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Ruthenium Complexation in an Aluminium Metal–Organic Framework and Its Application in Alcohol Oxidation Catalysis

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Abstract: A ruthenium trichloride complex has been loaded into an aluminium metal–organic framework (MOF), MOF-253, by post-synthetic modification to give MOF-253-Ru. MOF-253 contains open bipyridine sites that are available to bind with the ruthenium complex. MOF-253-Ru was characterised by elemental analysis, N_2 sorption and X-ray powder diffraction. This is the first time that a Ru complex has been coordinated to a MOF through post-synthetic modification and used as a heterogeneous catalyst. MOF-253-Ru catalysed the oxidation of primary and secondary alcohols, including allylic alcohols, with $PhI(OAc)_2$ as the oxidant under very mild reaction conditions (ambient temperature to 40 °C). High conversions (up to >99 %) were achieved in short reaction times (1–3 h) by using low catalyst loadings (0.5 mol % Ru). In addition, high selectivities (>90 %) for aldehydes were obtained at room temperature. MOF-253-Ru can be recycled up to six times with only a moderate decrease in substrate conversion.

Keywords: alcohol oxidation · heterogeneous catalysis · immobilization · metal–organic frameworks · ruthenium

Introduction

The last decade has witnessed an explosion in the field of metal–organic frameworks (MOFs) and porous coordination polymers (PCPs).[1] These materials are constructed from metal ions or clusters connected by polytopic organic ligands that assemble into three-dimensional, crystalline, porous frameworks. Much enthusiasm towards these materials has stemmed from their huge surface areas, which are typically higher than those of traditional porous solids, such as zeolites[2,3] and mesoporous materials.[4,5] An almost endless combination of metal ions and organic linkers has led to a vast library of MOF structures in recent years. As the focus shifts from synthesis to applications, it is expected that MOFs will find use in areas such as gas separation and storage, fine chemicals catalysis and drug delivery.[6]

MOFs were recognised as potential catalysts as early as 1990,[7] and several years later, Fujita and co-workers demonstrated for the first time the use of MOFs as heterogeneous catalysts.[8] Recently, there has been extensive activity in this field, and numerous reviews have appeared in the literature.[9]

As MOFs are hybrid materials, different parts of the framework can function as the active site. First, the metal node can act as a Lewis acid catalyst if coordinatively unsaturated sites are available.[8,10] Furthermore, organic molecules with coordinating groups can be grafted to these metal sites to introduce additional catalytic functionality to the MOF.[11] Second, the linker may contain functional groups, or metal complexes, that can act as a catalyst;[12] examples include pyridyl groups,[13] metalloporphyrins,[14] binaphthyl[15] and metal–salen complexes.[16] Third, guest-encapsulated species, such as metal[17] or metal oxide nanoparticles,[18] polyoxometalate clusters,[19] or metal complexes,[20] can be supported in the void spaces of the MOF.

The oxidation of alcohols to carbonyl compounds is one of the most fundamental processes in organic synthesis.[21] During the last decade, a number of green heterogeneous catalytic systems have been developed that use molecular oxygen or air as the oxidant.[22] These typically employ metal-based heterogeneous catalysts containing ruthenium,[23] gold[24] or platinum.[25] However, many of these systems require harsh reaction conditions and substrate selectivity can be difficult to control. The selective oxidation of primary alcohols to aldehydes at room temperature with

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heterogeneous catalysts is still rather limited and represents a challenging area in green chemistry.[26] Oxidation catalysis with MOFs has been particularly prolific over the past several years.[27] The majority of these transformations have employed either metal nodes or encapsulated nanoparticles in the MOF as catalysts. For example, Van der Voort and co-workers used V-MIL-47 as a catalyst for the oxidation of cyclohexene with *tert*-butylhydroperoxide as the oxidant; however, the catalyst showed low selectivity.[28] Li, Tang and co-workers employed gold nanoparticles in Cr-MIL-101 for the selective aerobic oxidation of alcohols to the corresponding carbonyl compounds, including benzylic alcohols.[29] In this case, the oxidation of 1-phenylethanol with molecular oxygen, albeit at relatively high temperatures (160 °C), showed spectacular results with a turnover frequency (TOF) of 29 300 h^{-1}. There are also examples of enantioselective oxidation by using MOFs containing chiral linkers that can coordinate to transition-metal complexes.[9c,30] Hupp and co-workers synthesised a Zn-MOF containing a chiral Mn–salen linker, which catalysed the enantioselective epoxidation of 2,2′-dimethyl-2*H*-chromene, achieving a turnover number (TON) of 1430 with 82 % *ee*.[16a] Lin and co-workers used a similar Mn–salen linker as a catalyst for the enantioselective epoxidation of a variety of olefins, with up to 92 % *ee*.[16b]

Ruthenium compounds represent a versatile group of catalysts that are important in various organic transformations.[31,32] Ru complexes containing N-donor ligands, such as bipyridine (bpy) and phenanthroline, are particularly active as homogeneous oxidation and isomerisation catalysts.[33] It has been shown that certain ruthenium–bpy complexes can undergo deactivation through a ligand redistribution mechanism, in which multiple bpy ligands bind to the metal.[34] Supporting Ru in a MOF, on the other hand, would overcome this issue. As the bpy ligands are remotely distributed throughout the framework, inactive $[Ru(bpy)_{3-x}L_{2x}]$ (L = ligand) complexes should not form. MOF-253, recently reported by Yaghi and co-workers,[35] was selected as a suitable host, as it has a reasonably large Langmuir surface area ($2490\ m^2 g^{-1}$) and contains accessible bpy units in the framework. Furthermore, high chemical and thermal stability is expected of MOF-253 due to the Al^{3+} nodes.[36,37] In fact, the recyclability of this MOF as a catalyst was recently demonstrated for C–C cross-coupling reactions.[38]

Herein, we report the immobilisation of a ruthenium complex in a MOF (MOF-253-Ru) by post-synthetic modification (PSM). This material is an efficient catalyst for the oxidation of alcohols with $PhI(OAc)_2$ as the oxidant. A wide range of secondary alcohols were oxidised to ketones in good to excellent yields under mild conditions (RT to 40 °C). In addition, primary alcohols were selectively oxidised to aldehydes at room temperature within 1–2 h. The MOF catalyst can be easily recycled and displays only a minor loss of catalytic activity over six cycles.

Results and Discussion

Synthesis and characterisation of ruthenium complexes: Srivastava and co-workers previously reported that reaction of $[RuCl_4(dmso)_2][(dmso)_2H]$ with bpy results in immediate formation of $[Ru(bpy)Cl_3(dmso)]$ (**1**).[39] We used the same procedure to synthesise a similar complex, $[Ru(bpydc)Cl_3(dmso)]$ (**2**; bpydc = 2,2′-bipyridine-5,5′-dicarboxylic acid), in which bpy was replaced with bpydc (Figure 1 a). Unfortunately, attempts to synthesise MOFs with this ruthenium-functionalised linker were unsuccessful. It was then realised that ruthenium could be introduced into MOF-253, which contains the appropriate bpy ligand to coordinate ruthenium, by PSM.[15,40,41] Thus, we first synthesised MOF-253 as previously reported.[35] The structure of MOF-253 is built of infinite, one-dimensional chains of AlO_6 corner-sharing octahedra that connect through bpydc linkers to give rhombic-shaped pores with a free diameter of 13 × 11 Å (Figure 2). The structure crystallises in an orthorhombic unit cell ($a = 22.63$, $b = 5.58$, $c = 18.60$ Å; $V = 2348.84\ Å^3$).[42] The X-ray powder diffraction (XRPD) patterns of as-synthesised MOF-253 are shown in Figure S1 in the Supporting Information. Reaction of MOF-253 with $[RuCl_4(dmso)_2][(dmso)_2H]$ (Figures 1 b and 2) resulted in the formation of a ruthenium-functionalised MOF (MOF-253-Ru), as confirmed by XRPD, elemental analysis, thermogravimetric analysis (TGA) and N_2 sorption measurements. The XRPD patterns of MOF-253 before and after ruthenium complexation are shown in Figure 3. Despite the low quality of these patterns—typical of Al-MOFs and most likely due to disorder within the crystal structure[43]—the peaks correspond closely with the strong peaks in the simulated pattern,[36] although there is a small shift towards higher 2θ values. As-synthesised MOF-253 contained amorphous species that were removed by washing with DMF and MeOH (Figure S1 in the Supporting Information).

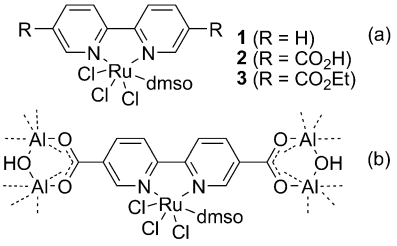


Figure 1. a) Ru-bipyridyl complexes. b) Schematic representation of Ru complex coordinated to the bpy site of MOF-253 in a post-synthetic step.

To gain some insight into the number and type of ligands coordinated to ruthenium in MOF-253-Ru, we compared its characterisation data (CHSN and Cl analyses and inductively coupled plasma–optical emission spectrometry (ICP-OES)) with those of homogeneous ruthenium complexes **1**–**3** (Figure 1 a and the Supporting Information). Because complex **1** is formed immediately at room temperature from $[RuCl_4(dmso)_2][(dmso)_2H]$ and bpy in ethanol, we anticipat-

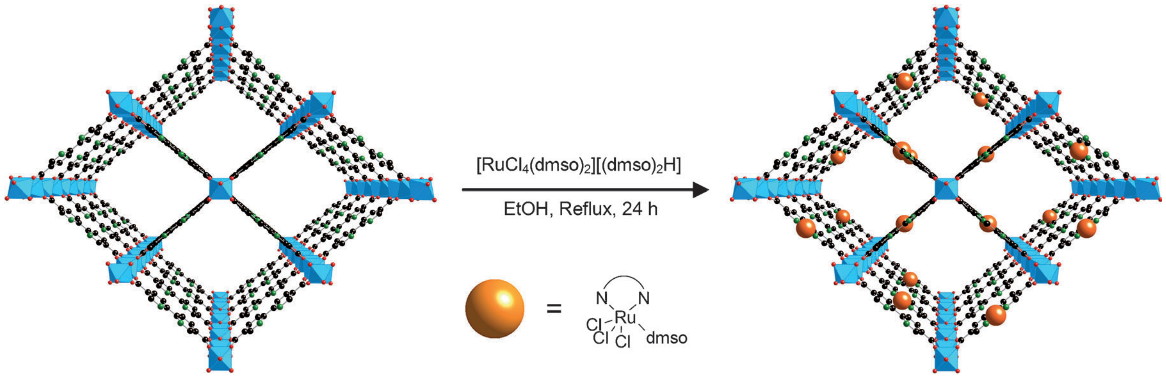


Figure 2. Representative structure and post-synthetic modification of MOF-253. Blue octahedra represent Al atoms; grey, red and green spheres represent C, O and N atoms, respectively; orange spheres represent the Ru complex, [$RuCl_3$(dmso)]. H atoms and guest molecules are omitted for clarity. The figure was drawn by using structural data taken from the literature, [36].

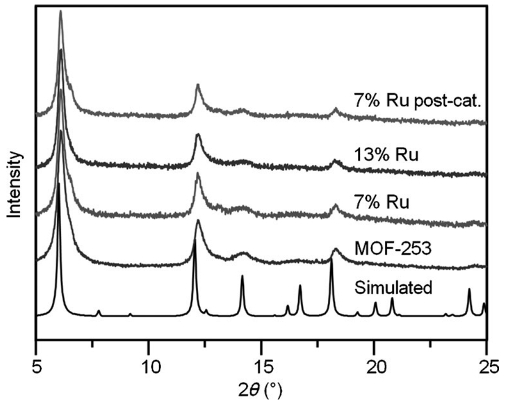


Figure 3. From bottom to top: XRPD patterns of simulated MOF-253, washed MOF-253, MOF-253-Ru7, MOF-253-Ru13 and MOF-253-Ru7 after six catalytic cycles.

ed that reaction of [$RuCl_4(dmso)_2$][$(dmso)_2H$] with MOF-253 would result in formation of a complex with similar stoichiometry inside MOF-253. Indeed, a stoichiometry matching that of [$RuCl_3$(dmso)] was confirmed by elemental analysis, which indicated formation of the complex [Ru(bpydc)Cl_3(dmso)] (Figure 1 b) within the MOF. Different amounts of Ru were loaded into MOF-253 to determine the maximum possible catalyst loading. Two samples were prepared containing 7 and 13 mol % Ru (i.e., Ru complexes occupied 7 and 13 % of the bpydc linkers in the MOF, respectively),[44] and named as MOF-253-Ru7 and MOF-253-Ru13. MOF-253-Ru13 was prepared using a large excess of Ru (Ru/linker = 1.5:1). Remarkably, the sample contained only 13 mol % Ru, which indicated that only a fraction of the bpydc sites were functionalised. The material remained crystalline upon incorporation of Ru (Figure 3).

The thermal stability of MOF-253 and MOF-253-Ru in air was investigated by TGA. The thermogravimetry (TG) curves of the MOF-253-Ru samples, displayed in Figure 4 (top), showed 7–9 % weight loss between 100 and 300 °C, which corresponds to decomposition of the Ru complex. Collapse of the framework occurred at significantly lower temperatures (330 °C) for MOF-253-Ru relative to MOF-253 (400 °C).

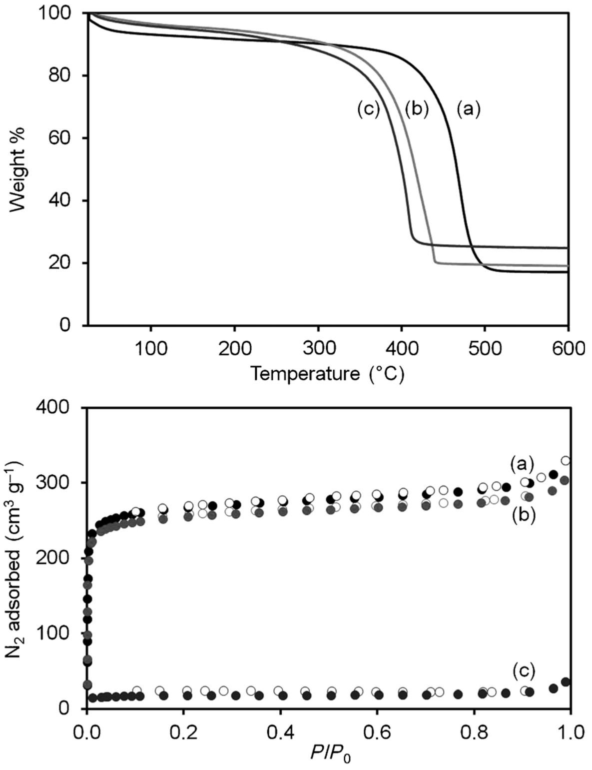


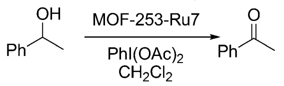
Figure 4. Top: TG curves; bottom: N_2 adsorption (●) and desorption (○) isotherms for MOF-253 (a), MOF-253-Ru7 (b) and MOF-253-Ru13 (c).

The N_2 sorption isotherms of MOF-253 and MOF-253-Ru samples are shown in Figure 4 (bottom). The Langmuir surface areas of MOF-253, MOF-253-Ru7 and MOF-253-Ru13 were calculated to be 1202, 1145 and 80 m^2g^{-1}, and the pore volumes were estimated to be 0.51, 0.47 and 0.05 cm^3g^{-1}, respectively. The surface area of MOF-253 was considerably lower than the reported value of 2490 m^2g^{-1}.[35] The CHN analysis (see the Supporting Information) and observed weight losses in the TGA (Figure 4) matched closely with the chemical formula of MOF-253, [Al(bpydc)(OH)·0.5H_2O], thereby indicating that no excess linker was present in the pores of MOF-253. Therefore, this lower surface area is not related to the activation procedure, but rather to the crystal defects of the MOF. The surface area decreased slightly upon low Ru loading, whereas higher loading led to a rapid drop in surface area. The pore openings in MOF-253-Ru13 are most likely blocked by the [Ru(bpydc)Cl_3(dmso)] complexes so that neither more Ru complexes nor N_2 molecules could enter the pores, thus resulting in the low surface area. SEM images of MOF-253 revealed uniform spherical particles, around 0.2–0.5 μm in diameter (Figure S2 a in the Supporting Information). There was little change in particle size or morphology for MOF-253-Ru7 (Figure S2 b in the Supporting Information). However, at higher Ru loading (13 mol %), aggregation of the MOF particles occurred, thereby leading to larger particles 1 μm in diameter (Figure S2 c in the Supporting Information). In addition, the MOF-253-Ru13 particles were inhomogeneous and the surfaces were covered with smaller rod-shaped crystallites. This is evidently related to the increase in the amount of the ruthenium complex present in the sample, and may explain the low surface area of MOF-253-Ru13.

Oxidation catalysis with MOF-253-Ru: A preliminary study was carried out using the homogeneous Ru complexes [Ru(bpy)Cl_3(dmso)] (**1**) and [RuCl_3(dbpydc)(dmso)] (**3**; dbpydc = diethyl 2,2′-bipyridine-5,5′-dicarboxylate) to find suitable conditions for the oxidation of alcohols (Scheme S1 in the Supporting Information). The oxidation of 1-phenylethanol was tested as a model reaction. Over 99 % conversion was achieved by using 1 mol % Ru (**1** and **3**) and (diacetoxy)iodobenzene as the oxidant in dichloromethane at 40 °C in 1.5 h (Table S1 in the Supporting Information). This reaction was then extended to the heterogeneous catalyst MOF-253-Ru7. The results are displayed in Table 1. The reaction in the absence of Ru with or without MOF-253 gave only traces of acetophenone (Table 1, entries 1 and 2). Addition of 1 mol % MOF-253-Ru7 resulted in complete oxidation to acetophenone within 3 h (Table 1, entry 3). The catalyst loading could be decreased to 0.25 mol % Ru, which afforded conversions of > 95 % within 3 h (Table 1, entries 4–6). Almost quantitative oxidation was achieved after 2 h with 0.5 mol % Ru (Table 1, entry 5 in parentheses). A catalyst loading of 0.05 mol % Ru (Table 1, entry 7) gave a TON of 1980 (10 h). Moreover, the reaction could be performed at room temperature with 0.5 mol % Ru (Table 1, entry 8) or by using 1 equivalent of oxidant (Table 1, entry 9), although longer times were required (4 and 4.5 h, respectively).

The method was expanded to other secondary alcohols by using the reaction conditions shown in Table 1, entry 5 and

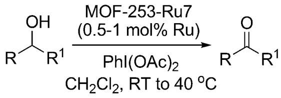
Table 1. Optimisation of reaction conditions for the oxidation of 1-phenylethanol with MOF-253-Ru7 as the catalyst.[a]



Entry	Ru [mol %]	*t* [h]	Yield [%][b]
1	–	3	4
2	MOF-253 (no Ru)	3	3
3	1.00	3	99
4	0.75	3	99
5	0.50	3 (2)	99[c] (97)
6	0.25	3	95
7[d]	0.05	10	99
8[e]	0.50	4	97
9[f]	0.50	4.5	98

[a] All reactions were conducted by using MOF-253-Ru7 (7 mol % or 2.2 wt % Ru), 1-phenylethanol (0.5 mmol, 60 μL), $PhI(OAc)_2$ (0.75 mmol, 242 mg) and dichloromethane (1 mL) at 40 °C. [b] Based on analysis by gas chromatography (GC). [c] Initial turnover frequency (TOF) = 480 h^{-1}. [d] 2.5 mmol of 1-phenylethanol (1 M) was used. [e] Reaction at 22 °C. [f] Reaction was conducted with 1 equivalent of $PhI(OAc)_2$.

Table 2. Oxidation of various alcohols by using MOF-253-Ru as the catalyst.[a]



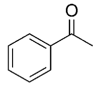
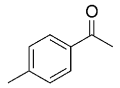
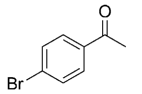
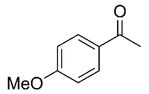
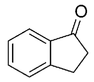
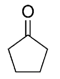
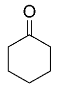
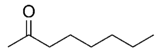
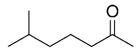
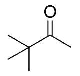
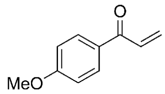
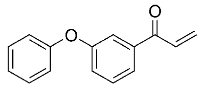
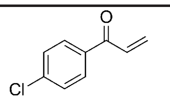
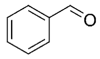
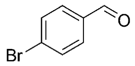
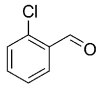
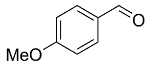
Entry	Product	*t* [h]	*T* [°C]	Conversion/yield[b] [%]	TOF [h^{-1}]
1		2	40	97/97	97
2		2	40	99/99	99
3	 Br	3	40	93/93 (89)	62
4	 MeO	3	40	95/95 (90)	63
5		2	40	92/92 (88)	92
6		3.5	40	98/98	56
7		4.5	40	97/97	43
8		4.5	40	99/99	44
9		2	40	99/95[d]	99
10		2	40	95/88[d]	96
11[c,d]	 MeO	4	40	82/78 (75)[e]	41
12[c,d]		5	40	64/60 (54)[e]	16

Table 2. (Continued)

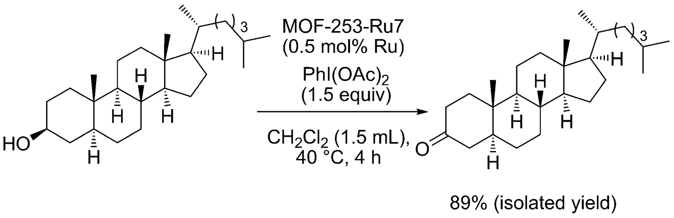
Entry	Product	t [h]	T [°C]	Conversion/yield[b] [%]	TOF [h^{-1}]
13[c,d]		5	40	55/51 (43)[e]	11
14[c,f]		1.5	22	99/90[g]	66
15[c,f]		2	22	98/91[g]	49
16[c,f]		2	22	95/88[g]	48
17[c,f]		1.5	22	90/84[g]	60

[a] All reactions were conducted by using MOF-253-Ru7 (0.5 mol% Ru, 0.0025 mmol, 11.5 mg), the substrate alcohol (0.5 mmol, 60 μL), PhI-$(OAc)_2$ (0.75 mmol, 242 mg) and CH_2Cl_2 (1 mL) at the temperature indicated. [b] Based on GC analysis with dodecane as the internal standard; yield of the isolated product is given in parentheses. [c] 1 mol% Ru used as the catalyst. [d] Yield based on ^1H NMR spectroscopy of the crude reaction mass in the presence of 1,4-dimethoxybenzene as the internal standard; yield of the isolated product is given in parentheses. [e] α,β-Unsaturated aldehydes were formed in small quantities (up to 4%). [f] 1.5 mL of CH_2Cl_2 was used. [g] Carboxylic acids formed in 6—9% yield.

Table 2, entry 1. Benzylic *sec*-alcohols[45] containing aromatic rings bearing electron-donating and electron-accepting groups were also oxidised to the corresponding ketones with nearly full conversion after 2–3 h (Table 2, entries 2–5). A variety of aliphatic cyclic and acyclic *sec*-alcohols were oxidised in excellent yield within 2–5 h (Table 2, entries 6–10). Chemoselective oxidation of the alcohol moiety for several allylic alcohols was achieved with moderate to good yields in 4–5 h by using 1 mol% Ru (Table 2, entries 11–13).

Oxidation of primary alcohols to the corresponding aldehydes in high yields is a challenging task. A major problem usually encountered is the formation of variable amounts of carboxylic acids, particularly when using heterogeneous catalysts that typically require high reaction temperatures. High yields and selectivities for aldehydes at room temperature with MOFs as catalysts have only been achieved by Pt@MOF-177,[46] which required reaction times of 24 h. Unfortunately, Pt@MOF-177 collapsed after the first reaction cycle and could not be reused. A MOF containing Ru paddlewheels also demonstrated high selectivities for the oxidation of alcohols to aldehydes; however, relatively low TONs (≈10) were attained and long reaction times (24 h) were required.[47] Alcohols were also selectively oxidised to aldehydes with high conversions by Au/MIL-101 in short reaction times (1–3 h) at relatively high temperatures (80 °C).[29] By using similar conditions to those used with secondary alcohols (40 °C), oxidation of primary benzylic alcohols catalysed by MOF-253-Ru7 gave low selectivity for the corresponding aldehyde as a result of over-oxidation to the carboxylic acid. However, excellent conversions and selectivities were achieved at room temperature by using 1 mol% Ru (Table 2, entries 14–17). Therefore, this work represents a considerable step forward in the application of MOFs as heterogeneous catalysts for the selective oxidation of alcohols under mild conditions. On the other hand, these previous MOF catalysts employed molecular O_2[29,46] or H_2O_2[47] as the oxidant, which results in fewer byproducts and less waste in comparison to $PhI(OAc)_2$. Unfortunately, oxidation of primary aliphatic alcohols, such as 1-nonanol or 2,2-dimethylpropan-1-ol, afforded only traces of the corresponding aldehydes.

A more complex alcohol, cholestanol, was oxidised to the corresponding ketone in excellent yield after 4 h in the presence of 0.5 mol% Ru by using MOF-253-Ru7 (Scheme 1).



Scheme 1. Oxidation of cholestanol to cholestanone catalysed by MOF-253-Ru7.

Since MOF-253 possesses one-dimensional channels, only the two shortest dimensions of the molecule need to be considered. For cholestanol these are 8.1 × 6.5 Å, significantly smaller than the channels of the MOF (11 × 13 Å). Therefore, the substrates should be able to enter the pores of MOF-253. According to the proposed mechanisms, the reaction proceeds through initial coordination of the oxidant to the metal complex, followed by reaction of this complex with the substrate.[48] The pore size is large enough to accommodate the oxidant–Ru substrate complex.

The heterogeneous nature of the catalyst was verified by hot filtration tests. At 72% conversion of 1-phenylethanol into acetophenone (30 min), the catalyst was removed by filtration and the reaction was continued. After 3 h, no significant increase in acetophenone formation was observed (a reaction profile is shown in Figure S4 in the Supporting Information). ICP-OES, however, revealed 0.9 ppm Al and 1.6 ppm Ru present in the supernatant, corresponding to 0.1 and 0.7% of the initial amounts of Al and Ru, respectively, in MOF-253-Ru7. Consequently, although metal leaching does occur, it does not contribute significantly to the oxidation of the alcohol. The evolution of ruthenium leaching over time upon heating at 35 °C in CH_2Cl_2 or in a mixture of CH_2Cl_2 and AcOH (1 M) is presented in the Supporting Information (Figure S5). It was observed that in the former case, a ruthenium leaching of 0.6% occurs during the first 2 h. Interestingly, after this time the leaching slows down considerably, and the amount of ruthenium remains constant at least up to 10 h under the same conditions. Similar results were obtained when MOF-253-Ru7 was heated at 35 °C in the mixture CH_2Cl_2/AcOH (1 M), the difference being a slightly increased ruthenium leaching (1.4%) during the first couple of hours. These results may indicate that the material contains some ruthenium species weakly bound to the MOF, which are easily displaced. However, most of the ruthenium species remain within the MOF. These species are catalytically active, since the material could be recycled for at least six runs (see below).

Recycling experiments were performed by using a 6.5 mmol scale of 1-phenylethanol. After the required reaction time, the catalyst was recovered, washed with solvent and dried under vacuum at room temperature for 16 h between each cycle. The catalyst was reused six times with only a moderate decrease in conversion (Table S2 in the Supporting Information, first cycle: 97%, sixth cycle: 85%). Analysis of the used catalyst revealed no change in either crystallinity or surface area (Figures 3 and 5), which indicated that the Al leaching did not affect the integrity of the framework. On the other hand, the Ru content decreased from 7 to 5 mol% after six cycles, according to elemental analysis. SEM images of MOF-253-Ru7 after six cycles showed little change in the particle size (Figure S2d in the Supporting Information). Elemental analysis also revealed that the dmso and Cl ligands on the Ru complex in the MOF had been exchanged during catalysis (Supporting Information).

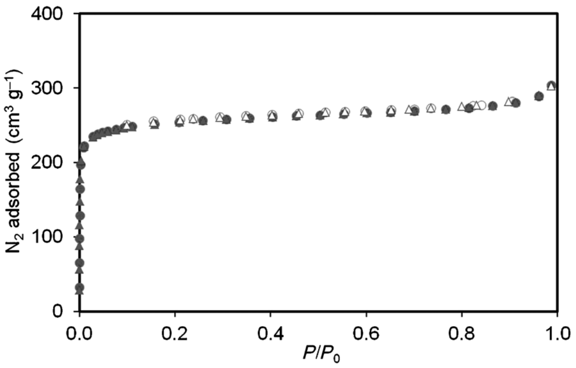


Figure 5. N_2 adsorption (●,▲) and desorption (○,△) isotherms for MOF-253-Ru7 before catalysis (●,○) and MOF-253-Ru7 after six cycles (▲,△).

Finally, the effect of porosity on the catalytic properties of MOF-253-Ru was examined. Since MOF-253-Ru13 has a significantly lower surface area ($80\ m^2g^{-1}$) than MOF-253-Ru7 ($1145\ m^2g^{-1}$), we expected it would be an inferior catalyst. MOF-253-Ru13 was employed as a catalyst for the oxidation of 1-phenylethanol by using the reaction conditions from Table 1, entry 5 (0.5 mol% catalyst loading). As we suspected, after 1 h only 36% of the substrate had been converted to acetophenone, compared with 62% conversion achieved with MOF-253-Ru7 after 1 h. This suggests that ruthenium within the pores of MOF-253-Ru13 is less accessible to the substrate, as a result of pore blockage. Catalysis will therefore mainly occur on the surface of the MOF-253-Ru13 particles. However, this variation in catalytic activity may also be attributable to the difference in particle size and morphology between the samples (Figure S4 in the Supporting Information).

Conclusion

In this work, we have established a method for introducing ruthenium complexes into MOF-253. The MOF remains crystalline and retains a high surface area upon coordination of small amounts of [$RuCl_3$(dmso)]. In addition, we have shown that our synthesised MOF-253-Ru can catalyse the oxidation of a wide range of alcohols with high selectivities for ketones and aldehydes. Oxidation of primary alcohols to aldehydes at room temperature and in short reaction times is unprecedented in MOF catalysis. The MOF-253-Ru catalyst is truly heterogeneous and can be successively recycled up to six times without significant loss of activity, crystallinity or surface area. In addition, samples containing low Ru loadings and higher surface areas were significantly more active as oxidation catalysts than samples with high Ru loadings and low surface areas. Because the bpydc ligands are fixed to the MOF, deactivation of the catalyst through formation of inactive [$Ru(bpy)_{3-x}L_{2x}$] species is avoided. Although the coordination of metal complexes into MOFs by PSM is a practical method that leads to materials with enhanced functionality, this work demonstrates that even stronger metal binding sites in the framework are required for practical applications associated with heterogeneous catalysis.

Experimental Section

General: All chemicals and solvents were used as received without further purification. XRPD was carried out on a PANalytical X'Pert PRO diffractometer in reflectance Bragg–Brentano geometry equipped with a pixel detector and using $Cu_{K\alpha1}$ radiation. The samples were dispersed on zero-background Si plates. Nitrogen sorption was carried out at 77 K on a Micromeritics ASAP2020 device. Samples of MOF-253 and MOF-253-Ru were degassed at 250 and 50 °C for 16 h, respectively, prior to sorption measurements. TGA was performed on a PerkinElmer TGA 7 apparatus equipped with a platinum pan, and all samples were heated at a rate of $2\,°C\,min^{-1}$ in air. CHSN analysis was performed on a Carlo Erba Flash 1112 elemental analyser, Cl analysis was carried out by Schöniger flask combustion followed by titration, and ICP-OES was used for metal determination with a Varian Vista MPX ICP-OES instrument. Medac Ltd. (UK) carried out the elemental analysis. Field-emission SEM was performed on a JEOL JSM-7000F microscope operated at 5 kV. The samples were pre-coated with a thin carbon film. High-resolution mass spectra were recorded on a Bruker microTOF ESI–time-of-flight mass spectrometer. GC was performed on a Varian 3800 chromatograph with a CP-CHIRASIL-DEX CB chiral column (30 m) and a flame ionisation detector. Dodecane was used as an internal standard. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz, on a Bruker Avance 400 spectrometer. Chemical shifts (δ) are reported in ppm, with the residual solvent peaks in $CDCl_3$ ($\delta_H = 7.28$; $\delta_C = 77.00$ ppm) as an internal reference; coupling constants (J) are given in hertz.

Synthesis of MOF-253: The synthesis conditions used were similar to those described in the literature, [35]. $AlCl_3{\cdot}6H_2O$ (151 mg, 0.625 mmol) and bpydc (153 mg, 0.625 mmol) were added to a Teflon-capped 20 mL glass vial containing *N,N'*-dimethylformamide (DMF, 10 mL) and stirred for 30 min at room temperature, followed by sonication for 10 min. The mixture was heated at 120 °C for 24 h in an oil bath on a hotplate. The resulting white powder was rinsed in fresh DMF and the supernatant decanted. The Al-MOF was washed in DMF at 80 °C for 3 h, followed by washing in methanol by Soxhlet extraction for 24 h, after which the solid was rinsed in fresh methanol and heated overnight at 200 °C under vacuum to give [Al(bpydc)(OH)], MOF-253 (165 mg, 90 %).

Synthesis of MOF-253-Ru7 and MOF-253-Ru13: The preparation of MOF-253-Ru7 was carried out as follows: [Al(bpydc)(OH)] (1.078 g, 3.652 mmol) and [RuCl$_4$(dmso)$_2$][(dmso)$_2$H] (0.163 g, 0.292 mmol) were heated at reflux in absolute ethanol (100 mL) for 24 h while stirring. A dark-brown solid was collected by centrifugation. The solid was washed by stirring in fresh ethanol for 2 h, followed by centrifugation. This process was repeated three times. The powder was then dried at 50 °C under vacuum for 16 h to yield the product, [Al(bpydc)(OH)]·0.07RuCl$_3$(dmso) (1.085 g, 97 %). MOF-253-Ru13 was prepared in a similar manner; exact amounts are supplied in the Supporting Information.

General procedure for the oxidation of primary, secondary and allylic alcohols: A dried sealable tube equipped with a magnetic stirring bar was charged with MOF-253-Ru7 (0.5–1 mol % Ru), an alcohol (0.5 mmol), (diacetoxyiodo)benzene (242 mg, 0.75 mmol), dodecane (20 µL) and dichloromethane (1 mL). The reaction mixture was stirred at 22 or 40 °C for the appropriate reaction time. After cooling to room temperature the mixture was centrifuged and the conversion was determined by GC.

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[42] Cell parameters determined by Dicvol04 within the HighScore Plus suite. Figure of merit, FOM(9) = 18.2.

[43] The crystallinity of MOF-253 can be improved if acetic acid is introduced into the reaction mixture. However, after activation of the MOF with methanol, most of the Bragg reflections disappear from the XRPD pattern. Therefore, this activation procedure, although necessary, most likely disrupts some of the MOF crystals leading to misalignment between neighbouring unit cells and particles. Consequently, many of the low-intensity reflections, as well as those at higher 2θ, are lost.

[44] 7 and 13 mol % of Ru within MOF-253 correspond to 2.2 and 3.8 wt % Ru, respectively.

[45] Interestingly, it has been reported that under homogeneous conditions a ruthenium complex afforded low yield in the oxidation of *sec*-alcohols by $PhI(OAc)_2$. This system was an excellent catalyst to oxidise primary alcohols: B.-L. Lee, M. D. Kärkäs, E. V. Johnston, A. K. Inge, L.-H. Tran, Y. Xu, Ö. Hansson, X. Zou, B. Åkermark, *Eur. J. Inorg. Chem.* **2010**, 5462–5470.

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