



Green Chemistry

PAPER

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Post-functionalized iridium–Zr-MOF as a promising recyclable catalyst for the hydrogenation of aromatics†

Cite this: *Green Chem.*, 2014, **16**, 3522

Received 2nd April 2014,

Accepted 1st May 2014

DOI: 10.1039/c4gc00581c

www.rsc.org/greenchemAntonia M. Rasero-Almansa,^a Avelino Corma,^b Marta Iglesias^{*a} and Félix Sánchez^{*c}

The multifunctional heterogeneous catalyst iridium–Zr-based MOF is able to effectively catalyze the hydrogenation of aromatic compounds in high yields under mild conditions. The catalyst was found to be highly active and reusable, giving similar reactivity and selectivity after at least five catalytic uses.

Introduction

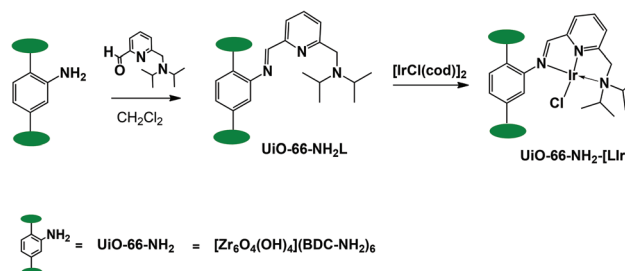
Zr-based MOF (UiO66–NH₂) was selected as a support owing to its many outstanding physical and chemical properties. It has a large specific surface area and pore size as well as good chemical resistance to water and organic solvents, a highly desirable and most promising combination for catalytic applications.¹ These highly stable new materials, after the adequate post-synthetic modification, can act as heterogeneous catalysts that combine the properties of soluble organometallic complexes with those of the MOF as a support. Recently we described that post-functionalized rhodium and iridium–Zr-based MOFs can be applied as multifunctional catalysts for one-pot and cascade reactions².

In order to extend the benefits of the Zr-based MOFs to other catalytic processes, we shifted our attention to the application of Ir–Zr-MOF-supported catalysts for other reactions. Among such processes, aromatic hydrogenation to form cyclohexane derivatives is one of the most important steps from an environment preservation standpoint,^{3,4} in both the petrochemical industry, for clean diesel fuel generation, and the pharmaceutical industry, for safe drug synthesis. The field is also of interest in relation to hydrogen storage.⁵ The hydrogenation of benzene and arenes is generally accomplished using heterogeneous catalysts almost exclusively,^{4a,6} molecular catalysts immobilized on heterogeneous surfaces,⁷ supported nanoparticle,⁸ or soluble nanoparticle⁹ systems, sometimes inadvertently derived from molecular precursors,¹⁰ represents

an important industrial catalytic transformation, particularly for the production of cleaner-burning, low-aromatic diesel fuels.^{4a} In this paper we report the catalytic activity of iridium complexes immobilized on functionalized Zr-MOF in the hydrogenation of arenes. Moreover, the Ir–Zr-MOF can be recycled *via* centrifugation and used at least for 5 cycles.

Results and discussion

UiO66–NH₂¹¹ was selected since the presence of NH₂ groups in the linker (2-aminoterephthalic acid) allows the functionalization of the material by conventional reactions, and functionalized-Zr-MOFs can be prepared according to well established procedures. In addition, UiO66–NH₂ possesses Lewis acid sites (zirconium), and the introduction of metal complexes on UiO66–NH₂ gives rise to a bifunctional catalyst which combines acidity and metallic sites capable of hydrogenation/dehydrogenation. UiO66–NH₂ was prepared by mixing ZrCl₄ and BDC–NH₂ in DMF, crystallization at 120 °C for 12–24 h, activation by DMF exchange with tetrahydrofuran and drying under vacuum (BET surface area = 800 m² g^{−1}). The resulting Zr–NH₂-MOF was suspended in CH₂Cl₂ and treated with the aldehyde^{2,12} (Scheme 1) at room temperature for 24 h. Meanwhile, iridium complexation by the imino-pincer ligand was



Scheme 1 Preparation of iridium–Zr-MOF.

^aInst. Ciencia de Materiales de Madrid, CSIC, C/Sor Juana Inés de la Cruz, n° 3, 28049 Madrid, Spain. E-mail: marta.iglesias@icmm.csic.es

^bInst. Tecnología Química, UPV-CSIC, Avda. de los Naranjos, s/n, 46022 Valencia, Spain. E-mail: acorma@itq.upv.es

^cInst. Química Orgánica General CSIC, C/Juan de la Cierva, n° 3, 28006 Madrid, Spain. E-mail: felix-igo@iqog.csic.es

† Electronic supplementary information (ESI) available: Details of characterization. See DOI: 10.1039/c4gc00581c

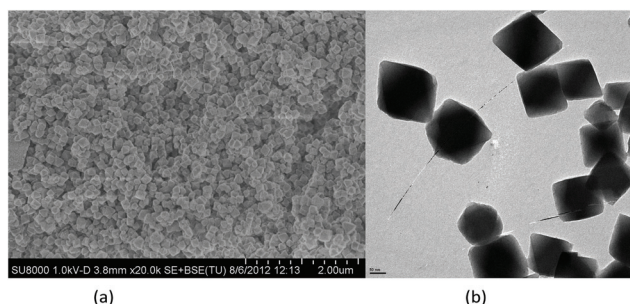


Fig. 1 SEM (a) and TEM (b) images for UiO66-NH₂-[Ir].

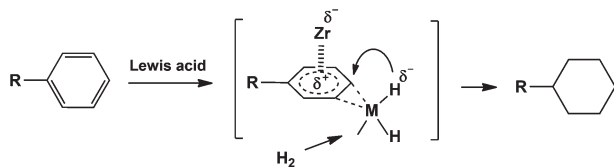
almost quantitative as we have previously described;² details for preparation and characterization can be found in the ESI.† The modified samples show thermal stabilities comparable to that of UiO66-NH₂ with decomposition temperatures near 350 °C in air. All steps occur without apparently losing the framework integrity (XRD patterns in Fig. S2†).

N₂ adsorption results further confirmed the stability of the porous structure after metal doping (ESI Fig. S6†). SEM and TEM micrographs showed the materials have preserved their structure (Fig. 1).

Iridium-MOF catalyst for hydrogenation of aromatics

The efficient synthesis of cyclohexane derivatives *via* the catalytic hydrogenation of aromatic compounds is of both scientific and industrial importance. However, the complete hydrogenation of aromatics still requires highly energetic (>100 °C) and dangerous reaction conditions (50 atm H₂) due to the lack of efficient catalysts. Recent publications suggest that palladium,¹³ ruthenium,¹⁴ rhodium,¹⁵ iridium¹⁶ and nickel¹⁷ may be used to achieve the hydrogenation of aromatic compounds under milder conditions. The utilization of platinum-based catalysts has been less investigated.¹⁸

On the other hand, it is well known that Lewis acids can activate aromatic compounds¹⁹ and a sequential step is hydrogenation by hydrogen atoms which were activated by the metal as depicted in Scheme 2. These two types of activation could work cooperatively, resulting in high activity for producing cyclohexane derivatives. Our bifunctional Zr-[IrL]-catalyst has zirconium as Lewis acid and iridium which can act as the active metal. Herein we report the highly efficient catalytic hydrogenation of aromatic compounds, under mild conditions (in ethanol at 6 bar of H₂ and 60–90 °C) by simultaneous activation of molecular hydrogen and the aromatic substrate with iridium and zirconium as Lewis acid respectively.



Scheme 2 General reaction pathway for the hydrogenation of aromatic compounds.

We selected aniline as our model compound to explore the Zr-[IrL] catalyzed aromatic hydrogenation reaction, the selective conversion to cyclohexanamine, in standard conditions with ethanol as a solvent, was 100% after 10 h. However, when temperature increased to 90 °C alkylation of amine to *N*-ethylcyclohexanamine was the major product. At this temperature, reaction in isopropanol or 2-butanol also resulted in *N*-isopropylcyclohexanamine or *N*-(pentan-2-yl)cyclohexanamine,^{2,20} for eliminating this secondary reaction we can use *t*-butanol as a solvent or 60 °C temperature and 6 bar H₂.

Zr-[IrL] was also tested in the hydrogenation of a series of other representative monosubstituted benzenes with electron withdrawing or donating groups. Substrates with electron donating groups are hydrogenated faster than those with electron withdrawing groups (Table 1 and Fig. 2). We found that

Table 1 Hydrogenation of aromatic substrates^a

	Cat. ^b (mol%)	Substrate	Product	Conv. (%) (h)	TOF ^d (h ⁻¹)
1	[IrL] (1)			100 (8) ^c	42
2	[ZIrL] (0.20)			85 (5) 98 (10)	85
3	ZIrL] (0.20)			90 (10)	80
4	[ZIrL] (0.20)			100 (5)	98
5	[ZIrL] (0.20)			49 (6) 65 (24)	60
6	[ZIrL] (0.20)			85 (6)	110
7	[ZIrL] (0.20)			90 (5)	235
8	[ZIrL] (0.20)			90 (22)	10
9	[ZIrL] ⁺ (0.20)			75 (24) ^c	8
10	[ZIrL] (0.20)			Traces (20)	—
11	[ZIrL] (0.20)			0 (24)	12
12	[ZIrL] (0.20)			67 + 17 (19)	n.d.

^a Reaction conditions: solvent: ethanol or isopropanol, *T*: 60 °C, PH₂: 6 bar. ^b Based on Ir. ^c Reaction in *t*-butanol at 90 °C, reaction in isopropanol (90 °C) yields 60% of *N*-alkylated product. ^d mmol subs mmol⁻¹ cat. h⁻¹.

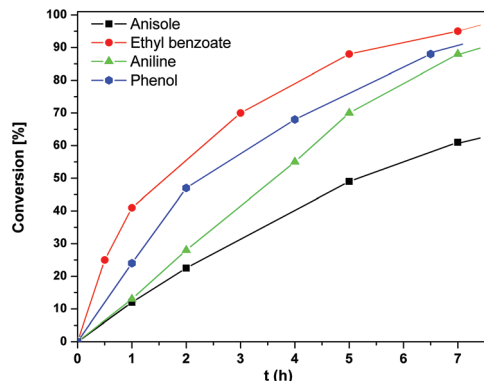


Fig. 2 Kinetic profile for the Zr-[IrL]-catalyzed aromatic hydrogenation.

Zr-[IrL] catalyzes the quantitative hydrogenation of aromatic hydrocarbons such as toluene, and phenol which was reduced to cyclohexanol with only traces of cyclohexanone detected as well as ethyl benzoate (Table 1, entries 4, 6, and 7); styrene is quickly reduced to ethylbenzene (Table 2, entry 1), which was hydrogenated to ethylcyclohexane at 90 °C (Table 1, entry 8). Nitrobenzene and benzonitrile were transformed to cyclohexylamine and cyclohexylmethanamine respectively in good yield and selectivity (Table 1, entries 3 and 9). Bromobenzene or diethyl phthalate did not react under these reaction conditions, even at 90 °C (Table 1, entries 10 and 11) while methyl 2-methoxybenzoate yields the corresponding cyclohexane carboxylate besides 20% of hydrogenolysis of the C–O bond (Table 1, entry 12). Comparing the soluble Ir-complexes, used as reference catalysts (Table 1, entry 1), with the corresponding supported on Zr-[IrL]-MOF, a considerable increase in the reactivity was observed.

In order to determine the selectivity of different functional groups against arenes, we explored the catalyzed-hydrogenation for other unsaturated carbon bonds (C=C, C=O) and

Table 2 Hydrogenation experiments with Zr-[IrL]-catalysts^a

Entry	Substrate	Product	Conv. (%) (h)	TOF (h ⁻¹)
1			100 (0.5)	935
2			100 (2)	325
3			100 (0.5)	1000
4			100 (24)	13
5			85 (2)	850
6			20 (24) 100 (20) ^b	10

^a 0.2 mol% of catalyst based on Ir; PH₂: 2 bar, 40 °C. ^b 90 °C.

cyano and nitro groups attached to an aromatic ring (Table 2). Thus, olefinic double bonds of styrene and α -methylstyrene were fully converted to ethylbenzene and isopropylbenzene respectively; also carbonyl compounds as benzaldehyde or acetophenone yield the corresponding alcohols, and benzonitrile or nitrobenzene the corresponding amines; in all cases these groups were hydrogenated before the reduction of arene was initiated.

Recycling experiments and heterogeneity of catalyst

After the hydrogenation reaction, Zr-[IrL] was separated from the reaction mixture by filtration or centrifugation, thoroughly washed with ethanol and reutilized as a catalyst in subsequent runs under identical reaction conditions. The results included in Fig. 3a indicate that after the first cycle the activity slightly decreased and then no efficiency loss was observed in the arene hydrogenation for up to five runs. Moreover, the filtrate solutions collected at the end of each catalytic run were analyzed by ICP-MS and in none of them Ir was detected, which confirms the absence of iridium in the solution, whilst in FT-IR spectra of the recovered solid the catalyst appears as a band at ~ 2000 cm⁻¹ corresponding to the $\nu(\text{Ir-H})$ bond (Fig. S10†).

A control experiment was also performed to show that the hydrogenation reactions are stopped by the removal of Ir-Zr-MOF from the reaction solution (Fig. 3b). Moreover, they provide easy separation and high reusability performance in these reactions by keeping their stability against leaching throughout the catalytic runs.

The characterization of the isolated samples from the fifth catalytic run in the hydrogenation of aniline (using XRD, SEM and TEM) reveals that (i) the crystallinity of the host UiO66 framework is mainly retained (Fig. 4) and (ii) there is some bulk iridium formed within the framework of UiO66, at the end of the fifth catalytic run (SEM and TEM images in Fig. 5 and 6). Higher SEM and TEM resolution for Ir-Zr-MOF crystallites is difficult due to local damage by electron beams, which cause distortion and movement.

Recent studies have shown that metal-organic frameworks are also to be considered as suitable host materials to controlled growth of catalytic clusters or nanoparticles within MOF cavities.²¹ To date it has already been demonstrated that the zeolitic imidazole framework (ZIF-8 MOF) or MIL101(Cr) can act as a suitable host material for Au,²² Ag,²³ Ni,²⁴ Ir²⁵ and

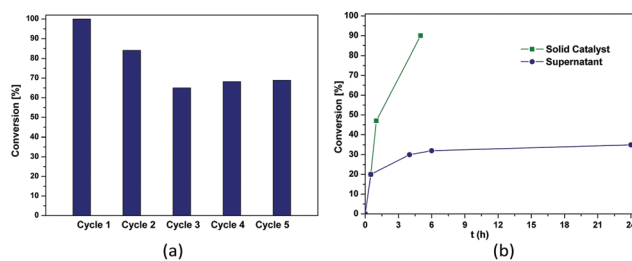


Fig. 3 (a) Recycling experiments for the catalyzed hydrogenation of aniline and (b) hot filtration test for the hydrogenation of ethyl benzoate.

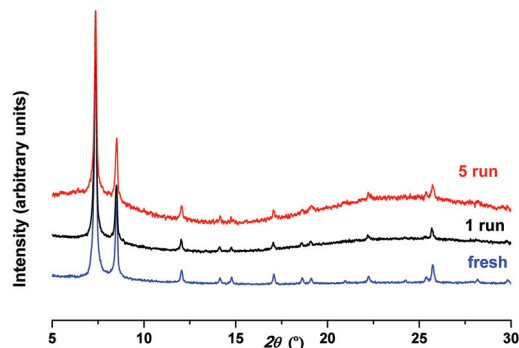


Fig. 4 PXRD for a fresh catalyst and recovered after 1 run and 5 runs.

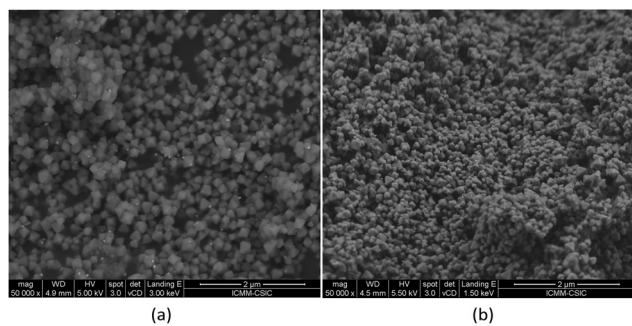


Fig. 5 SEM images of fresh (a) and recovered catalyst (b).

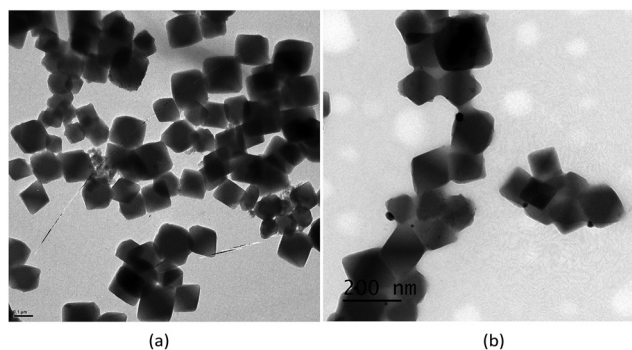


Fig. 6 TEM images of fresh (a) and recovered catalyst (b).

Pd²⁶ nanoparticles. The chemically robust Zr-based MOF (UiO66-NH₂) also might result in a host matrix to stabilize guest iridium nanoparticles (IrNPs).

We have reduced the Zr-[Lr]-MOF with NaBH₄ (ethanol at 273 K for 2 h) or H₂ (6 bar, 120 °C) in order to obtain nanoparticles of iridium supported on the Zr-MOF (Zr-MOF-IrNPs) and we have found that PXRD analysis (Fig. 7) shows the typical reflections of UiO66-NH₂, which confirm the stability of the support under the chosen conditions, but reduced catalysts were not active for hydrogenation of aniline and any product formation was not observed after 24 h; and as a consequence when the hydrogenation of aniline was performed with Zr-[Lr]-MOF at 120 °C, recycling is not possible because the activity decreases considerably after the first run.

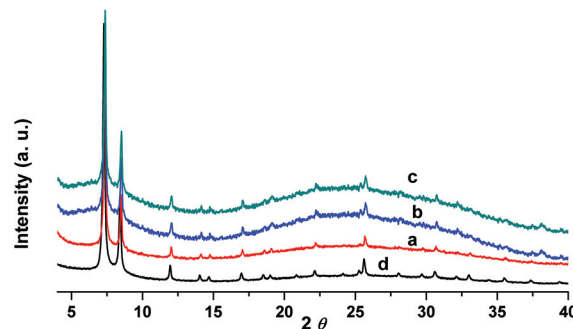


Fig. 7 PXRD for Zr-[Lr]-MOF: (a) recovered after the first run, (b) recovered after the fifth run, (c) Zr-MOF-IrNPs after 6 bar H₂ at 120 °C and (d) Zr-MOF-IrNPs obtained for reduction with NaBH₄.

The morphology of the different Ir-Zr-MOF samples was examined by dynamic light scattering (DLS) (Fig. S11[†]), SEM (Fig. S12[†]) and TEM (Fig. S13[†]). The TEM images of material obtained by reduction with NaBH₄ or by hydrogenation at 120 °C show a lot of larger nanoparticles, and we have found that they are inactive in hydrogenation reactions whilst TEM images of recovered catalysts in operation conditions (60 °C/6 bar) show that most of the particles have a size similar to that found in the fresh catalyst, which seems to corroborate the view that the molecular structure of heterogenized complexes was preserved, as could be also confirmed by FT-IR in which a band corresponding to the Ir-H bond can be observed. The presence of larger particles could be responsible for the decrease of activity after the first cycle of reactions.

X-ray photoelectron spectroscopy (XPS) analysis was performed on the fresh and recovered Zr-[Lr]-MOF solids. The samples were kept in vacuum overnight prior to XPS measurements. The spectra were calibrated with respect to the C1s peaks in each sample. The survey scan XPS spectrum of the Zr-[Lr]-MOF samples (Fig. S15[†]) shows the presence of iridium in addition to the UiO66 framework elements (Zr, C, N). XPS analysis showed N-1s (399.1 eV) and C-1s signals, the latter comprising sp² carbon (284.6 eV), and sp³ carbon neighboring oxygen (287.9 eV). The XPS core level for the iridium

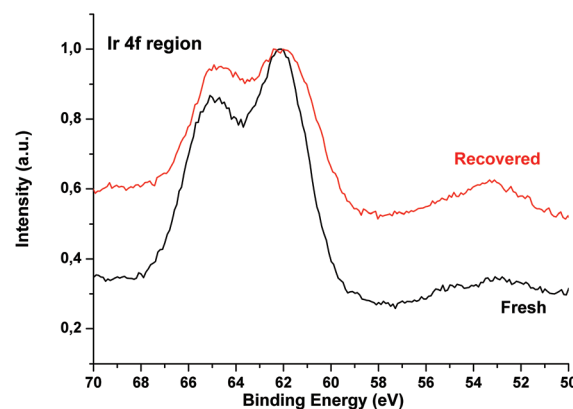


Fig. 8 XPS Ir(4f) region for the original catalyst and recovered after reaction.

(Ir(4f) region) showed no difference in peak positions between the original catalyst and the solid recovered from the reaction (peaks at 64.8 and 62.1 eV, readily assigned to Ir4f_{7/2} and Ir4f_{5/2}) indicating the Ir^{δ+} oxidation state in the samples²⁷ (Fig. 8).

Conclusions

The use of the iridium pincer complex active phase and Zr-MOF as a support has allowed us to obtain a new catalyst for the direct hydrogenation of aromatic compounds at low temperatures and initial hydrogen pressures. These catalysts are versatile and can be easily recycled with high conversion efficiency for up to five cycles and represent an attractive choice for green industrial and synthetic applications.

Experimental

Reagents and materials

Starting materials were purchased and used without further purification from commercial suppliers (Sigma-Aldrich and Alfa Aesar). Dried, distilled and deoxygenated solvents were used.

Materials preparation

Synthesis of Zr-based metal-organic framework was performed in a 250 mL round bottom flask using a procedure similar to that previously described.¹¹ X-ray diffraction (Phillips X'Pert, CuK α radiation) was used to confirm the expected crystalline structure of the materials. All substances and reagents used were commercially available and used as received. The reaction and analytic methodology are given in ESI.† General considerations and characterization methods are presented in ESI.†

Catalytic measurements

General procedure. Hydrogenation of aromatics was performed in an Autoclave Engineers (100 mL). The reactants were added to the suspension of catalysts (0.2 mol% based on iridium) in ethanol (15–40 mL); the reactor was hermetically sealed, pressurized (6 bar H₂) and heated (60 °C) under continuous stirring (*ca.* 1000 rpm). Small liquid aliquots (\approx 100 μ L) were taken. The progress of the reaction was monitored by GC-MS (Fig. S16†).

In particular, hydrogenation of aniline (50 μ L, 0.5 mmol) was performed with 10.5 mg (1.05×10^{-3} mmol Ir) of Zr-MOF-LIr in 2-propanol (15 mL). The reaction mixture was filtered, and the solvent was removed under reduced pressure to give the crude product, pure for GC-MS. When the reaction is carried out with 10 times more substrate, the reaction is complete in 36 h.

The recycling of Zr-MOF-LIr

After completion of the reaction the catalyst was recovered by separation of solid MOF-Ir from liquid after extensively centrifuging. The recovered catalyst was washed with ethanol three

times, dried at 80 °C for 12 h and reused. The Zr-MOF-LIr catalyst showed consistent activity for four cycles.

The hot filtration test of Zr-MOF-LIr catalyst

A mixture of Zr-MOF-LIr (6.7 mg, 7.0×10^{-4} mmol Ir), ethyl benzoate (50 μ L, 0.35 mmol), and ethanol (15 mL) was put into a reactor (Autoclave Engineers) and was extensively stirred (*ca.* 1000 rpm) at 60 °C, 6 bar H₂ for 0.5 h. The conversion was \sim 20%. Then the solid catalyst was quickly separated after filtration of the reactant mixtures. The liquid was kept at 60 °C with extensive stirring for 24 h. The conversion was 35%. It was found that the blank thermal reaction without any catalyst for this reaction at 60 °C was *ca.* 8% (see Fig. 3).

Acknowledgements

We thank the MINECO of Spain (project MAT2011-29020-C02-02), Consolider-Ingenio 2010-(CSD-0050-MULTICAT). for financial support. A.M.R.A. thanks MINECO for the FPI program.

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