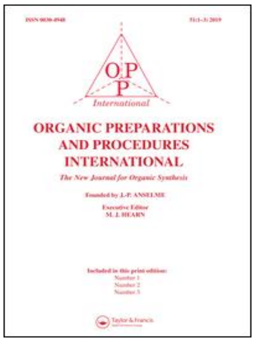

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EXPERIMENTAL PAPER

Selective Oxidation of Hydrocarbons and Alcohols Using Phen-MCM-41 as an Efficient Co-Catalyst in Combination with NHPI-Based Nano-Magnetic Catalyst

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Oxidation reactions are essential processes in organic transformations.[1–2] Thus, utilization of practical and effective methods, especially for catalytic oxidation, has attracted great attention during recent decades. In this regard, *N*-hydroxy imides (NHIs), and particularly *N*-hydroxyphthalimide (NHPI), have been widely applied as promising and suitable catalysts for the oxidation of organic substrates.[3–4] Since initial reports by Ishii and his co-workers,[5–6] NHPI-mediated oxidative systems have developed to become powerful catalytic methods. Conceptually, this fosters the catalytic oxidation process through the production of its active free-radical form, which is known as the phthalimide *N*-oxyl (PINO) radical.[7] Traditionally, generation of PINO radicals involves the use of co-catalysts, mainly including such transition metal salts as Co(II),[8] Cu(II),[9] Mn(IV)[10] and V(V) salts.[11] However, in spite of satisfactory results, employing these transition-metal complexes is not very favorable from economic and environmental standpoints. Accordingly, metal-free catalytic systems have been significantly explored over the last two decades[12] and several effective initiators or co-catalysts have been utilized such as 2,2′-azobisisobutyronitrile (AIBN),[13] 1,4-diamino-2,3-dichloro-anthraquinone,[14] and *o*-phenanthroline and its analogs.[15]

Undoubtedly, the ability to recover and reuse the catalyst is an essential topic in the design of any catalytic system.[16–17] Hence, during the last years several methods have been reported about immobilization of NHPI on solid surfaces and polymers,[18–24] as well as into ionic liquids.[25–26] We have recently reported the immobilization of NHPI onto functionalized SiO_2 coated Fe_3O_4 nanoparticles,[27] and also on NaY nano-zeolite[28] as efficient recoverable catalysts for the oxidation of benzyl alcohols and hydrocarbons.

In an innovative and useful strategy, Karimi and co-workers reported simultaneous use of silica-immobilized NHPI together with a supported cobalt complex, in order to achieve selective oxidation of methylaromatic compounds.[29] It is obvious that applying a similar catalytic system through a metal-free approach would be highly favorable, especially from the viewpoint of green chemistry.

Accordingly, inspired by the efforts of Xu and his co-workers[14–15] and in continuation of our attempts to extend NHPI-based heterogeneous catalytic oxidation,[27–28] in

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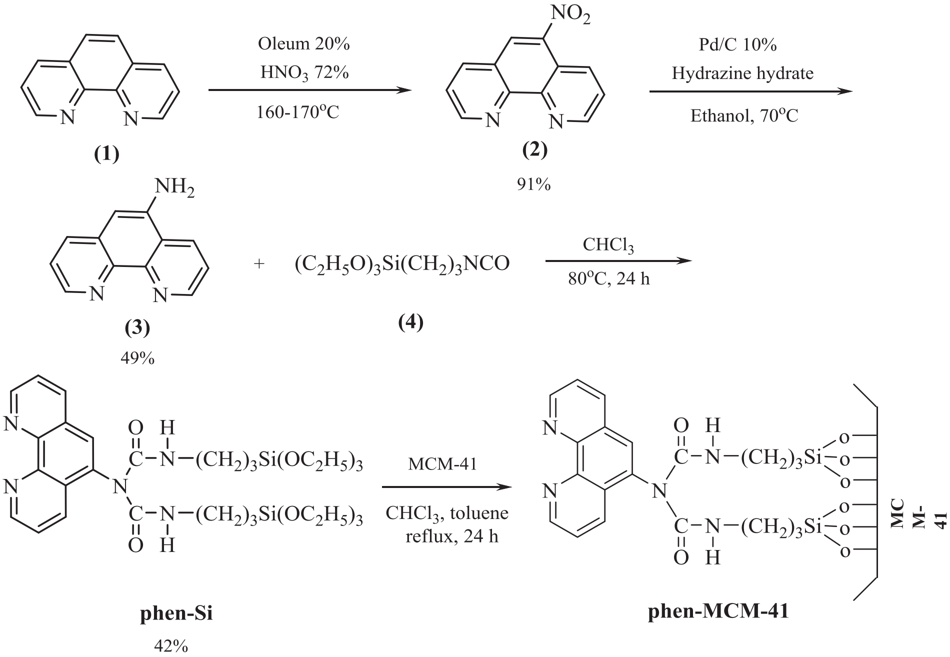


Scheme 1. Immobilization of functionalized phenanthroline onto MCM-41 (phen-MCM-41).

the present study Mobil Composition of Matter No. 41 (MCM-41) supported phenanthroline (phen-MCM-41) was prepared as a reusable co-catalyst. In combination with NHPI-immobilized on $Fe_3O_4@SiO_2$ it constituted an effective heterogeneous system for the metal-free catalytic oxidation of hydrocarbons and alcohols.

Immobilization of functionalized *o*-phenanthroline onto the MCM-41 was performed according to the procedure summarized in Scheme 1. At first, to obtain the required 5-amino-phenanthroline (**3**), the nitration reaction of *o*-phenanthroline monohydrate was carried out by use of fuming nitric acid and sulfuric acid. Then, reduction of the corresponding nitro compound (**2**) in the presence of 5% Pd/C and hydrazine monohydrate led to the formation of 5-amino-1,10-phenanthroline. In the next step, 5-(*N,N*-bis-3-(triethoxysilyl)propyl)ureyl-1,10-phenanthroline (phen-Si) was obtained through the reaction of 5-amino-1,10-phenanthroline with 3-(triethoxysilyl)propyl isocyanate (**4**) in $CHCl_3$ at 80 °C for 24 h. Finally, to prepare phen-MCM-41, the mesoporous MCM-41 reacted with phen-Si in toluene at reflux temperature for 24 h.

This co-catalyst was characterized by FT-IR, TGA, FESEM-EDX, XRD and BET techniques. FT-IR spectra of the phen-MCM-41 showed characteristic peaks attributed to the amide groups, C=N and C=C of phenanthroline and Si–O framework of MCM-41 which is in accordance with FT-IR data reported in the literature.[30] An X-ray diffraction (XRD) technique was utilized to survey the crystalline structure of pure MCM-41 and phen-MCM-41 (Figure 1). In agreement with the XRD patterns of pure MCM-41, the XRD pattern of the phen-MCM-41 demonstrated a strong peak at 2θ of less than 3° together with some small peaks that are similar to the XRD pattern of the mesoporous MCM-41 indicating the presence of MCM-41 in the co-catalyst structure.[31] The negligible shift of this peak for phen-MCM-41 may originate from the accommodation of

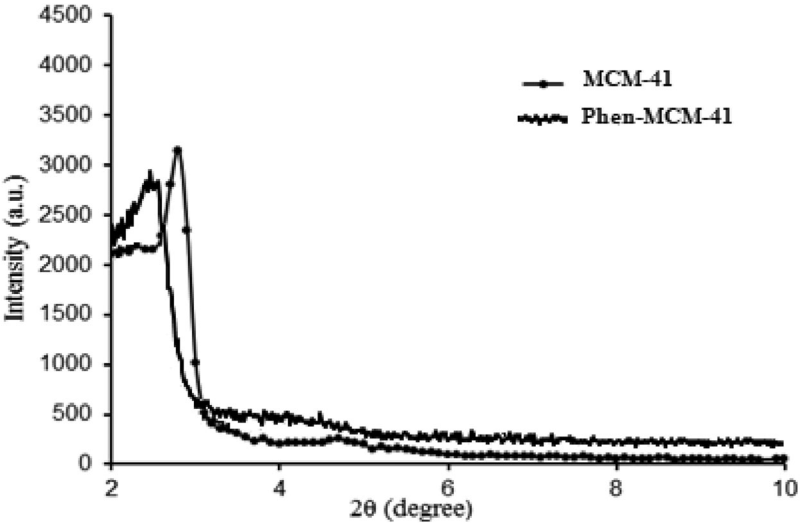


Figure 1. XRD patterns of the MCM-41 and phen-MCM-41.

the phenanthroline moiety inside MCM-41 channels which corresponds with the previous reports.[32–34]

Assessment of the thermal stability, as well as the amount of immobilized organic moiety on the surface of MCM-41 was accomplished by thermogravimetric analysis (TGA). As displayed in Figure 2, a weight loss of about 6% was observed at the temperature range of 50-200 °C, attributed to moisture and absorbed water. Additionally, another mass loss of *ca.* 18% at the range of 200-550 °C arises from the degradation of the organic moiety attached to the MCM-41. Based on this result, the amount of phen-Si immobilized on the MCM-41 surface (mmol of grafted phen-Si per 1 g MCM-41) was 0.49 mmol

Nitrogen adsorption-desorption isotherms of phen-MCM-41 at 77K are displayed in Figure 3. According to the IUPAC classification,[35] the attained isotherms of phen-MCM-41 are type IV, which refers to mesoporous materials. BET results of pure MCM-41 and phen-MCM-41 have been summarized in Table 1. As can be seen in the table, a notable decrease took place in the specific surface area and total pore volume for phen-MCM-41 in comparison with the initial state, which can be accounted for by the blockage and narrowing of some pores of mesoporous MCM-41 during the immobilization process.

Figure 4 shows the field emission scanning electron microscopy (FESEM) micrographs of mesoporous phen-MCM-41. The average size of the phen-MCM-41 is in the range of 50-70 nm. Furthermore, agglomeration and accumulation of the particles seems to occur after immobilization of the organic fragment on the surface of MCM-41.

The energy dispersive X-ray (EDX) spectrum was employed for elemental analysis of phen-MCM-41. According to the EDX pattern of phen-MCM-41 (Figure 5), the evident Si peak confirms the presence of MCM-41 solid support in the obtained co-catalyst.

The efficiency of the catalytic system including Fe_3O_4@NHPI and phen-MCM-41 was investigated in the oxidation reactions of hydrocarbons and alcohols (Scheme 2). Considering the obtained optimum results for Fe_3O_4@NHPI,[27] we examined the optimal amount of phen-MCM-41 as co-catalyst. The oxidation reaction of ethylbenzene was chosen as a model reaction (Table 2). The oxidation of ethylbenzene was carried out

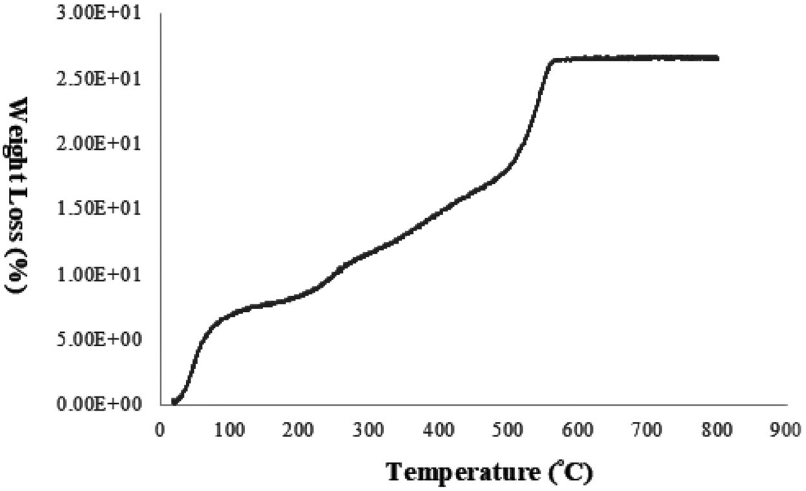


Figure 2. TGA curve of the phen-MCM-41.

using different amounts of phen-MCM-41 (Table 2, entries 1-3) and Br_2 with an aqueous solution of H_2O_2 in the presence of Fe_3O_4@NHPI as catalyst, in refluxing acetonitrile (80 °C). As shown in Table 2, 15 mg of the co-catalyst seems to be sufficient to promote the oxidation process (Table 2, entry 2, see Experimental section and reference 27 for scale of the reaction). Under these conditions, acetophenone was obtained as exclusive product after 4.5 h. Additionally, utilizing a higher amount of co-catalyst (Table 2, entry 3) did not considerably change the conversion of ethylbenzene. It is noteworthy that the oxidation reaction in the absence of phen-MCM-41 led to a very low amount of conversion (Table 2, entry 4).

After that, the obtained optimal conditions were employed to oxidize a number of organic compounds (Table 3). As shown in Table 3, under optimum conditions different hydrocarbons were converted into the corresponding carbonyl products. As mentioned above, oxidation of ethylbenzene exclusively led to the formation of acetophenone with 97% conversion (entry 1). Tetralin and indane were strikingly converted to 1-tetralone and 1-indanone, respectively (entries 2-3). In these two cases, low amounts of 1-tetralol and 1-indanol were detected as minor products. Oxidation of toluene was performed with 40% conversion and 97% selectivity toward benzoic acid (entry 4). Moreover, *p*-xylene was oxidized to the corresponding carbonyl compounds, comprising mainly terephthalic acid in conjunction with terephthaldehyde (entry 5). Cyclohexane showed only 30% conversion with 55% selectivity in respect of cyclohexanone after 8 h (entry 6), along with the formation of adipic acid as the other product. Furthermore, in order to evaluate the effectiveness of these catalytic systems for other organic substrates, oxidations of alcohols were also investigated under these conditions. Despite the low conversion of cyclohexanol (35% conversion with 70% selectivity for adipic acid, entry 7), benzyl alcohol and diphenyl methanol exhibited desirable conversion and selectivity (entries 8-9). Oxidation of benzyl alcohol (entry 8) resulted in 77% conversion with 98% selectivity toward benzaldehyde, as well as slight formation of benzoic acid. Diphenyl methanol successfully converted to benzophenone as the only product (entry 9).

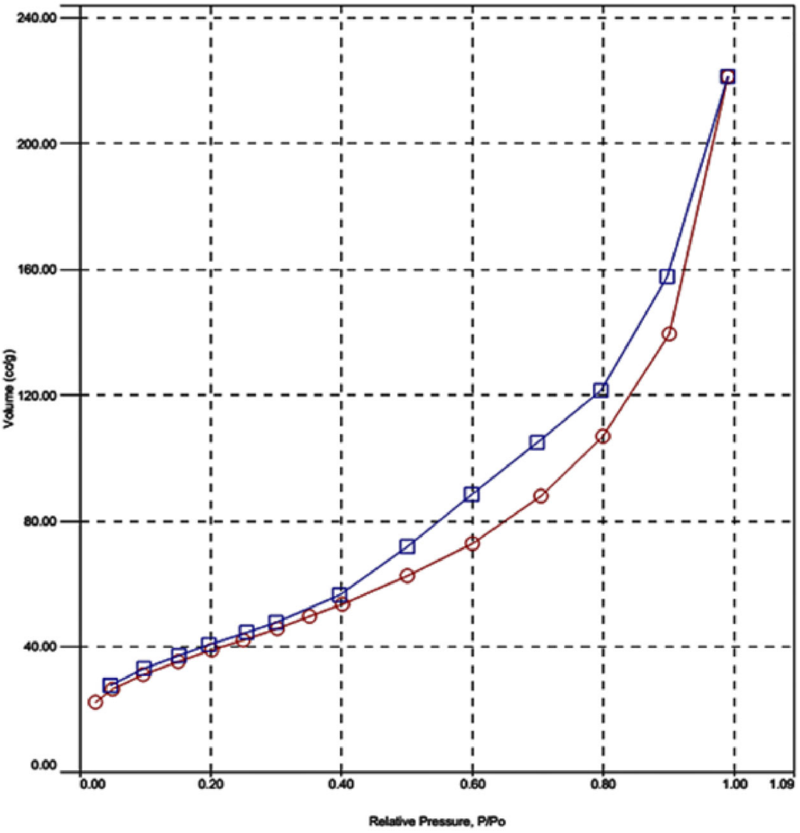


Figure 3. Nitrogen adsorption-desorption isotherms of the phen-MCM-41.

Table 1. BET results of MCM-41 and phen-MCM-41.

Sample	BET surface area (m^2 g^{-1})	BJH pore diameter (nm)	Total pore volume (cm^3 g^{-1})
MCM-41	771.43	2.34	0.46
phen-MCM-41	145.58	3.62	0.36

From the mechanistic view, considering the work of Xu[15] and our own previous reports,[27–28] we can describe a possible route for this catalytic process (Scheme 3). At first, interaction of phen-MCM-41 with Br_2 results in the formation of a cation-radical species which is accompanied by the subsequent proton and electron transfer between this cation-radical and Fe_3O_4@NHPI to produce PINO radicals. The next stage involves the abstraction of hydrogen from the substrate by PINO to convert it into a radical. This radical readily reacts with oxygen, provided from *in situ* decomposition of hydrogen peroxide in the presence of Br_2, thereby leading to peroxy radicals. Eventually, hydrogen abstraction by these radicals from the NHPI-based catalyst affords PINO radical and hydroperoxide which is then followed by an elimination process to achieve the desired product.

Critical parameters in the evaluation of heterogeneous catalysis efficiency are recoverability and reusability. After completion of the reaction the nano magnetic catalyst was readily separated by use of an external supermagnet[27] and the separation of co-catalyst

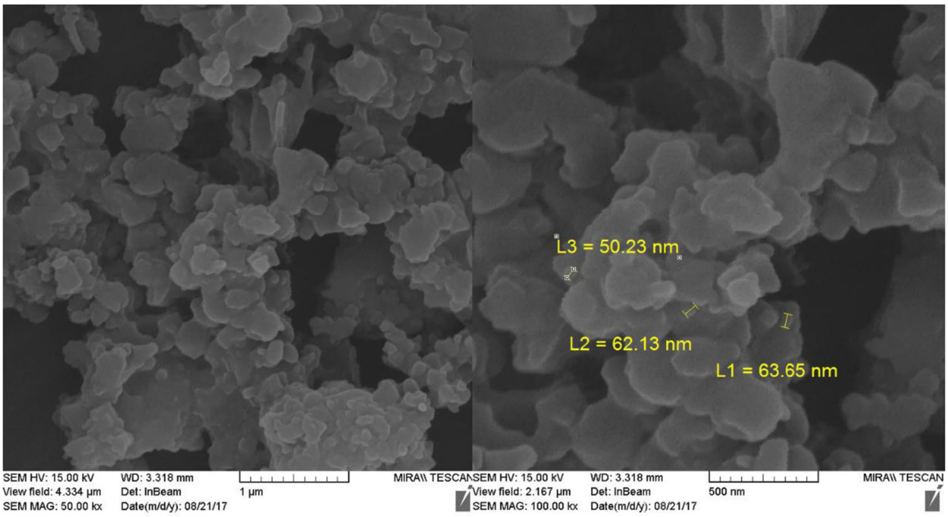


Figure 4. FESEM images of phen-MCM-41.

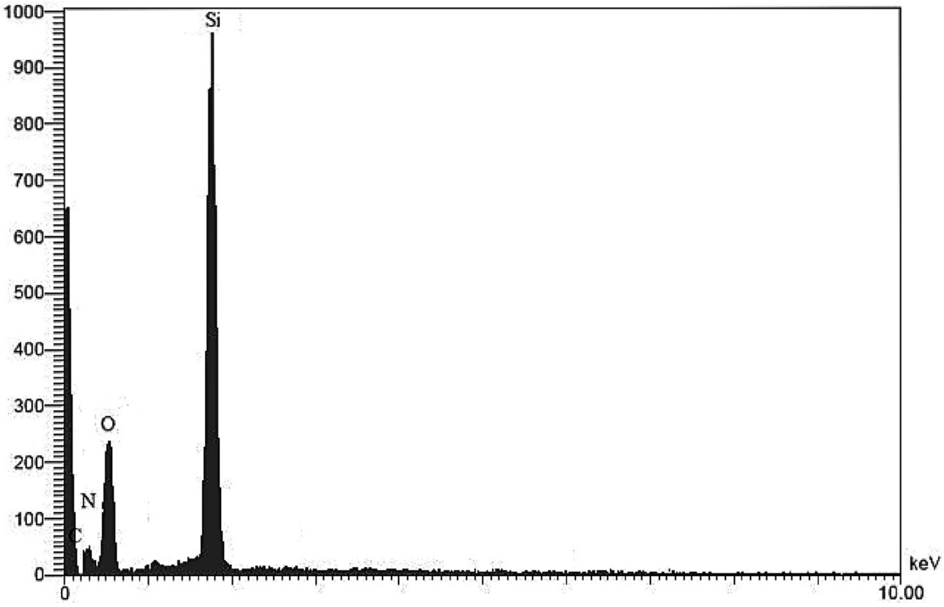
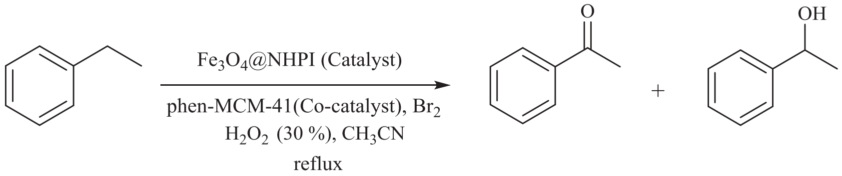


Figure 5. EDX pattern of phen-MCM-41.

was then achieved via centrifugation. After several washings with ethanol and distilled water, the isolated phen-MCM-41 was dried in a vacuum oven at 80° C. Subsequently, it was ready to be employed for the next reaction. On the basis of our experimental results, this co-catalyst could be successfully recovered and reused up to 5 times with negligible loss of activity in respect of fresh co-catalyst (Figure 6).

In conclusion, immobilized phen-Si on MCM-41 (phen-MCM-41) together with Fe_3O_4@NHPI was utilized as an efficient heterogeneous catalytic system to oxidize organic substrates. The prepared phen-MCM-41 was fully characterized by FT-IR, XRD,



Scheme 2. Oxidation of ethylbenzene as model reaction for optimizing the amount of phen-MCM-41.

Table 2. Optimizing the amount of co-catalyst using oxidation reaction of ethylbenzene.

Entry	Amount of co-catalyst (mg)	Conv (%)[a]	Sel (%)[b]
1	10	78	76
2	15	97	100
3	20	98	100
4	–	5	62

[a] After completion of the reaction (4.5 h), amounts of conversion and selectivity were measured by GC-MS analysis.

[b] Selectivity toward the acetophenone.

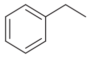
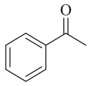
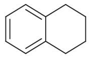
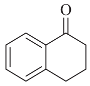
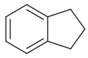
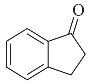
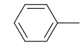
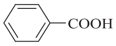
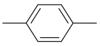
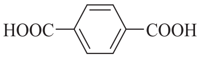
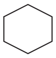
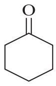
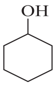
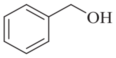
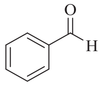
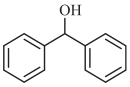
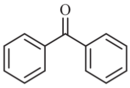
TGA, FESEM, BET and EDX analyses and exhibited considerable activity as a co-catalyst in oxidation reactions of hydrocarbons and alcohols. These starting materials were selectively converted to the corresponding carbonyl-containing products with moderate to excellent yields. Moreover, reusability and recoverability of this heterogeneous co-catalyst was studied. The recovered phen-MCM-41 was effectively reusable for next runs up to 5 times with no significant effect on its co-catalytic feature.

Experimental section

1,10-Phenanthroline monohydrate, fuming sulfuric acid, 5% Pd/C catalyst and 3-(triethoxysilyl)propyl isocyanate were supplied from Merck Company. Other commercially available chemicals and solvents were purchased from local suppliers. All chemicals were applied without further purification. MCM-41 was synthesized according to a reported procedure.[36]

Melting points were determined on an Electrothermal IA 9100 apparatus. ^1H and ^{13}C NMR spectra were determined in $CDCl_3$ by means of a Bruker Avance III 400 MHz spectrometer. Thermogravimetric analysis (TGA) was carried out using a Rheometric Scientific STA-1500 instrument. Fourier transform infrared spectroscopy (FT-IR) was accomplished on a Bruker Vector 22 spectrometer using KBr pellets. X-ray powder diffraction (XRD) analyses were conducted on a Philips PW 1830 X-ray diffractometer within a range of Bragg's angle (0.8-80°) at room temperature. Nitrogen adsorption/desorption isotherms were recorded using a NOVA 2200e analyzer, after out-gassing the samples for 14 h at 60 °C under vacuum. Field emission scanning electron microscopy (FESEM) was performed by use of a JEOL JSM6390 instrument, equipped with an energy-dispersive X-ray (EDX) analyzer (acceleration voltage 10 kV). Finally, products of oxidation reactions were identified by an Agilent Technologies 7890A/5975C gas chromatography (GC), coupled with DB-5 MS capillary column.

Table 3. Oxidation of hydrocarbons and alcohols using phen-MCM-41 and Fe_3O_4@NHPI.[a]

Entry	Starting material	Major product	Time (h)	Conversion[b] (%)	Selectivity (%)[b,c]
1			4.5	97	100
2			2	85	94
3			2.25	83	91
4[d]			7.5	40	97
5[d]			6	39	54
6			8	30	55
7[d]			5.5	35	70
8			3.5	77	98
9			3	97	100

[a] Reaction conditions: Fe_3O_4@NHPI (10 mg), starting material (1 mmol), phen-MCM-41 (15 mg), Br_2 (3 mol%), oxidant (2 mmol) in 5 mL CH_3CN at 80 °C.

[b] Data about the conversion of starting materials and selectivity of corresponding products were obtained by GC-MS analysis.

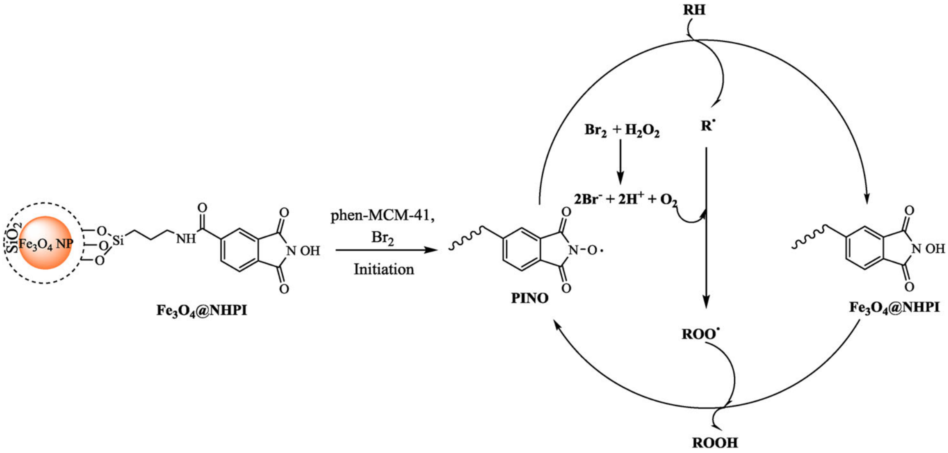
[c] Selectivity toward the ketone derivatives and benzaldehyde.

[d] Selectivity toward the corresponding acid product.

5-Nitro-1,10-phenanthroline (**2**), 5-amino-1, 10-phenanthroline (**3**), and 5-(*N*,*N*-bis-3-(triethoxysilyl) propyl) ureyl-1,10-phenanthroline (phen-Si) were prepared according to the procedure reported in the literature[37] and these known compounds were identified on the basis of their ^1H and ^{13}C NMR spectra, which were submitted for review.

Functionalization of MCM-41 with phen-Si (phen-MCM-41)

According to the previous report,[30] 0.5 g of MCM-41 was suspended in 80 mL of anhydrous toluene. Then, phen-Si (0.344 g, 0.5 mmol), dissolved in 8 mL of anhydrous $CHCl_3$, was added and the reaction mixture was stirred for 24 h under an inert atmosphere (argon gas) at reflux temperature. Afterwards, the resulting mixture was filtered and the obtained solid was washed several times with toluene and dried overnight under vacuum. IR (KBr, cm^{-1}): 2928 and 2886 (C-H stretch), 1703 (C=O stretch), 1650 (C=N phenyl), 1545 (C=C phenyl), 1088 (Si–O–Si)



Scheme 3. A plausible mechanism for the catalytic oxidation by use of Fe_3O_4@NHPI and phen-MCM-41 in the presence of H_2O_2.

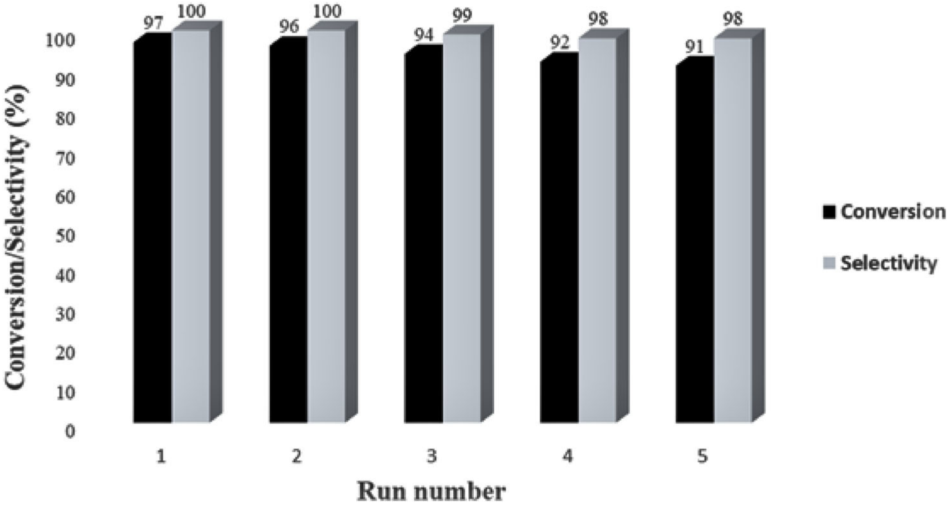


Figure 6. Reusability study of phen-MCM-41 for oxidation of ethyl benzene under optimized conditions.

General procedure for the catalytic oxidation of benzyl alcohols and hydrocarbons in the presence of silica coated magnetic nanoparticle supported NHPI (oxidation catalyst) and phen-MCM-41 (co-catalyst)

Oxidation of hydrocarbons and alcohols was accomplished in a 50 ml round bottomed flask equipped with a condenser and a mechanical stirrer. In all cases, hydrogen peroxide (aqueous solution 30% (w/w) of H_2O_2) was utilized as the oxidant. Typically, to an acetonitrile (5.0 ml) solution of ethyl benzene (1 mmol, 0.107 g) was added the catalyst (0.010 g), phen-MCM-41 (0.015 g), Br_2 (0.019 mmol, 0.001 mL) and H_2O_2 (2 mmol, 0.2 mL). Next, the reaction mixture was heated under reflux and the progress of the reaction was monitored via TLC (silica gel, ethyl acetate:hexane 1:3) and GC. After completion of the reaction, the catalyst was magnetically isolated followed by several washings with ethanol and water. After that, the residue was centrifuged to recover the co-catalyst (phen-MCM-41). Finally, the products were analyzed by GC–MS measurements. All of the products were known compounds, identified on the basis of their GC-MS analyses. Data and details of these GC–MS analyses were submitted for review and are available upon request from the corresponding author.

Acknowledgments

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References

1. J. E. Bäckvall, "*Modern Oxidation Methods*," passim, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2012.
2. T. Mallat and A. Baiker, *Chem. Rev.*, **104**, 3037 (2004). doi:10.1021/cr0200116
3. F. Recupero and C. Punta, *Chem. Rev.*, **107**, 3800 (2007). doi:10.1021/cr040170k
4. S. Coseri, *Cat. Rev. Sci. Eng.*, **51**, 218 (2009). doi:10.1080/01614940902743841
5. Y. Ishii, K. Nakayama, M. Takeno, S. Sakaguchi, T. Iwahama and Y. Nishiyama, *J. Org. Chem.*, **60**, 3934 (1995). doi:10.1021/jo00118a002
6. Y. Ishii, S. Sakaguchi and T. Iwahama, *Adv. Synth. Catal.*, **343**, 393 (2001). doi:10.1002/1615-4169(200107)343:5<393::AID-ADSC393>3.0.CO;2-K
7. R. Amorati, M. Lucarini, V. Mugnaini, G. F. Pedulli, F. Minisci, F. Recupero, F. Fontana, P. Astolf and L. Greci, *J. Org. Chem.*, **68**, 1747 (2003). doi:10.1021/jo026660z
8. B. B. Wentzel, M. P. J. Donners, M. C. Feiters, P. L. Alsters and R. J. M. Nolte, *Tetrahedron*, **56**, 7797 (2000). doi:10.1016/S0040-4020(00)00679-7
9. B. Orlińska, *Tetrahedron Lett.*, **51**, 4100 (2010). doi:10.1016/j.tetlet.2010.05.128
10. J. Jiang, Y. Jing, Y. Zhang, N. Zhang, J. Jiao, W. Zhu, H. Xue, Y. Zong and G.Yang, *Catal. Lett.*, **141**, 544 (2011). doi:10.1007/s10562-010-0507-9
11. P. J. Figiel and J. M. Sobczak, *J. Catal.*, **263**, 167 (2009). doi:10.1016/j.jcat.2009.02.007
12. L. Melone and C. Punta, *Beilstein J. Org. Chem.*, **9**, 1296 (2013). doi:10.3762/bjoc.9.146
13. Y. Aoki, N. Hirai, S. Sakaguchi and Y. Ishii, *Tetrahedron*, **61**, 10995 (2005). doi:10.1016/j.tet.2005.08.087
14. G. Yang, Q. Zhang, H. Miao, X. Tong and J. Xu, *Org. Lett.*, **7**, 263 (2005). doi:10.1021/ol047749p
15. X. Tong, J. Xu and H. Miao, *Adv. Synth. Catal.*, **347**, 1953 (2005). doi:10.1002/adsc.200505183
16. M. G. Clerici and O. A. Kholdeeva, *Liquid Phase Oxidation via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications*, passim, John Wiley & Sons, 2013.
17. M. Arshadi and M. Ghiaci, *Appl. Catal. A*, **399**, 75 (2011). doi:10.1016/j.apcata.2011.03.043
18. B. Gao, S. Meng and X. Yang, *Org. Process. Res. Dev.*, **19**, 1374 (2015). doi:10.1021/acs.oprd.5b00108
19. I. Hermans, J. Van Deun, K. Houthoofd, J. Peeters and P. A. Jacobs, *J. Catal.*, **251**, 204 (2007). doi:10.1016/j.jcat.2007.06.025
20. M. Jian, C. Jianlan, L. Dongmei and X. Meina, *RSC Adv.*, **6**, 68170 (2016). doi:10.1039/C6RA14936G
21. S. Su, J. R. Giguere, S. E. Schaus and J. A. Porco, *Tetrahedron*, **60**, 8645 (2004). doi:10.1016/j.tet.2004.05.109
22. X. Li, L. Guo, P. He, X. Yuan and F. Jiao, *Catal. Lett.*, **147**:856 (2017). doi:10.1007/s10562-016-1967-3

23. M. Zhou, X. Li, L. Bao, X. Yuan and H. A. Luo, *Catal. Lett.*, **146**, 383 (2016). doi:10.1007/s10562-015-1635-z
24. K. Kasperczyk, B. Orlinska, E. Witek, P. Łatka, J. Zawadiak and L. Proniewicz, *Catal. Lett.*, **145**, 1856 (2015). doi:10.1007/s10562-015-1578-4
25. S. Koguchi and T. Kitazume, *Tetrahedron Lett.*, **47**, 2797 (2006). doi:10.1016/j.tetlet.2006.02.077
26. J. R. Wang, L. Liu, Y. F. Wang, Y. Zhang, W. Deng and Q. X. Guo, *Tetrahedron Lett.*, **46**, 4647 (2005). doi:10.1016/j.tetlet.2005.04.136
27. R. Hosseinzadeh, M. Mavvaji, M. Tajbakhsh and Z. Lasemi, J. Iran. *Chem. Soc.*, **15**, 893 (2018). doi:10.1007/s13738-017-1288-5
28. R. Hosseinzadeh, M. Mavvaji, M. Tajbakhsh and Z. Lasemi, *React. Kinet. Mech. Cat.*, **124**, 839 (2018). doi:10.1007/s11144-018-1354-8
29. F. Rajabi, J. H. Clark, B. Karimi and D. J. Macquarrie, *Org. Biomol. Chem.*, **3**, 725 (2005). doi:10.1039/b419322a
30. R. Hosseinzadeh, N. Aghili and M. Tajbakhsh, *Catal. Lett.*, **146**, 1194 (2016). doi:10.1007/s10562-016-1743-4
31. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowics, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. Mccullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992). doi:10.1021/ja00053a020
32. M. Pirouzmand, M. M. Amini and N. Safari, *J. Porphyrins Phthalocyanines*, **11**, 118 (2007). doi:10.1142/S1088424607000151
33. W. Kaleta and K. Nowinska, *Chem. Commun.*, 535 (2001). doi:10.1039/b007111k
34. Z. Mehraban and F. Farzaneh, *Microporous Mesoporous Mater.*, **88**, 84 (2006). doi:10.1016/j.micromeso.2005.09.002
35. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, **57**, 603 (1985). doi:10.1351/pac198557040603
36. S. Vashnia, H. Tavakoli, R. Cheraghali and H. Sepehrian, *Separ. Sci. Technol.*, **49**, 241 (2014). doi:10.1080/01496395.2013.828310
37. K. Binnemans, P. Lenaerts, K. Driesen and C. Görller-Walrand, *J. Mater. Chem.*, **14**, 191 (2004). doi:10.1039/B311128H