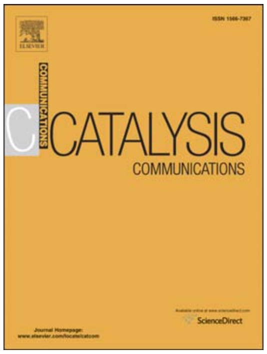

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Liquid phase oxidation of *n*-octane to C8 oxygenates over modified Fe-MOF-5 catalysts

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Abstract

The Metal Organic Framework materials Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 were prepared. The XRD results showed the expected pattern of MOF-5 with a very sharp peak at a 2θ value below 10° which indicate that the material are highly crystalline. The SEM and TEM images showed that the catalysts are cubic in shape. The synthesised Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 were testing in the oxidation of *n*-octane using H_2O_2 as an oxidant in acetonitrile as solvent. Conversions of 10.5, 4.2 and 3.6 % were obtained for Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 respectively. It was observed that primary carbon activation increased with decreasing Fe content, as C-1 selectivities of 9.5, 12.9 and 19.8 % were achieved for Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 respectively. Only C8 oxygenate products were observed, which include 1-octanol, 2-octanol, 3-octanol, 4-octanol, octanal, 2-octanone, 3-octanone, 4-octanone and octanoic acid. Furthermore, these catalysts were tested in the oxidation of cyclohexane using H_2O_2 in acetonitrile. Selectivities of 48.3 % for cyclohexanol, 47.1 % for cyclohexanone and 4.6 % for hydroperoxycyclohexane were recorded at a conversion of 40 % using Fe_4-MOF-5 as a catalyst.

Keywords: n-octane; cyclohexane; MOF-5; octanol; octanone; oxidation

1. Introduction

Recently, there has been much interest in MOF (metal organic framework) materials. These types of materials come in different shapes and types and possess special and important physical and chemical properties [1-7]. They tend to be softer that the traditional aluminosilicate zeolite materials like ZSM-5, mordenite and faujasite, hence they resemble

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more closely the behaviour of enzymes. There are porous materials with 3D structures of interconnected metal and different inorganic linkers and have a very wide range of applications, which include gas storage, catalysis etc. [8-12].

One of the most promising MOFs is MOF-5, which type of MOF materials have been reported to have a high potential in the catalytic field [13]. An iron copper MOF-5 has been reported in the oxidation of xanthene using t-butylhydroperoxide and the catalyst was found to be stable and reusable under reaction conditions [14]. In this study we now report the synthesis of Fe-MOF-5 and Fe-Zn-MOF-5 with different iron content and the testing of them in the oxidation of *n*-octane and cyclohexane using H_2O_2 in acetonitrile solvent. The activation of medium chain length alkanes is becoming increasingly important as these paraffins are major low value by-products from gas and coal to liquid plants, the number of which is increasing [15], and paraffins can offer green routes to valuable oxygenates. Terminally functionalised alcohols are high value products and are difficult to achieve, since secondary carbon atoms are more reactive that the primary ones. Systems reported that show high selectivity to terminal carbon activation usually achieve this with very low conversion, typically less than 1% [16].

2. Experimental

2.1 Materials

All the reagents and solvents used were commercially supplied (Sigma, Aldrich, Fluka and Merck). The GC standards used and acetonitrile were of high purity. The acetonitrile was purged with nitrogen before any catalytic testing to remove oxygen.

2.2 Synthesis of Fe-MOF-5

The synthesis of Fe-MOF-5 was achieved following the reported method [17] by mixing 1.2 g $Fe(NO_3)_3$ and 0.334 g terephthalic acid in 40 ml DMF under vigorous stirring followed by addition of 2.2 ml TEA drop wise. The mixture was stirred for 2 hour when a brownish precipitate was formed. The precipitate was filtered, washed and added to chloroform and stood overnight. Thereafter, the precipitate was filtered and dried. The general formula of MOF-5 is $Zn_4O_{13}C_{24}H_{12}$, and the coefficient for the metals must be kept at 4 molar equivalents. Zn was added to balance the value of metals when the amount of Fe used was less than 4. The synthesis of the Fe-Zn-MOF-5 materials was conducted using the above mentioned procedure with the inclusion of $Zn(NO_3)_2$ and the appropriate amount of $Fe(NO)_3$.

2.3 Catalysts characterization

Fourier Transform-Infrared (FT-IR) spectroscopy data was obtained within the range of 4000 – 400 cm^{-1} using a Nicolet 400D spectrophotometer. Powder X-Ray Diffraction (XRD) was performed using a Philips PW 1730/10 diffractometer, using Co Kα radiation, equipped with a long line focus operating with amperage of 20 mA and voltage of 40 kV. Data was collected in the range of 2 to 50° (2θ). Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) data was collected on a PerkinElmer (Optima 5300 DV) instrument. Samples were digested in HCl and the analyses were done in triplicate Scanning Electron Microscope (SEM) data was obtained using a Philips XL30 ESEM at 20 kV operating at a low vacuum mode of 1 Torr. Transmission Electron Microscope (TEM) images were obtained from a JEOL JEM 1010. Brunauer-Emmet-Teller (BET) surface area measurements were obtained using a Micromeritics Gemini instrument. The catalysts were degassed overnight under nitrogen at 200 °C.

2.4 Catalytic testing

All the reactions were performed under nitrogen. In a typical test run, 13 ml of acetonitrile was added into a two-neck round bottom flask (100 ml) fitted with a stopper and a condensor. The oxidation was performed by adding a mass of 0.1 g catalyst, 1 mL cyclohexane and 1 mL H_2O_2 (30 wt%) as an oxidant. The products were analysed by a PerkinElmer Auto System GC equipped with Flame Ionisation Detector using a Pona 50 x 0.20 mm x 0.5 μm column. The residual H_2O_2 was determined by titrating 1 mL of the reaction solution acidified with 6M H_2SO_4 with 0.1 M $KMnO_4$. The carbon balance for all oxidation reactions was found to be +/- 98 % (above 98 % of the reacted *n*-octane corresponded to the total moles of products formed on a carbon basis).

3. Results and discussion

3.1 Catalyst characterisation

The FT-IR results (Table 1) show a peak around 1570 cm^{-1} which is due to carboxylate anions in the catalyst material. The peak of the –COOH group of the terephthalic acid (linker), which appears around 1760 – 1690 cm^{-1}, was not observed in the Fe-MOF-5 catalyst confirming that there is coordination between the linker and metal ion [17].

The XRD results in Fig. 1 show a sharp peak below 10° which indicates that the materials are highly crystalline [18]. The diffractograms also show the MOF-5 pattern which is in agreement with literature [18]. The SEM images in Fig.2 A - C reveal that the material is cubic in shape and well crystalline, with a size range between 100 – 300 µm. The TEM images in Fig. 2 D - F are in agreement with the SEM images, again showing that the material is cubic in shape [19, 20]. The BET surface areas (Table 1) of the synthesised catalysts were found to be around 599, 575 and 501 m^2/g for Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 respectively, which is in agreement with literature [21]. The difference in surface areas of the catalysts can be attributed to the presence of Zn in the catalysts, and surface area decreases with increasing Zn content. The ICP results confirmed the expected Fe content in the materials and also the expected Fe:Zn ratios for Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 respectively.

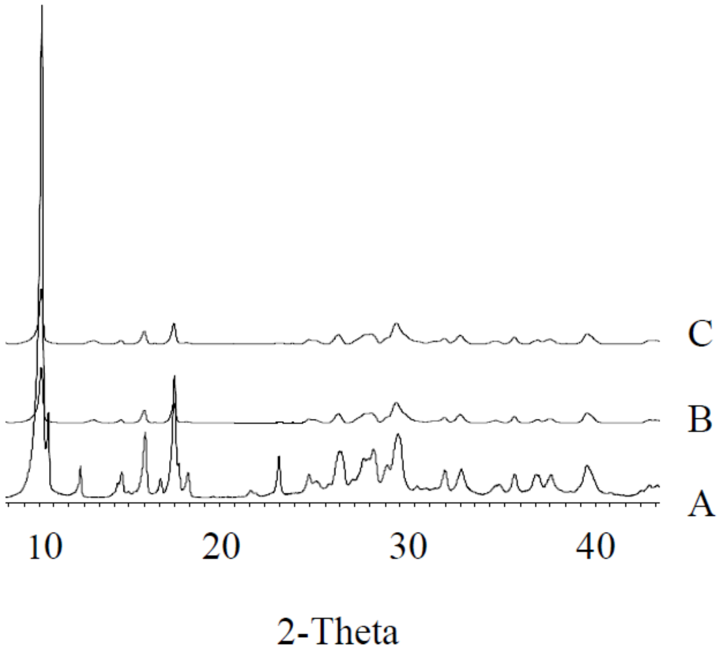

Fig. 1 : Powder X-Ray Diffractograms of A) Fe_4-MOF-5, B) Fe_2-Zn_2-MOF-5 and C) $Fe_{0.9}$-$Zn_{3.1}$-MOF-5

Table: 1 FT-IR, BET and ICP results of MOF-5 catalysts

Catalyst	FTIR (cm^{-1})	BET (m^2/g)	ICP (molar)	
			Fe	Zn
Fe_4-MOF-5	1570	599	4	0
Fe_2-Zn_2-MOF-5	1569	575	2	2
$Fe_{0.9}$-$Zn_{3.1}$-MOF-5	1570	501	0.9	3.1

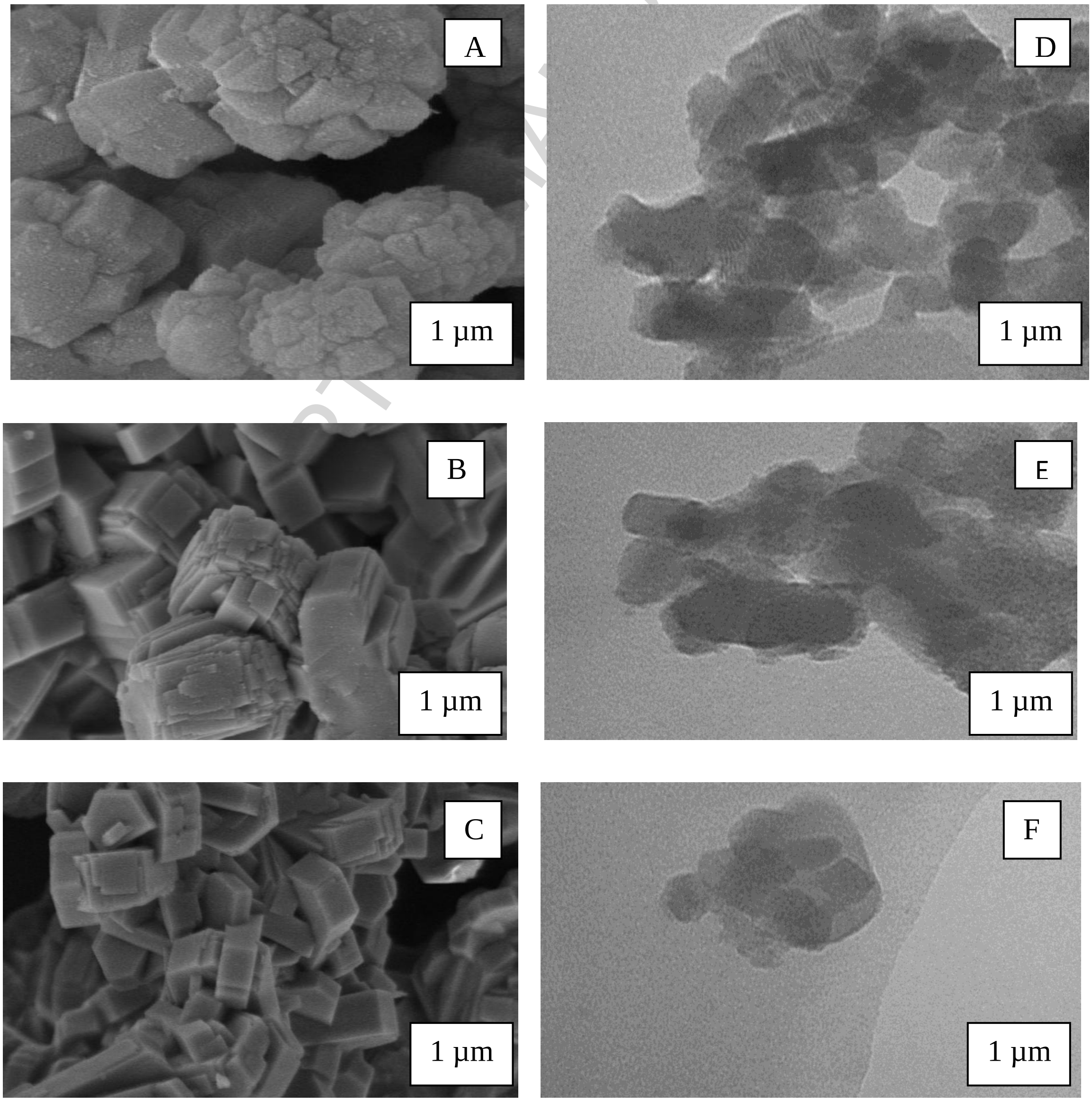

Fig. 2: A) SEM image of A) Fe_4-MOF-5, B) Fe_2-Zn_2-MOF-5 and C) $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 and TEM images of D) Fe_4-MOF-5, E) Fe_2-Zn_2-MOF-5 and F) $Fe_{0.9}$-$Zn_{3.1}$-MOF-5

3.2 Catalytic testing

Table 2: Oxidation of *n*-octane using Fe-MOF-5 catalysts[a]

Catalysts	% Fe	Conversion %	Selectivity %			
			C1	C2	C3	C4
Fe_4-MOF-5	1	10.5	8.9	35.1	29.5	26.5
Fe_2-Zn_2-MOF-5	0.5	4.2	12.9	32.9	31.5	22.7
$Fe_{0.9}$-$Zn_{3.1}$-MOF-5	0.2	3.6	19.8	28.8	29.6	21.8
Fe_4-MOF-5[b]	1	10.3	9.2	35.1	29.4	26.3

[a]:Reaction conditions: catalyst = 0.1 g,octane /H_2O_2 =1 (molar ratio), acetonitrile (13 ml), reaction time = 4 hours at 80 °C, blank reaction (without a catalysts) showed no conversion of n-octane, conversion error range 1.7 -2.4 %

b: Recycled catalyst, conversion and selectivities shown after 3rd recycle.

Table 3: Product distribution over Fe-MOF-5 catalysts

Catalysts	Selectivity (%)							
	1-ol	2-ol	3-ol	4-ol	al	2-one	3-one	4-one
Fe_4-MOF-5,	5.5	7	9.5	7.7	3.4	28.1	20	18.8
Fe_2-Zn_2-MOF-5	7	7.4	10.2	7.6	5.9	25.5	21.3	15.1
$Fe_{0.9}$-$Zn_{3.1}$-MOF-5	10.7	7.7	9.3	7.9	9.1	21.1	20.3	13.9
Fe_4-MOF-5[a]	5.1	6.6	9.4	8.1	4.1	28.5	20	18.2

[a]Recycled catalyst, selectivities shown after 3rd recycle.

Table 4: octanone(s):octanol(s) ratios using Fe-MOF-5 catalysts

Catalysts	octanone(s):octanol(s)
Fe_4-MOF-5	2.4
Fe_2-Zn_2-MOF-5	2.1
$Fe_{0.9}$-$Zn_{3.1}$-MOF-5	1.8
Fe_4-MOF-5[a]	2.4

[a] Recycled catalyst

The C8 oxygenates (4-octanone, 3-octanone, 2-octanone, octanal, 4-octanol, 3-octanol, 2-octanol and 1-octanol) were the only products observed, with a small amount of octanoic acid, which was found to be less than 1 % in selectivity. Furthermore, the selectivity to octanones decreased, and the selectivity to octanols increased with decreasing Fe content. This is likely due to fewer catalytic sites being available for further oxidation of the octanols formed.

The oxidation results (Table 2) show that the conversion of *n*-octane increases as the Fe content of the MOF-5 increases. Thus, Fe_4-MOF-5 showed a conversion of 10.5 %, while Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 showed 4.2 and 3.6 % of conversion respectively. The Fe_4-MOF-5 catalyst shows the highest carbon activation at C2, followed by C3, C4 and lastly C1 with 35.1, 29.5, 26.5 and 8.9 % selectivity respectively. When Fe_2-Zn_2-MOF-5 was used, a different trend was observed. Activation at C3 showed higher selectivity compared to C2 and a trend of C3 > C2 > C4 > C1 with 32.9, 31.9, 22.7 and 12.9 % selectivity, respectively, was observed. This change can be attributed to the presence of Zn atoms in the catalyst that might be occupying the external corners of the cube creating a specific environment for Fe atoms [22]. A change in products distribution was further observed when $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 was used. Here there was a very small difference between activation of C3 and C2 as they show a selectivity of 29.6 and 28.8% respectively. Also for C4 and C1, there was no significant difference between the sites as they show 21.8 and 19.8 % selectivity respectively. The results also showed that as the Fe content decreases, the selectivity to C1 activation increases. One of the major advantages of these catalysts is the fact that they are recyclable, which allows the interest to focus mainly on selectivity. The $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 gave a 4% conversion with 20% selectivity to terminal products. The unreacted n-octane can be recycled back to the reaction thus improving the yield to terminal products.

Catalysts Fe_4-MOF-5 and Fe_2-Zn_2-MOF-5 in Table 3 showed the following product distribution trend: 2-octanone > 3-octanone > 4-octanone > 3-octanol > 4-octanol > 2-octanol > 1-octanol > octanal. However, a different trend was observed when $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 was used: 2-octanone > 3-octanone > 4-octanone > 1-octanol > 3-octanol > octanal > 4-octanol > 2-octanol. This change can be attributed to the low amount of Fe and high amount of Zn atoms in $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 which may promote Fe atoms to be situated in a more hindered environment that promotes the C1 activation.

The octanone(s)/octanol(s) ratios showed the values of 2.4, 2.1 and 1.8 for Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 respectively. These results suggest that the production of octanols is increasing as the Fe content in the catalysts decreases, likely due to fewer Fe sites, hence reduced further reaction of the primary products, octanols, to octanones. The H_2O_2 conversion was found to be 69, 61 and 45 % for Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5, respectively, giving an H_2O_2 efficiency of 15.2, 6.9 and 7.8% for Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 respectively. The H_2O_2 efficiency thus decreases with decreasing iron content. It is known that H_2O_2 reacts with Fe to produce radicals [23] and water. The loss of H_2O_2 efficiency can be attributed to the higher Fe content that reacts with H_2O_2 to produce more water instead of products (oxygenates).

Table 5: oxidation of cyclohexane using Fe-MOF-5 catalysts

Catalysts	% Fe	Conversion %	Selectivity % cyclohexanol	cyclohexanone	hydroperoxycyclohexane
Fe_4-MOF-5,	1	40	48.3	47.1	4.6
Fe_2-Zn_2-MOF-5	0.5	36	49.8	47.0	3.2
$Fe_{0.9}$-$Zn_{3.1}$-MOF-5	0.2	33	51.1	45.2	3.7

Reaction conditions: catalyst = 0.1 g, H_2O_2 /cyclohexane 1 (molar ratio),

acetonitrile (13 ml), reaction time = 4 hours at 80 ºC

The oxidation of cyclohexane over Fe-MOF-5 showed only a slight drop in conversion as the Fe content decreases (Table 5). Conversions of 40, 36 and 33 % were observed for Fe_4-MOF-5, Fe_2-Zn_2-MOF-5 and $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 respectively, clearly showing the higher reactivity of secondary carbon atoms. The products distribution of all catalysts was found to be similar, with the cyclohexanol selectivity being the highest with a selectivity between 48.3 – 51.1 %, followed by cyclohexanone with a selectivity between 45.2 – 47.1 % and, lastly, hydroperoxycyclohexane with the selectivity between 3.2 – 4.6 %. The most noticeable change in product distribution is that the $Fe_{0.9}$-$Zn_{3.1}$-MOF-5 showed slightly higher cyclohexanol selectivity of 51.1 % and a correspondly lower cyclohexanone selectivity at 45.2 %. This can be due to the lower number of Fe sites, hence deeper oxidation is reduced.. The selectivity to hydroperoxycyclohexane in our results might be due to the higher temperature which resulted in over-oxidation. The H_2O_2 conversion was found to be 48-70 % with a H_2O_2 efficiencies of between 57- 69 %

3.3 Recycling and leaching test of Fe_4-MOF-5

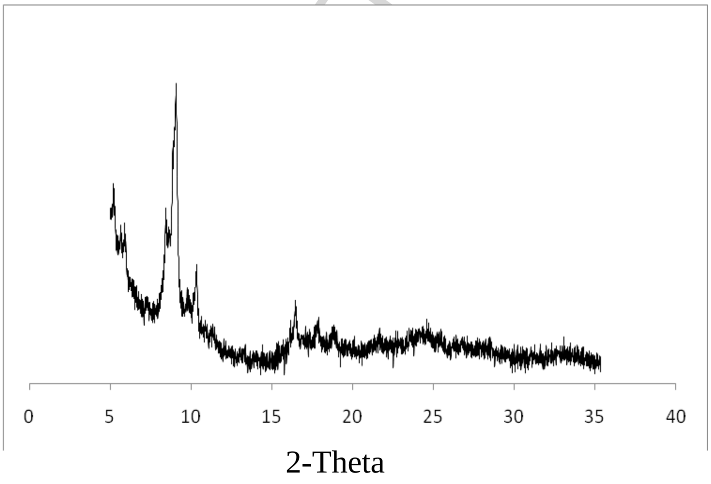

Fig. 3: Powder X-Ray Diffractogram of used Fe_4-MOF-5

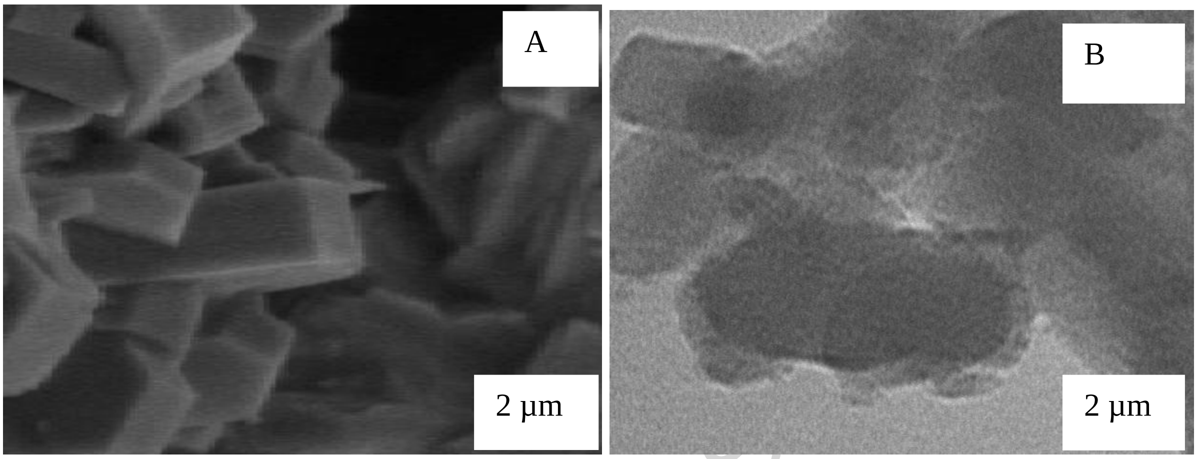

Fig. 4: Images A) SEM and B) TEM of used Fe_4-MOF-5

The catalyst Fe_4-MOF-5 was recycled three times to establish the stability of the catalyst. The reaction results showed (Table 3) that there was effectively no loss of activity when the catalyst was used for the third time compared to the conversion over the fresh catalyst. The products distribution over the used catalyst (second and the third cycle) was found to be very similar to that of the fresh catalyst. Furthermore, XRD, SEM and TEM results showed that the used catalyst still has MOF-5 phase and shows no distortion in shape. The ICP results of the reaction solution showed that there was no Fe in the reaction solution, which suggests that the Fe does not leach out from the catalyst, and therefore the catalyst is stable.

4. Conclusion

The XRD results confirmed the synthesis of the Fe-MOF-5 and modified Fe-Zn-MOF-5 and the SEM and TEM images showed that the catalyst is cubic in shape. The catalytic tests showed that decreasing the Fe content in Fe-MOF-5 increases the activation for C1 in the oxidation of *n*-octane, with a decrease in conversion. Only C8 oxygenated products were obtained with a highest selectivity to primary oxygenates of 19.8%. All the tested Fe-MOF-5 catalysts showed a similar product distribution in the oxidation of cyclohexane. Furthermore, the catalysts are stable, can be recycled and do not leach.

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References

[1] D. Farrusseng, S. Aguado, C. Pinel, Angew. Chem. Int. Ed. 48 (2009) 7502 - 7513.

[2] K. Y. Müller-Buschbaum, Y. Mokaddem, Solid State Sci. 10 (2008) 416 - 420.

[3] A. M. Spokoyny, O. K. Farha, K. L. Mulfort, L. J. Hupp, C. A. Mirkin, Inorg. Chim. Acta.364 (2010) 266 - 271.

[4] Wang, T. Zhang, T. Song, C. Li, J. Xu, L. Wang, Micropor. Mesopor. Mater. 155 (2012) 281 - 286.

[5] B. Xiao, H. Hou, Y. Fan, M. Tang, Inorg. Chim. Acta 360 (2007) 3019 - 3025.

[6] N. Zhao, W. Li, C. Sun, H. Bian, H. Wang, Z. Chang, H. Fan, Solid State Sci. 14 (2012) 317 - 323.

[7] T. Loiseau, G. Férey, J Fluor. Chem. 128 (2007) 413 - 422.

[8] W. Gao, D. Xing, D. Zhou, M. Shao, S. Zhu, Chem. Commun. 14 (2011) 601 - 605.

[9] N. Jin, J. Seo, K. Hong, H. Chun, Micropor. Mesopor. Mater. 150 (2012) 32 - 37.

[10] S. Nayak, H. P Nayek, C. Pietzonka, G. Novitchi, S. J. Dehnen, J. Mol. Struct. 1004 (2011) 82 - 87.

[11] A. Torrisi, R. G. Bell, C. Mellot-Draznieks, Micropor. Mesopor. Mater. 168 (2013) 225 - 238.

[12] L. Wang, T. Song, C. Li, J. Xia, S. Wang, L. Wang, J. Xu, J. Solid State Chem. 190 (2012) 208 - 215.

[13] L. Zhang, Y. H. Hu, Mater. Sci. Eng. B 176 (2011) 573 - 578.

[14] A. M. Dhakshinamoorthy, M. Alvaro, H. Garcia, J. Catal. 267 (2009) 1 - 4.

[15] B. Pillay, M. R. Mathebula, H. B. Friedrich, Appl. Catal. A 361 (2009) 57 - 64.

[16] B. Moden, B. Zhan, J. Dakka, J. G. Santiesteban, E. Eglesia, Phys. Chem. C 111 (2007) 1402 - 1411.

[17] N. T. S. Phan, K. K. A. Le, T. D. Phan, Appl. Catal. A 382 (2010) 246 - 253.

[18] D. Saha, S. Deng, Z. Yang, J. Porous. Mater. 16 (2006) 141 - 149.

[19] J. Li, S. Cheng, Q. Zhao, P. Long, J. Dong, Int. J. Hydrogen Energy. 34 (2009) 1377 - 1382.

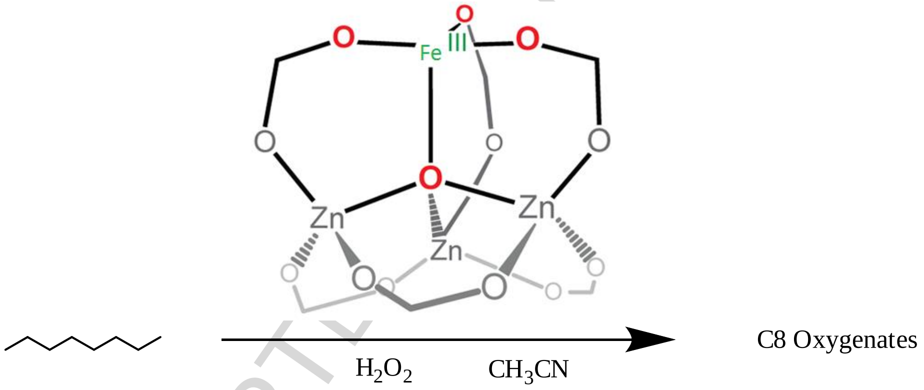
[20] Y. Liu, Z. Ng, E. A. Khan, H. K. Jeong, C. B. Ching, Z. Lai, Micropor. Mesopor. Mater. 118 (2009) 296 - 301.

[21] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Eur. J. 17 (2011) 6256 - 6262.

[22] O. Ardelea, G. Blanita, M. Mihet, I. Coldea, D. Lupu, P. Palade, Rev. Roum. Chim. 56 (2011) 655 - 657.

[23] C. Jiang, Z. Gao, H. Qu, J. Li, X. Wang, P. Li, H. Liu, J. Hazard. Mater. 250-251 (2013) 76 - 81

Activation of n-octane and cyclohexane over modified Fe-MOF-5 using hydrogen peroxide as an oxidant



Graphical abstract

Highlights

Metal Organic Framework materials containing Fe and Fe/Zn were prepared

n-octane was selectively oxidized with H_2O_2 to C8 oxygenates only

Up to 20% selectivity to primary (C-1) functionalized oxygenates was obtained

The catalysts are stable, can be recycled and no leaching of metals was observed