd^0 clusters (i.e., a general process aging the palladium catalysts), can be ruled out in principle, at least to a great extent, because the color change of the catalyst related to Pd^0 formation was not observed. The integrity of the material is indeed demonstrated by the finding that it can be reused without significant diminution of catalyst activity and selectivity (see the second and fourth entries in Table 1). In addition, chemical analysis of the Pd-MOF recovered after exhaustive water washing and vacuum drying showed that the palladium content of the material agrees with the expected $Pd(2\text{-pymo})_2$ formula.

To obtain final proof that the structure of Pd-MOF remained unchanged after the catalytic tests and that no metal leaching occurred, we filtered the catalysts from the substrate at the temperature of the reaction (150 °C) at partial conversion. We found that no further conversion occurred after the substrate was reheated. We note, however, that the "filtered while hot test" has been recently questioned due to unavoidable temperature decrease during filtration and the rapid co-adsorption of palladium species with just minor temperature decrease (the so-called "boomerang effect") [24,25]. In any case, our present findings indicate that in the event that any leaching of Pd species from the Pd-MOF structure to the solution occurs and is responsible (at least in part) for the catalytic activity, Pd-MOF acts as a very good, slow-release palladium reservoir (see below for turnover frequency [TOF] values). At present, the most reasonable proposal for the reaction mechanism is based on the mechanism for homogeneous palladium complexes (after all, Pd-MOF is an example of a macromolecular complex) and assumes that during the catalytic cycle, a reversible change in the palladium oxidation state from Pd^{II} to Pd^0 occurs that must cause a stress in the local MOF structure due to a reversible change from tetracoordination (for Pd^{II}) to dicoordination (for Pd^0), without producing the collapse of the solid structure. Thus, the solid will tolerate a certain number of faults in the crystal during the catalytic cycle.

The TOF for the Pd-MOF catalyst was calculated for a separate run with a tenfold lower catalyst concentration (0.25 mol% Pd), and a value of 1230 h^{-1} (20.5 min^{-1}) was obtained. The Pd-MOF catalyst was found to be also active (and reusable) for the same coupling reaction even at room temperature (third and fourth entries in Table 1), with longer times where needed to achieve total conversion. In view of its performance, we can conclude that Pd-MOF is an active phosphine-free heterogeneous catalyst.

3.2. Alcohol oxidation

The activity of Pd-MOF in partial oxidation of alcohols is demonstrated for the case of 3-phenyl-2-propen-1-ol (cinnamyl alcohol). Cinnamyl alcohol is a suitable substrate to probe the activity and chemoselectivity of a catalyst for the aerobic alcohol oxidation [26,27]. Besides alcohol oxidation, in the case of allylic alcohols, palladium catalysts can promote undesirable side processes, such as polymerization and C=C double-bond isomerization, that lower the selectivity of the reaction. Controls filtering the solid at the reaction temperature also demonstrated that Pd-MOF is not dissolved in toluene under these conditions. With Pd-MOF as the catalyst, total conversion of this product using air at atmospheric pressure was reached after 20 h, with a 74% selectivity to cinnamylaldehyde. This selectivity value is similar to that found for palladium-catalyzed oxidations of allylic alcohols [26].

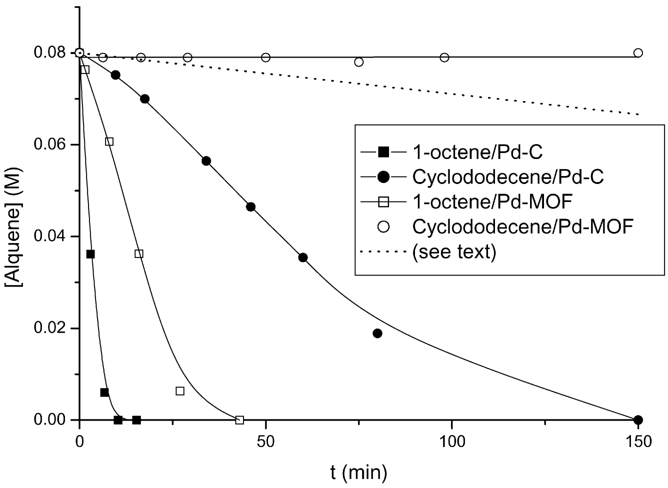


Fig. 2. Hydrogenation of 1-octene and cyclododecene over Pd-MOF and Pd-C. For reaction conditions see footnote [g] in Table 1.

3.3. Shape-selective olefin hydrogenation

The third test reaction carried out with Pd-MOF was alkene hydrogenation. We chose the reactants to explore the potential shape-selective properties of the material. Aimed at this purpose, and following the method proposed by Chang et al. [28], we compared the hydrogenation rates of 1-octene and cyclododecene. Nevertheless, the intrinsic reactivity of the two molecules was studied first. To do that, we used a conventional Pd/C catalyst (5 wt% Pd) with no shape selectivity. As can be seen in Fig. 2, 1-octene is converted 32 times faster than cyclododecene, as determined from the slope of the time-conversion plots at short reaction times [0.4 mmol alkene, 0.2 mol% Pd, $P(H_2) = 2$ atm, 35 °C]. Using the Pd-MOF as the hydrogenation catalyst, we observed total conversion of 1-octene after 40 min (Fig. 2; Table 1). In contrast, we did not observe (within the limits of experimental error) any disappearance of cyclododecene or formation of cyclododecane even after 5 h at the same reaction conditions. In any case, we have plotted (dotted line) in Fig. 2 the expected kinetic curve for hydrogenation of cyclododecene on the basis of the relative rate of hydrogenation obtained before with Pd/C. As can be seen, the experimental points are clearly well above the simulated curve, indicating that hydrogenation rate for cyclododecene in Pd-MOF is lower than what could be expected from its chemical reactivity. Consequently, for Pd-MOF, 1-octene is selectively converted toward the bulkier cyclododecene, which is not hydrogenated. These results indicate that the active centers located at the internal surface of Pd-MOF are accessible through the pore openings for 1-octene, whereas cyclododecene should not diffuse inside the pores. Molecular dockings using HyperChem at MM + level have confirmed the difficulties of cyclododecene to diffuse inside the pores of Pd-MOF. Note that these results also definitively exclude the hydrogenation activity of Pd-MOF as being due to soluble Pd species that could leach from the solid to the solution rendering the process homogeneous rather than heterogeneous (as discussed in Section 3.1).

It is also worth mentioning here that the low selectivity of 1-octene to octane (59% at 40 min) is due to the competition between hydrogenation and isomerization of the C=C double bond to 2-octene. Both processes have in common the intermediacy of palladium hydrides reacting with the C=C double bond and differ in the subsequent removal of a hydride (isomerization) or the addition of a second hydrogen atom. We have observed that the 2-octene formed is ultimately hydrogenated to octane, so that the selectivity/conversion ratio increases with time. Thus, it is therefore possible to attain 100% selectivity to octane formation after 2 h.

4. Conclusion

In the context of the current interest in MOF and in developing the full potential of these materials, we have shown that Pd-MOF exhibits the typical behavior of heterogeneous palladium catalysts, promoting the C–C cross coupling, aerobic oxidation, and hydrogenation reactions. The presence of palladium atoms in well-defined microporous channels opens the possibility of performing shape-selective catalysis with these materials.

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