

Metal-Organic Frameworks (MOFs) as Heterogeneous Catalysts for the Chemoselective Reduction of Carbon-Carbon Multiple Bonds with Hydrazine

Amarajothi Dhakshinamoorthy,^a Mercedes Alvaro,^a and Hermenegildo Garcia^{a,*}

^a Instituto de Tecnología Química CSIC-UPV and Departamento de Química, Universidad Politécnica de Valencia, Av. De los Naranjos s/n, 46022 Valencia, Spain
Fax: (+34)-96-387-7809; phone: (+34)-96-38-7807; e-mail: hgarcia@qim.upv.es

Received: May 25, 2009; Revised: July 24, 2009; Published online: October 1, 2009

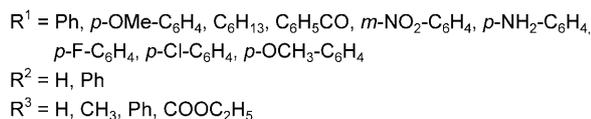
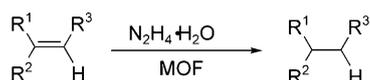
Abstract: The as-synthesized metal-organic frameworks (MOFs), particularly that based on aluminum coordinated with benzenedicarboxylic acid, constitute selective catalysts for the reduction of carbon-carbon multiple bonds in alkenes, alkynes and α,β -unsaturated esters with hydrazine hydrate in acetonitrile under mild conditions. The present protocol enjoys advantages such as convenient reaction conditions and benign, reusable and cost effective catalyst.

Keywords: alkynes; hydrazines; metal-organic frameworks; olefins; reduction

Metal-organic frameworks (MOFs) have attracted much interest in the recent years as promising new materials due to the presence of channels and cavities of nanometer scale defining pore systems analogous to those found in zeolites.^[1,2] The crystal structure of MOFs is formed by a metal ion or a metallic cluster coordinated to multidendate organic ligands. Over the past decade, the elevated surface area and pore volume and the flexibility of design characteristic of MOFs have opened a new arena in research aimed mainly at preparing new MOF structures and studying their applications in gas storage.^[3] But still there is a general debate about the potential advantages of MOF in catalysis due to the relative low thermal and chemical stability of MOFs and the fact that structural metal atoms do not generally have free coordination positions to act as catalytic sites. However, several groups have shown that MOFs as heterogeneous catalysts can exhibit high activity and selectivity in various reactions such as oxidation,^[4] epoxide ring opening^[5] and asymmetric hydrogenation^[6] among others.^[7] In addition, MOFs have also been used as supports to incorporate metal nanoparticles and the resulting encapsulated nanoparticles exceed in activity

the conventional metal-supported catalysts while presenting substrate shape selectivity due to the confinement of the metal nanoparticles inside a restricted space.^[8] In recent years, the need to develop clean and green chemical processes has become mandatory in order to avoid environmental concerns^[9] and as a consequence, heterogeneous catalysts based on MOFs could exhibit remarkable advantages with respect to analogous homogeneous transition metal catalysts. Compared to the homogeneous phase reactions, the use of heterogeneous catalysts simplifies the work-up procedure by allowing simple filtration, facilitating product separation and catalyst reuse.^[10]

Reduction of non-polarized carbon-carbon multiple bonds is a general reaction in organic chemistry that is normally effected by hydrogen gas and heterogeneous noble or transition metal catalysts such as Rh/C, Pd/C, nickel Raney, or PtO₂. One of the few alternatives to the use of hydrogen gas for the reduction of carbon-carbon multiple bonds is the use of diimide (diazene, HN=NH), hydrazine or its derivatives.^[11] The use of hydrazine, soluble in water and organic solvents, as hydrogen source can be advantageous and convenient for laboratory hydrogenations and in the production of fine chemicals.^[12] Experimentally, the use of hydrazine has the advantage of avoiding flammable gases and that no noble metal catalysts are needed. It is generally accepted that non-polarized double bonds are reduced by diimide and hydrazine *via* a cycloaddition mechanism.^[11,12] Also, addition of a base increases the liberation of hydrogen from hydrazine hydrate by increasing the concentration of the hydrazine in basic form.^[13] In the present study, the catalytic activity of various MOFs in the hydrogenation of alkenes and alkynes using hydrazine hydrate as reducing agent in acetonitrile has been tested. Herein we will show the activity and potential of as-synthesized MOFs without noble metal, as reusable heterogeneous catalyst for hydrazine-mediated hydrogenation as shown in Scheme 1.

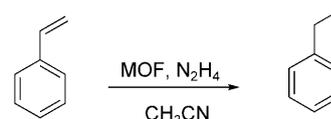


Scheme 1. Hydrogenation of C=C double bond in presence of MOFs using hydrazine hydrate as reducing agent.

The present study highlights that aluminium MOF is active and selective towards the title reaction without losing the crystalline nature of MOF and hence it can be reused without further modification. The crystal structure of $\text{Al}_2(\text{BDC})_3$ (BDC: *p*-benzenedicarboxylate) is constructed from corner sharing octahedral Al linked by BDC ligands.^[14] $\text{Al}_2(\text{BDC})_3$ has the pore dimension of 8.5 Å with the surface area of 1590 m² g⁻¹ with good thermal stability.^[14b] Recently, many groups have reported the use of MOFs for hydrogen storage but here is the first example where MOFs are being used as hydrogenation catalysts without any further modification or loading inside the framework with other metals. At this point, we believe that the activity of the catalyst may depend on (i) availability of significant numbers of accessible sites due to the open MOF crystal structure, (ii) reversible coordination of organic linkers with the metal atom and iii) the influence of the electrostatic field in the cavity by the partially charged framework.

In the initial stage of our work, we have focused on control experiments to optimize suitable conditions for an efficient and mild catalytic hydrogenation using hydrazine hydrate in the presence of various MOFs based on Fe, Cu, Zn or Al metals. For performing these initial studies, styrene was chosen as a model substrate. With styrene and $\text{Al}_2(\text{BDC})_3$ as catalyst in the absence of reducing agents no styrene conversion occurred after 24 h at room temperature as well as at 75 °C. This blank experiment indicates that styrene is stable under the reaction conditions and that $\text{Al}_2(\text{BDC})_3$ do not promote its acid-catalyzed oligomerization. On the other hand, performing the reduction with an excess reducing agent in the absence of MOFs leads the formation of 26% of ethylbenzene. Under similar conditions, the conversion of ethylbenzene was improved (37%) by adding aqueous ammonia to the reaction mixture. The beneficial influence of ammonia on the reduction of hydrazine is in accordance with earlier reports on hydrogen liberation by the addition of base, indicating that the free hydrazine base is the actual reducing agent.^[11b] In contrast to the previous results, when styrene was reacted with hydrazine hydrate in the presence of $\text{Al}_2(\text{BDC})_3$ up to 98% conversion with 99% selectivity towards ethylbenzene was obtained (see Table 1). Interestingly, if

Table 1. Hydrogenation of styrene to ethylbenzene using MOFs as catalysts at various conditions.^[a]



Entry	Catalyst	N ₂ H ₄ ·H ₂ O (μL)	Conversion ^[b] [%]	Selectivity [%]
1	–	–	–	–
2	$\text{Al}_2(\text{BDC})_3$	–	< 4	98
3	–	36	37	99
4	$\text{Al}_2(\text{BDC})_3$	36	67	99
5	$\text{Al}_2(\text{BDC})_3$ ^[c]	36	98	99
6	$\text{Fe}(\text{BTC})$	36	52	99
7	$\text{Cu}_3(\text{BTC})_2$ ^[c]	36	6	99
8	Zn-MOF ^[c]	36	14	99
9	$\text{Al}_2(\text{BDC})_3$ ^[d]	–	< 4	95
10	$\text{Al}_2(\text{BDC})_3$ ^[e]	36	71	99
11	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ^[f]	36	6	98
12	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ^[g]	36	16	98

^[a] Reaction conditions: styrene (0.05 mL), catalyst (75 mg), acetonitrile (5 mL), 0.04 mL of 25% aqueous ammonia, 25 °C, 24 h.

^[b] Determined by GC.

^[c] 150 mg of catalyst were used.

^[d] Isopropyl alcohol was used as reducing agent.

^[e] After fourth cycle.

^[f] 166 mg were used.

^[g] 50 mg were used.

the hydrogenation is carried out with soluble aluminium sulfate as homogeneous catalyst at the same styrene/Al molar ratio as when using $\text{Al}_2(\text{BDC})_3$ a 6% conversion of styrene to ethylbenzene was observed under identical conditions as for $\text{Al}_2(\text{BDC})_3$. Analogously, if instead of $\text{Al}_2(\text{BDC})_3$ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is used as catalyst, styrene conversion was 16% under the same conditions. These experiments clearly demonstrate that both highly microporous catalyst and hydrazine hydrate are essential to achieve an optimum conversion of styrene to ethylbenzene. Even though homogeneous transition metal complexes and heterogeneous catalysts with a noble metal in combination with molecular hydrogen could be an efficient alternative, the present strategy demonstrates the utility of Al-based MOF as a potential catalytic system for the chemoselective reduction of carbon-carbon multiple bonds under mild conditions avoiding the use of hydrogen gas.

Besides $\text{Al}_2(\text{BDC})_3$, three other MOFs differing in the structural metal were also tested as heterogeneous catalysts for the reduction of styrene. The structure of $\text{Cu}_3(\text{BTC})_2$ (BTC: 1,3,5-benzenetricarboxylate) is constituted by a cluster of two metal atoms with paddle wheel shape that has a square planar coordinati-

on.^[15a,b] The BTC ligand acts as a trigonal planar ligand connecting the diatomic metal clusters^[15b] which defines nano cages of about 2.5 nm with windows of 0.8 nm. The structure of Fe(BTC) is constituted by the trimers of iron octahedra sharing a common vertex μ_3 -O linked by the benzene-1,3,5-tricarboxylate moieties in such a way that this leads to two types of mesoporous cages having free apertures of 25 and 29 Å, accessible through microporous windows of 5.5 and 8.6 Å.^[15c] The Zn-MOF has a zeolitic zinc imidazolate framework in which the bonding angles of the imidazolate ligand mimic those of the SiO_4^{4-} building blocks in zeolites. In contrast to $\text{Al}_2(\text{BDC})_3$ and Fe(BTC) or $\text{Cu}_3(\text{BTC})_2$, Zn-imidazolate has Zn–N bonds that are stronger than metal–O bonds. This stronger coordination bonds results in a higher thermal stability of Zn-MOF compared to the other three MOFs.^[15] The purpose of using Fe(BTC), $\text{Cu}_3(\text{BTC})_2$ and Zn-MOF is to determine the most active material of the series. Although all the screened MOFs were active, $\text{Al}_2(\text{BDC})_3$ appears as the most efficient in terms of the percentage conversion with better selectivity than the other three MOFs. It is important to note that under the best conditions, an excess of four equivalents of hydrazine hydrate is sufficient to reach almost complete conversion. In other precedents using an organocatalyst, larger hydrazine excesses have been used.^[11] Hydrazine was unique since other reducing agents such as ammonium formate and isopropyl alcohol were unsuccessful to effect hydrogenation of styrene in combination with MOFs.

The reusability of $\text{Al}_2(\text{BDC})_3$ was also investigated under optimized conditions. At the end of the reaction time, the solid was collected, washed with fresh solvent, dried at ambient conditions and used for another consecutive run without further treatment. The catalyst exhibited some stability up to four runs with a gradual decrease in the styrene percentage conversion upon reuse from 98% for the fresh catalyst to 71% in the fourth reuse. This gradual deactivation can be attributed to the pore blocking caused by the presence of water^[14] both in hydrazine hydrate as well as in aqueous ammonia or by the poisoning with undesired by-products arising from oligomerization of the alkenes.

Figure 1 presents the powder XRD pattern of the fresh and reused $\text{Al}_2(\text{BDC})_3$ sample in four consecutive hydrogenation reactions of styrene to ethylbenzene. As it can be seen in this Figure 1, the crystallinity of $\text{Al}_2(\text{BDC})_3$ is preserved during the course of the reaction. We observed, however, some minor changes in the XRD pattern. In the literature, there are precedents in which the same XRD pattern variation has been recorded and shown that these peak intensity changes are due to variations in the pore dimension through the process called breathing.^[14] In another precedents in the use of MOFs as catalysts, variations

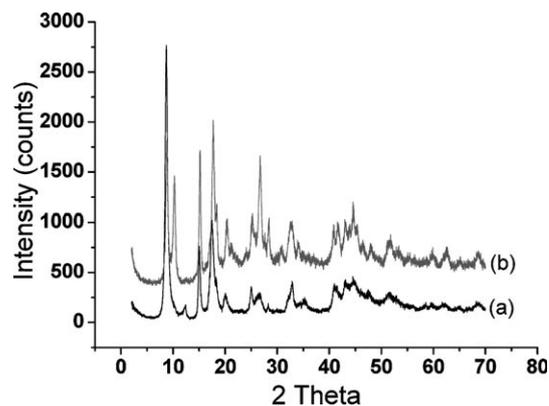


Figure 1. Powder XRD patterns of pure (a) and four times reused (b) $\text{Al}_2(\text{BDC})_3$.

in the relative intensity of the some XRD peaks have been attributed to the influence of the presence of organic compounds inside MOF micropores after their use as catalyst.^[4c] Whatever the reason, Figure 1 supports the claim that the $\text{Al}_2(\text{BDC})_3$ structure resists the reagents and reaction conditions used in the styrene hydrogenation.

The optimized protocol was extended to other substrates to determine the scope of the catalytic activity of $\text{Al}_2(\text{BDC})_3$ and also to study the chemoselectivity of the reduction (Table 2). The presence of electron-withdrawing or electron-donating groups on styrene does not affect the yield of the resulting ethylbenzene that was obtained with very high selectivity. *t*-Stilbene, β -methylstyrene and *t*-anethole were successfully reduced to their corresponding products in good yields with more than 98% selectivity. Similarly, 1,1-diphenylethylene was hydrogenated successfully without dimerization that is a common side process observed for this alkene occurring even under mild Lewis acids.^[16] Interestingly, aliphatic and cyclic olefins, namely 1-octene and *cis*-cyclooctene, are reduced to *n*-octane and cyclooctane, respectively, in good yield without any isomerization of the C=C double bond to internal positions in the case of 1-octene. In related precedents using Pd-catalyzed hydrogenation in MOFs, isomerization of the C=C double from terminal to internal positions has been observed to occur.^[2b,8b] As this catalytic system affords high yields for terminal and disubstituted alkenes and does not give double bond isomerization, it is a valuable alternative when metal-catalyzed hydrogenations are problematic.

We also extended this protocol to alkynes such as phenylacetylene and diphenylacetylene. Reaction of phenylacetylene with some excess hydrazine hydrate (4 equivalents) under the present experimental conditions yields ethylbenzene as reduced product. On the other hand, diphenylacetylene gives bibenzyl as the

Table 2. Reduction of multiple bonds in various substrates with $\text{Al}_2(\text{BDC})_3$ in acetonitrile with hydrazine hydrate.^[a]

Entry	Substrate	Product	Yield [%] ^[b]	Selectivity [%] ^[b]
1			81	100
2			90	100
3			82	99
4			84	99
5			94	99
6			68	100
7			78	99
8			71	98
9			75	99
10			93	99
11			92	100
12			90	> 99
13			77	> 99
14			30	20
15			82 ^[c]	95
16			46	96
17		–	–	–
18		–	–	–

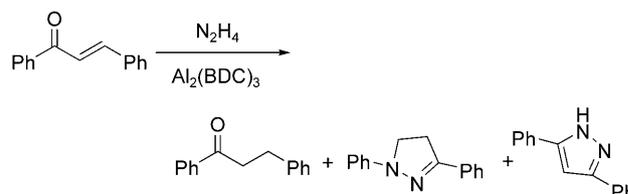
^[a] Reaction conditions: substrate (0.48 mmol), hydrazine hydrate (4 equiv.), $\text{Al}_2(\text{BDC})_3$ (150 mg), 25% aqueous ammonia (0.04 mL), acetonitrile (5 mL), 25 °C, 24 h.

^[b] Determined by GC. Yield [%] is calculated using nitrobenzene as external standard.

^[c] Excess hydrazine (8-fold) hydrate is used.

only product although the product yield is only moderate (see entry 16 in Table 2).

In order to check the chemoselectivity, the hydrogenation was carried out under optimized conditions for *m*-nitrostyrene (entry 2 in Table 2), ethyl cinnamate and its amino derivative (entries 12 and 13 in Table 2). Interestingly, all the three substrates are converted to their corresponding reduced products with complete chemoselectivity. On the other hand, hydrogenation of chalcone and nitrobenzene to their corresponding reduced products was also investigated. Chalcone was reduced to 1,3-diphenylpropanone with



Scheme 2. Reaction of *trans*-chalcone with hydrazine hydrate in the presence of $\text{Al}_2(\text{BDC})_3$. Pyrazole and dihydropyrazole originate from the condensation of hydrazine with the carbonyl group.

30% selectivity along with the formation of pyrazoles as by-products as shown in Scheme 2. Thus, we have found that hydrazine as reducing agent for C=C double bonds is not compatible with the presence of carbonyl groups in the substrate. This limitation could be predicted in view of the general reactivity of aldehydes and ketones with hydrazines.^[17]

Finally, attempts were also made to reduce nitro and cyano compounds to amines using hydrazine as reagent and $\text{Al}_2(\text{BDC})_3$ as catalyst but these attempts were unsuccessful. The failure to effect the reduction of nitro- and cyanobenzene (entries 17 and 18 in Table 2) indicates that our catalytic system is highly chemoselective for the reduction of unpolarized multiple bonds, while it does not reduce nitro and cyano groups. On the other hand, the percentage conversion of 1-phenylcyclohexane was low when compared with other alkenes reported here. This may be reasonably explained by the fact that the position of the double bond also plays a vital role in the reaction rate and again it clearly indicates that the mechanism does not involve benzylic intermediates.

In order to have some insight into the reaction mechanism, we have carried out the hydrogenation of various substituted styrenes and determined the influence of the nature of the substituent on the initial reaction rate. The results are given in Figure 2. This clearly indicates that both electron-donating and electron-withdrawing substituents exhibit similar reactivity, thus ruling out the intermediacy of carbocations or the development of a partially positively charged transition state during the course of the reaction.

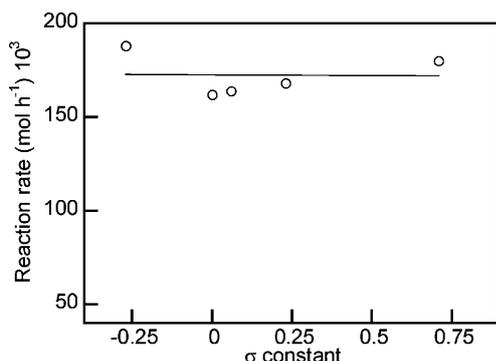


Figure 2. Effect of substituents on percentage conversion of styrenes.

Concerning the reaction mechanism, an earlier precedent has provided experimental evidence based on XP spectroscopy for the interaction of hydrazine with aluminium.^[18] In a similar fashion considering the basicity of hydrazine and the Lewis acidity of Al^{3+} , in the present case, we assume that this acid-base interaction forming an adduct is the key step of the process. Subsequently, this active Lewis adduct will transfer a hydride species either through an Al-H hydride intermediate or directly to the C=C double bond effecting the reduction. An alternative reaction mechanism in which both hydrazine and alkene species are coordinated to the Al^{3+} center also cannot be excluded at the present stage. Scheme 3 summarizes our proposal.

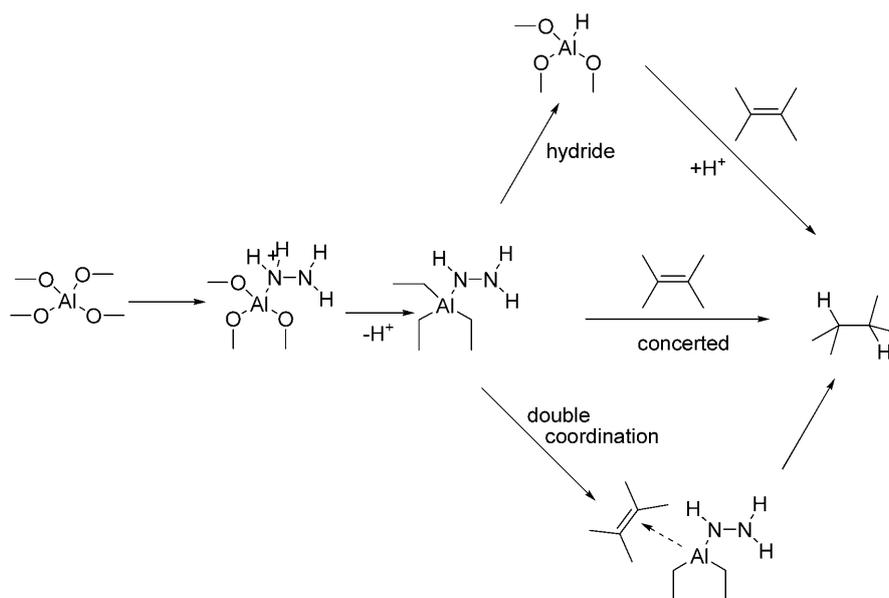
In conclusion, we report a novel approach for the hydrogenation of carbon-carbon multiple bonds to their corresponding reduced products with good

yields and high chemoselectivity with hydrazine hydrate as reducing agent under basic conditions using $\text{Al}_2(\text{BDC})_3$ as heterogeneous catalyst. This protocol does not require the use of hydrogen gas and is efficient being applicable to a wide range of substrates. The advantages of the present protocol include (i) cheap and reusable catalyst, (ii) lower hydrazine hydrate excess compared to the large excesses typically used, (iii) the reagent by-product is nitrogen, (iv) simple work-up and the separation of the products from the reaction system can be achieved by simple filtration and (v) this catalytic system is highly selective and does not affect cyano and nitro groups. Therefore this method based on the use of MOFs as catalyst can be considered an environmentally friendly alternative to heterogeneous hydrogenations.

Experimental Section

All reagents and starting materials were obtained commercially from Aldrich and used without any further purification. The percentage conversion, purity and relative yields of the final products were determined using a Hewlett-Packard 5890 series II gas chromatograph with FID detector and high purity helium as carrier gas. The products were identified by comparison with authentic samples and by GC-MS analysis on a Hewlett Packard 6890 series.

MOFs and starting materials were purchased from Sigma Aldrich and used as received. $\text{Fe}(\text{BTC})$ (Cat.: 69,087-2), $\text{Cu}_3(\text{BTC})_2$ (CAS: 51937-85-0) and $\text{Al}_2(\text{BDC})_3$ (CAS: 654061-20-8) and $\text{Zn}(\text{imidazolate})$ (Cat.: 691348).



Scheme 3. Plausible catalytic mechanism for the hydrogenation of carbon-carbon multiple bonds or alkenes with $\text{Al}_2(\text{BDC})_3$ catalyst.

General Procedure

The reaction was carried out by charging a 50-mL round-bottom flask with 150 mg of catalyst in 5 mL of acetonitrile, 0.48 mmol of the corresponding substrate and the corresponding equivalent amount of hydrazine hydrate with 0.04 mL of 25% aqueous ammonia. The reaction mixture was stirred at room temperature for the required time at 450 rpm. The reaction mixture was extracted with diethyl ether (15 mL). The products were analyzed by GC and GC-MS. The yield was calculated using nitrobenzene as external standard and determination of the response factor of reagents and products with respect to this standard.

The reusability of $\text{Al}_2(\text{BDC})_3$ was tested for the reduction of styrene. At the end of the reaction, the mixture was filtered, washed with diethyl ether (5 mL), dried at 60°C for 2 h and reused directly without further purification for the second run with fresh styrene. It was used for four consecutive runs with a gradual loss in activity.

Powder XRD patterns of fresh and reused $\text{Al}_2(\text{BDC})_3$ were recorded in a Philips X'Pert diffractometer using the CuK_α radiation at a scan rate of $0.2^\circ \text{ min}^{-1}$. Nitrogen adsorption isotherms were determined after outgassing the solids under vacuum at 200°C until constant weight using a Micromeritics ASAP 2000 instrument.

Acknowledgements

Financial support by the Spanish DGI (CTQ06-6857 and CTQ2007-67805/PPQ) is gratefully acknowledged.

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