DOI: 10.1002/chem.201000588

Metal–Organic Frameworks as Efficient Heterogeneous Catalysts for the Regioselective Ring Opening of Epoxides

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

Abstract: An iron-based metal–organic framework, [Fe(BTC)] (BTC: 1,3,5benzenetricarboxylate) is an efficient catalyst in the ring opening of styrene oxide with alcohols and aniline under mild reaction conditions. Out of the various alcohols tested for ring opening of styrene oxide, methanol was found to be the most reactive in terms of percentage conversion and reactivity. The rate of the ring-opening reaction of styrene oxide decreases as the size of the alcohol is increased, suggesting the location of active sites in micropores.

Keywords: epoxides • green chemistry • heterogeneous catalysis • metal–organic frameworks • ringopening reactions [Fe(BTC)] was a truly heterogeneous catalyst and could be reused without loss of activity. The analogous compound $[Cu_3(BTC)_2]$ was also found to be effective, although with somewhat lower activity than [Fe(BTC)]. The present heterogeneous protocol is compared with a homogeneous catalyst to give an insight into the reaction mechanism.

Introduction

Epoxides are important synthetic intermediates for a large number of bifunctional alcohols that can be prepared conveniently from the corresponding alkenes.^[1] Also, epoxides from C₂ to C₄ alkenes are common commodities prepared in a large quantities and used as starting materials for the preparation of 1,2-diols and β -aminoalcohols.^[2] The most important reaction of epoxides is ring opening catalysed by acids or bases. For this process to be of synthetic use, the epoxide ring opening has to be performed under mild conditions with high regioselectivity towards the desired product. Herein, we describe liquid-phase epoxide ring opening catalysed by metal–organic frameworks (MOFs) as heterogeneous catalysts under mild reaction conditions.

MOFs are crystalline solids in which the structure is built by metal ions or clusters of metal ions held in place by organic di- or multitopic linkers. MOFs are at the top of the list of porous solids and exhibit very large surface areas (mostly internal) as well as the lowest framework densities. The synthesis of new MOFs and their use for hydrogen storage, CO₂ sequestration and gas separation is a current research front in chemistry.^[3] MOFs contain a large percentage of transition metals that can act as Lewis acids provided that they have free coordination positions not compromised in the construction of MOFs. MOFs have many similarities, from the structural point of view, with zeolites and related microporous solids. Zeolites constitute the best example of successful heterogeneous catalysts. Thus, there is interest in exploiting the possibilities of MOFs as heterogeneous catalysts.^[4-9] The main drawbacks of MOFs as solid catalysts compared with zeolites are the lower thermal and chemical stabilities of MOFs and the fact that for some structures the nodal metal ions or clusters do not have free coordination positions to interact with substrates and reagents.^[10] MOFs as catalysts have been recently reviewed and their advantages, limitations and the general applicability of MOFs as solid catalysts have been commented on in detail.^[11-13]

Herein, we have used three commercially available MOFs. One of them, [Fe(BTC)] (BTC: 1,3,5-benzenetricarboxylate), is composed of trimers of iron octahedra sharing a common vertex μ_3 -O linked by the BTC moieties in such a way that this leads to two types of mesoporous cages of free apertures of 25 and 29 Å, accessible through microporous windows of 5.5 and 8.6 Å.^[14] One of the coordination positions of Fe³⁺ ions is occupied by a solvent molecules and, therefore, it can be available to participate in catalysis by coordination with the substrate without compromising the stability of the crystal structure. Analogously, [Cu₃(BTC)₂]



8530

 [[]a] Dr. A. Dhakshinamoorthy, Dr. M. Alvaro, Prof. Dr. H. Garcia Instituto Universitario de Tecnología Química CSIC-UPV and Departamento de Química, Universidad Politécnica de Valencia Av. De los Naranjos s/n, 46022 Valencia (Spain) Fax: (+34)96387-7809 E-mail: hgarcia@qim.upv.es

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000588.

has the same organic linker as [Fe(BTC)], but the structure of $[Cu_3(BTC)_2]$ is composed of a cluster of two copper ions with a paddle-wheel shape that has square planar coordination. The BTC ligand acts as a trigonal planar ligand connecting diatomic metal clusters, which defines nanocages of about 2.5 nm with windows of 0.8 nm.^[15] Also, for each Cu²⁺ ions there is a coordination position occupied by a solvent molecule. The third MOF under study is $[Al_2(BDC)_3]$ (BDC: *p*-benzenedicarboxylate) and the crystal structure of $[Al_2(BDC)_3]$ is composed of corner-sharing octahedral Al linked by BDC ligands.^[16] $[Al_2(BDC)_3]$ has a pore size of 8.5 Å with the surface area of 1590 m²g⁻¹ with good thermal stability. In the case of $[Al_2(BDC)_3]$, the six coordination positions of the Al³⁺ ions are compromised with the BDC linkers.

We also describe that [Fe(BTC)] is an extremely efficient and regioselective heterogeneous catalyst for epoxide ring opening by alcohols and amines (Scheme 1). Taking into ac-

$$R^2 \xrightarrow{O} R^4$$
 RXH $R^2 \xrightarrow{XR} OH$ $R^2 \xrightarrow{XR} R^2$ $R^3 \xrightarrow{A} R^4$ $R^1 \xrightarrow{R^2} R^3$ R^4 $R^1 \xrightarrow{R^2} R^4$ R^3

 $R^1 = H, CH_3, Ph, C_7H_{14}$

 $R^2 = H, CH_3$

 $R_4^3 = H, CH_3, Ph$

 $R^4 = H, CH_3$

 ${\sf R}$ = methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-methyl-2-propyl, phenyl, 1-hexyl ${\sf X}$ = 0, NH

Scheme 1. Epoxide ring opening catalysed by [Fe(BTC)] with alcohols and amines.

count the availability of the components, the non-toxicity of iron and the mild conditions, the present protocol constitutes a good example of a green catalyst and an environmentally benign process.

Results and Discussion

Herein, we present the results obtained on epoxide ring opening catalysed by [Fe(BTC)] and $[Cu_3(BTC)_2]$ MOFs as heterogeneous catalysts with various alcohols and amines. In addition, we show that [Fe(BTC)] is a heterogeneous and reusable catalyst and also discuss the various factors determining the reactivity of epoxides under present experimental conditions.

Initially styrene oxide was selected as a model substrate and the epoxide ring opening by methanol as a nucleophile in the presence of different catalysts under various conditions was screened with the aim to achieve the maximum percentage conversion without compromising the product selectivity. The efficient transformation of styrene oxide with methanol to 2-methoxy-2-phenylethanol is shown in Table 1.

In the absence of catalyst, styrene oxide was recovered unreacted after 1 h. On the other hand, three MOFs were tested to find the most active one for the reaction. It was Table 1. Ring opening of styrene oxide with methanol catalysed by different catalysts $^{\left[a\right] }$

	0	OCH ₃					
	\sim	CH ₃ OH		Н			
		catalyst					
Entry	Catalyst	Time [min]	Conversion [%]	Selectivity [%]			
1	-	60	-	-			
2	[Fe(BTC)]	5	36	99			
3	[Fe(BTC)]	10	49	98			
1	[Fe(BTC)]	15	58	98			
5	[Fe(BTC)]	20	69	97			
5	[Fe(BTC)]	60	>99 (93) ^[b]	94			
7	[Fe(BTC)]	24 ^[c]	72 ^[c]	95			
3	[Fe(BTC)]	90 ^[c]	88 ^[c]	90			
)	[Fe(BTC)]	144 ^[d]	10	95			
10	[Fe(BTC)]	60	98 ^[e]	>98			
11	[Fe(BTC)] ^[f]	60	<2	98			
12	$[Cu_3(BTC)_2]$	10	25	98			
13	$[Cu_3(BTC)_2]$	60	93 (89) ^[b]	95			
14	$[Al_2(BDC)_3]$	30	21	98			
15	$[Al_2(BDC)_3]$	60	67	96			
16	iron citrate	60	24	99			
17	$Fe(NO_2)_2 \cdot 9H_2O^{[g]}$	10	>99	98			

[a] Conditions: styrene oxide (0.250 g, 2 mmol), catalyst (50 mg, 0.2 mmol of Fe), 40 °C, methanol (5 mL). [b] Determined by GC using nitrobenzene as the external standard. Values in parentheses refer to the yield. [c] Styrene oxide (2 mL, 16.6 mmol), methanol (5 mL) for 24 and 90 h reaction time at 40 °C. [d] Styrene oxide (10 mL, 83.3 mmol), methanol (6 mL) for 144 h reaction time at 40 °C. [e] Conversion after the third reuse. [f] Reaction with pyridine (0.1 mL, 1.22 mmol) under identical conditions as those described in footnote a. [g] 100 mg of catalyst used.

found that [Fe(BTC)] showed the best catalytic activity under mild reaction conditions with very high selectivity. Figure 1 shows the time–conversion plot in the presence of the MOFs tested as catalysts. Although, $[Cu_3(BTC)_2]$ was also notably active as an epoxide ring-opening catalyst, it showed somewhat lower activity than [Fe(BTC)]. The catalytic activity of $[Cu_3(BTC)_2]$ is not surprising because Cu^{2+} in this MOF has one free position available for coordination with a substrate and a recent study has shown that $[Cu_3-2]$



Figure 1. Time conversion plot for ring opening of styrene oxide with methanol catalysed by a) [Fe(BTC)]; b) $[Cu_3(BTC)_2]$ and c) $[Al_2(BDC)_3]$. Reaction conditions: styrene oxide (2 mmol), catalyst (50 mg), 40°C, methanol (5 mL).

Chem. Eur. J. 2010, 16, 8530-8536

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 8531

 $(BTC)_2$] behaves as a Lewis acid.^[17] Furthermore, we observed that $[Al_2(BDC)_3]$ exhibits much lower activity than [Fe(BTC)] and $[Cu_3(BTC)_2]$. This lower activity of $[Al_2(BDC)_3]$ can be easily understood when considering that the Al^{3+} ion in this MOF is fully coordinated by BDC linkers and does not have a free coordination position available to act as a Lewis acid.

The data obtained showed that [Fe(BTC)] is a highly active and selective heterogeneous catalyst in the ring opening of styrene oxide with methanol and the selectivity was always more than 95%. To provide evidence for the existence of Lewis acidic sites in [Fe(BTC)], a control experiment was performed for the ring opening of styrene oxide with methanol in the presence of pyridine as described in Table 1, entry 11. The percentage conversion was <2 after 1 h and this failure can be easily explained by the poisoning of the Lewis acid sites by strong interactions with pyridine. This is clear evidence to support the presence of Lewis acid sites in [Fe(BTC)].

In addition, a quantitative EPR spectroscopic study on [Fe(BTC)] was undertaken. Figure S1 in the Supporting Information shows the EPR spectrum recorded for [Fe(BTC)], which gives 2.01 as the *g* value, as well as that of the Cu- $(SO_4)\cdot12H_2O$ standard used to quantify the intensity of the signal. It was estimated that the solid contained about 28% of Fe^{III} species, thus confirming the +III paramagnetic state of Fe in [Fe(BTC)], which is in agreement with the stoichiometry of the solid and the elemental analyses results (see the Supporting Information), which show the presence of 25% iron in the material.

To determine the productivity of [Fe(BTC)] for the conversion of styrene oxide to 2-methoxy-2-phenylethanol, the reaction was carried out in methanol with an eight-fold excess of styrene oxide with respect to [Fe(BTC)] (see Table 1, entries 7 and 8). At 24 h reaction time, 72% of the styrene oxide was converted to 2-methoxy-2-phenylethanol with very high selectivity. After a prolonged time, the percentage conversion of styrene oxide was increased to 88% without much decrease in the product selectivity. As expected, an eight-fold increase of styrene oxide concentration decreases the rate of the reaction, but the fact that the reaction progresses after 90 h and a high conversion is achieved indicates that [Fe(BTC)] does not become deactivated. Only when a 40-fold excess of styrene oxide with respect to the typical styrene oxide/[Fe(BTC)] ratio is used, is deactivation of [Fe(BTC)] observed (see Table 1, entry 9).

For the sake of comparison, iron citrate and iron nitrate nonahydrate were used as model catalysts for Fe^{III} as Lewis acid sites for the same reaction. As shown Table 1, entry 16, iron citrate showed very low conversion and this may be due to poor solubility in the medium, the absence of micropores in the solid and/or the lack of free coordination positions of the Fe^{III} ion. In contrast, Fe^{III} nitrate becomes completely dissolved in the medium and showed very high activity, reaching an almost complete styrene conversion toward the 2-methoxy-2-phenylethanol in only 10 min. The result of $Fe(NO_3)_3$ clearly indicates the intrinsic activity of Fe^{III} as

Lewis acidic sites to promote styrene oxide ring opening. The remarkable difference between $Fe(NO_3)_3$ as a homogeneous catalyst and [Fe(BTC)] as a heterogeneous catalyst must be explained in terms of the impeded accessibility of Lewis acid sites within the micropores of MOFs when compared with homogeneous catalysts and the fact that Fe^{III} ion in [Fe(BTC)] has only one position available for coordination in comparison to dissolved Fe(NO₃)₃, in which Fe^{III} should have more freedom to coordinate with the epoxide. Additionally, the carboxylate groups coordinating Fe^{III} must also reduce the Lewis acidity of these metal sites by giving electron density to the Fe^{III} ions. In any case, comparison with iron citrate clearly reveals the benefits of large microporosity and the presence of free coordination positions in [Fe(BTC)] so as to bind with styrene oxide to promote the ring opening.

To verify whether the catalysis of [Fe(BTC)] is truly heterogeneous or is due to some leached iron species present in the liquid phase, the reaction was carried out under the optimised conditions described in Table 1 and the [Fe(BTC)] solid catalyst was filtered from the reaction mixture at 38 % formation of 2-methoxy-2-phenylethanol. After removal of the [Fe(BTC)] catalyst, the solution in the absence of solid was again stirred at 40 °C. After 1 h, no further product formation was observed in the absence of solid (see Figure 2).



Figure 2. Leaching test and evidence for heterogeneity in the catalysis of styrene oxide ring opening by methanol at 40° C a) in the presence of [Fe(BTC)] or b) after filtration of the solid at 38% conversion.

Hence, it can be concluded that catalysis occurs in the solid phase and the process is truly heterogeneous.

The reusability of [Fe(BTC)] was investigated for the ring-opening reaction of styrene oxide with methanol under identical conditions as described in Table 1. After the required time, the reaction mixture was allowed to settle down and the supernatant liquid was decanted and the solid used for another consecutive run without further treatment. After three consecutive reuses, the catalyst did not show any changes in its crystallinity. Further evidence in support of the catalyst stability was obtained from powder XRD results. Comparison of the XRD patterns of the fresh and

8532

FULL PAPER

three times reused [Fe(BTC)] is provided in Figure 3, which shows that there is a coincidence in the peak position, with some changes in the relative intensity of some peaks, partic-



Figure 3. Powder XRD of a) fresh [Fe(BTC)], b) three times used [Fe-(BTC)] and c) methanol-treated [Fe(BTC)].

ularly at low-angle values. These changes in the intensity of some of the diffraction peaks have been previously observed and attributed to the presence of some organic material in the micropore space of the used MOF.^[18,19]

To provide further support and study the influence of methanol on the crystallinity of [Fe(BTC)], the catalyst was stirred in the absence of styrene oxide under identical conditions mentioned in Table 1. The coincidence of the XRD patterns of [Fe(BTC)] used as the catalyst and that stirred in pure methanol lend support to the fact that the crystal structure is maintained without any damage during the course of the reaction, except some changes in the intensity of the peaks (Figure 3c). These changes in the peak intensity must have occurred due to the replacement of some water molecules with methanol.

After optimising the reaction conditions with methanol using styrene oxide as a probe substrate, we wanted to study the scope of this reaction and catalyst and its applicability to other epoxides, alcohols and amines. The results are shown in Table 2.

Styrene oxide reacted with ethanol but the rate of the reaction was lower than that of methanol. The ring-opening reaction employing ethanol can be sped up by heating the suspension at moderate temperatures. As the temperature increases, the percentage yield increases. Also an increase in the amount of catalyst resulted in a better yield of the product. Similarly, 1-propanol also reacted with styrene oxide to give a good yield, but 2-propanol as a nucleophile gave a slightly lower yield than with 1-propanol, ethanol and methanol. This may be due to the steric hindrance of two methyl groups and/or also to a impeded diffusion of 2-propanol within the [Fe(BTC)] micropores to reach the activated epoxide interacting with the Lewis acid sites. Similar behaviour was observed when comparing the yields of the 2-phenylethanol product when using 1-butanol and 2-methyl-2-propanol as nucleophiles. The use of 2-methyl-2-propanol results in a much lower yield. This may be reasonably explained by the fact that 2-methyl-2-propanol is even more crowded with methyl groups increasing the steric hindrance, which, in general, impedes nucleophilic substitution and in this case also makes diffusion through the MOF micropores more difficult. Importantly, in all cases, one regioisomer predominates over other regioisomers in the presence of [Fe(BTC)] as the catalyst. The regioselectivity of the epoxide ring opening can be rationalised by assuming a prevalent S_N1 mechanism.

To differentiate between S_N1 and S_N2 reaction mechanisms, 1,2-epoxy-2-methylpropane was selected as a substrate and the nucleophilic ring opening of this epoxide was carried out with methanol and aniline. With methanol as the nucleophile, the less-substituted alcohol was obtained as the major product over the more-substituted regioisomer. On the other hand, the reaction between 1,2-epoxy-2-methylpropane and aniline in aprotic solvent resulted in equal amounts of both isomers through S_N1 and S_N2 mechanisms (Scheme 2). Thus, when solvent (aprotic acetonitrile), nucle-



Scheme 2. Ring opening of 1,2-epoxy-2-methylpropane with aniline in the presence of acetonitrile as the solvent when using [Fe(BTC)] as the catalyst. Reaction conditions: 1,2-epoxy-2-methylpropane (0.250 mL, 2.8 mmol), aniline (0.260, 2.8 mmol), acetonitrile (4 mL), [Fe(BTC)] (50 mg), 40 °C, 16 h.

ophile (aromatic amine) and substrate (terminal epoxide with a CH_2 carbon) favour the $S_N 2$ mechanism, a mixture of the two products coming from $S_N 1$ (the mechanism generally operating under the conditions of the present study) and $S_N 2$ mechanisms are observed in equal amounts. It can be anticipated that stronger and less-bulky nucleophiles, such as aliphatic amines, should promote the formation of $S_N 2$ even further. However, we note that the stability of MOFs and particularly $[Al_2(BTC)_3]$ may be limited in the presence of aliphatic amines, since they undergo decomposition.^[9]

Reactions between *cis*-cyclooctene oxide and 1-octene oxide and methanol resulted in no reaction with [Fe(BTC)] as the catalyst. To understand the reasons for this failure, we performed a homogeneous reaction with Fe^{III} nitrate and observed that again *cis*-cyclooctene oxide failed to react. On the other hand, 1-octene oxide reacted with methanol in homogeneous medium with a reasonably good yield to give the expected product. Taking into account the results obtained in the homogeneous phase, we speculate that the length of the alkyl chain should have an effect on the reactivity when using [Fe(BTC)] as the catalyst due to the unfavoration.

www.chemeurj.org

CHEMISTRY

A EUROPEAN JOURNAL

Table 2.	Ring opening reaction of epox	ides with various	nucleophiles	s catalysed by	y [Fe(BTC)]. ^[a]
Enovido	Nucleanhile	Time [h]	T [PC]	Draduat	

Epoxide	Nucleophile	Time [h]	T [°C]	Product	Yield [%] ^[b]
	_OH	1	40	OH	93 (1)
	∕∩он	1 24 24 24	40 40 70 70	ОСОН	14 (1) 35 (1) 59 (2) 73 ^[c] (3)
\bigcirc	∕∕ОН	24	80	OF	67 ^[c] (4)
Č,	ОН	24	80	ОЧ	52 ^[c] (2)
	OH	30	90	OH	85 ^[c] (2)
	→он	24	80	ОН	30 ^[c] (2)
o	_ОН	1 1	40 40		 _[d]
	_ОН	1 1	40 40	OH O U	- 78 ^[d] (2)
	ОН	24	60		50 ^[c] (1)
	∕ОН	1	40	О ОН	48 (2)
<u>}</u>	∕он	24	60	ООН	72 ^[c] (3)
<u>}</u>	ОН	24	60	О ОН	64 ^[c] (3)
°,/	_OH	4	40	ООН	72 (2)
	_ОН	48 20	40 60	O OH	19 62 ^[c]
	NH ₂	144 24	40 80	NH OH	$52^{[e]}$ (4) $72^{[c]}$ (2)
	NH ₂	24	70 ^[f]	HN OH	49 ^[c] (2)

[a] Reaction conditions: epoxide (0.250 g, 2 mmol), alcohols (5 mL), catalyst (50 mg). [b] Yield is determined by GC using nitrobenzene as external standard. Selectivity was always >95%. Values in parenthesis correspond to the yield of the corresponding regioisomer. [c] 150 mg of [Fe(BTC)] was used. [d] Epoxide (0.250 g), methanol (5 mL), Fe(NO₃)₂·9H₂O (100 mg). [e] Styrene oxide (5 mL, 41.6 mmol), aniline (3.87 mL, 41.6 mmol), [Fe(BTC)] (25 mg, 0.1 mmol), acetonitrile (10 mL). [f] Styrene oxide (0.25 mL, 2 mmol), 1-hexylamine (0.275 mL, 2 mmol), [Fe(BTC)] (150 mg), acetonitrile (5 mL).

ourable diffusion of these molecules inside the micropores, particularly at the moderate temperatures of the reaction.

Sterically crowded 2,2,3-trimethyloxirane reacted with methanol to give the product in 48% yield at 40°C in 1 h. Further, the same substrate with ethanol and 1-propanol resulted in good conversion with 62% yield at 60°C for longer times (24 h). These experiments again suggest that the size of the molecule has a strong influence on the reactivity of epoxide with alcohols when the reaction is performed in MOFs as solid catalysts. Further, trans-stilbene oxide was treated with methanol at different temperatures and again the yield was increased with temperature.

Besides using alcohols as nucleophiles, we also wanted to determine the reactivity of anilines with styrene oxide. The reaction of a large excess of styrene oxide with aniline resulted in moderate yields with a substrate/catalyst ratio of 410. The same reaction resulted in higher yields when the temperature and catalyst concentration were increased. In addition, moderate yields were observed with styrene oxide and hexylamine with [Fe(BTC)] as the catalyst.

To gain insight into the reaction mechanism, the initial reaction rates for the ring opening of styrene oxide with various alcohols at 40°C were determined. As the initial reaction rates, measured as the percentage of styrene oxide conversion in 1 h, for methanol (99%), (14%), ethanol 1-propanol (7%), 2-propanol (7%) and 2methyl-2-propanol (4%) are dramatically different, the formation of a fully developed carbocation intermediate by the interaction of the epoxide with Fe^{III} as the Lewis acid is ruled out. Hence, the following mech-

8534

www.chemeurj.org

FULL PAPER

anism was proposed (Scheme 3): Initially, [Fe(BTC)] coordinates with styrene oxide through an acid–base interaction to produce an increase in the electrophilic nature of the carbon



Scheme 3. Proposed mechanism for the ring opening of styrene oxide with methanol catalysed by [Fe(BTC)].

attached to the phenyl group or the one with more alkyl substituents. Subsequently, this carbon with a partial positive charge is attacked by methanol or the corresponding alcohol to give the product. The observed regioselectivity is the result of the polarisation of the C–O bond with the increase in the partial positive charge.

Conclusion

Herein, we present a simple and efficient synthetic protocol for the epoxide ring opening of various substrates using [Fe-(BTC)] as a heterogeneous catalyst under mild reaction conditions. Compared with heterogeneous, non-porous iron citrate, [Fe(BTC)] exhibits a superior performance that derives from a combination of Lewis acid iron ions with one exchangeable coordination position and large porosity in terms of surface area and pore size. We have shown that [Fe(BTC)] is a general catalyst for a number of epoxides with alcohols and amines that smoothly open the ring regioselectively to give good yields. Steric encumbrance on the alcohol or impeded diffusion play an unfavourable role on the conversion. The regioselectivity in all of the cases studied was high, rendering the product expected from a Lewis acid catalysed S_N1 ring-opening mechanism. The Lewis acidity of [Fe(BTC)] has been supported by poisoning with pyridine and by observing paramagnetic Fe^{III} in EPR spectroscopy. The catalyst could be easily recovered after the reaction and reused for additional runs before deactivation of the catalyst. [Fe(BTC)] exhibits superior performance than other related MOFs. Considering the easy preparation of [Fe(BTC)] and the low toxicity of Fe^{III}, this reaction system is green and can be implemented for large-scale synthesis.

Experimental Section

General: All reagents, starting materials and MOFs were obtained commercially from Aldrich and used without any further purification unless otherwise noted. [Fe(BTC)] was characterised by IR spectroscopy, chemical analysis, EPR spectroscopy and XRD. Elemental analysis shows that the percentage of iron in the material was 25. The percentage conversion, purity and relative yields of the final products were determined by using a Hewlett Packard 5890 series II gas chromatograph with an FID detector and high purity helium as the carrier gas. The products were identified by GC-MS by using a Hewlett Packard 6890 series spectrometer. Powder XRD patterns of fresh and reused [Fe(BTC)] were recorded in a Philips X'Pert diffractometer using CuKa radiation at a scan rate of 0.2° min-1. ESR spectra were recorded by using a Bruker EMX instrument, with the following typical settings: frequency 9.476 GHz, sweep width 6900 G, time constant 5.12 ms, modulation frequency 100 kHz, modulation width 1 G, microwave power 19.93 mW. The regioselectivity of the ring opening was determined by mass spectrometry, which shows different fragmentation pattern changes depending on the position of the nucleophilic group. The Supporting Information provides a full set of mass spectra of the products. In the case of 2-methoxy-2-phenylethanol, the structure was confirmed by comparison with authentic sample.

Typical procedure for ring opening of epoxides with alcohols: A 50 mL round-bottomed flask was charged with catalyst (50 mg) in alcohol (5 mL) and substrate (2 mmol). The reaction mixture was stirred for the required time and temperature. After the required reaction time, the reaction mixture was cooled to room temperature and extracted with dichloromethane (10 mL). The mass balances of the recovered reaction mixture accounted for more than 90% of the initial substrate, as confirmed by GC using nitrobenzene as the external standard. The products were analysed by GC and characterised by GC–MS. The yields of the product were determined by using nitrobenzene as the external standard considering the response factors unity. A similar procedure was followed for other catalysts (iron citrate and Fe(NO₃)₃·9 H₂O) maintaining the same iron content as that for the [Fe(BTC)] catalyst.

Reaction procedure for amines as nucleophiles: The corresponding epoxide (2 mmol) was allowed to react with aniline/hexylamine in the presence of [Fe(BTC)] as the heterogeneous catalyst using acetonitrile as the solvent under the conditions indicated in Table 2. After the required reaction time, analysis and characterisation of the products was determined by GC and GC–MS.

Experimental procedure for reusability tests: The reusability of [Fe-(BTC)] was tested for the ring opening of styrene oxide with methanol. At the end of the reaction, the heterogeneous mixture was allowed to settle completely followed by decanting the supernatant liquid. The recovered catalyst was dried, then reused without further purification for the second run with fresh styrene oxide with methanol.

Acknowledgements

Financial support by the Spanish DGI (CTQ06-6857 and CTQ2007-67805) and European Commission Integrated Project (MACADEMIA) is gratefully acknowledged.

- [1] J. Huang, T. Akita, J. Faye, T. Fujitani, T. Takei, M. Haruta, Angew. Chem. 2009, 121, 8002; Angew. Chem. Int. Ed. 2009, 48, 7862.
- [2] A. K. Sinha, S. Seelan, S. Tsubota, M. Haruta, Angew. Chem. 2004, 116, 1572; Angew. Chem. Int. Ed. 2004, 43, 1546.
- [3] S. Hong, M. Oh, M. Park, J. W. Yoon, J.-S. Chang, M. S. Lah, *Chem. Commun.* 2009, 5397.
- [4] M. Savonnet, S. Aguado, U. Ravon, D. Bazer-Bachi, V. Lecocq, N. Bats, C. Pinel, D. Farrusseng, *Green Chem.* 2009, 11, 1729.
- [5] D. Jiang, T. Mallat, F. Krumeich, A. Baiker, J. Catal. 2008, 257, 390.
- [6] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, J. Catal. 2009, 267, 1.

© 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 8535

CHEMISTRY

A EUROPEAN JOURNAL

- [7] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Adv. Synth. Catal. 2009, 351, 2271.
- [8] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Adv. Synth. Catal. 2010, 352, 711.
- [9] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Appl. Catal. A 2010, 378, 19.
- [10] R.-Q. Zou, H. Sakurai, S. Han, R.-Q. Zhong, Q. Xu, J. Am. Chem. Soc. 2007, 129, 8402.
- [11] D. Farrusseng, S. Aguado, C. Pinel, Angew. Chem. 2009, 121, 7638; Angew. Chem. Int. Ed. 2009, 48, 7502.
- [12] J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450.
- [13] Z. Wang, G. Chen, K. Ding, Chem. Rev. 2009, 109, 322.

- [14] P. Horcajada, S. Surble, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Greneche, I. Margiolaki, G. Ferey, *Chem. Commun.* 2007, 2820.
- [15] I. A. Baburin, S. Leoni, G. Seifert, J. Phys. Chem. B 2008, 112, 9437.
- [16] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Ferey, *Chem. Eur. J.* 2004, 10, 1373.
- [17] L. Alaerts, E. Seguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs, D. E. De Vos, *Chem. Eur. J.* 2006, 12, 7353.
- [18] D. Jiang, A. Urakawa, M. Yulikov, T. Mallat, G. Jeschke, A. Baiker, *Chem. Eur. J.* 2009, 15, 12255.
- [19] K. Brown, S. Zolezzi, P. Aguirre, D. Venegas-Yazigi, V. Paredes-Garcia, R. Baggio, M. A. Novak, E. Spodine, *Dalton Trans.* 2009, 1422.

Received: March 6, 2010 Published online: June 14, 2010

8536 -