

# Nitration of substituted phenols by metal salts impregnated

## Yb-Mo-Montmorillonite KSF

Wan-Po Yin and Min Shi\*

*State Key Laboratory of Organometallic Chemistry,  
Shanghai Institute of Organic Chemistry,  
Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032 China  
E-mail: [Mshi@mail.sioc.ac.cn](mailto:Mshi@mail.sioc.ac.cn)*

**Dedicated to Prof. Ted S. Sorensen in University of Calgary**

---

### Abstract

Metal salts impregnated Yb-Mo-HKSF catalysts show high stabilities and catalytic abilities in nitration of various substituted phenols under mild conditions. In addition, these metal catalysts can be easily recovered and reused in the next batch of nitration of phenolic compounds. The process is convenient and represents a practical method for clean synthesis of nitrated phenols.

**Keywords:** Catalytic nitration, phenolic compounds, nitric acid, CuCl<sub>2</sub>, metal salts impregnated Yb-Mo-HKSF

---

### Introduction

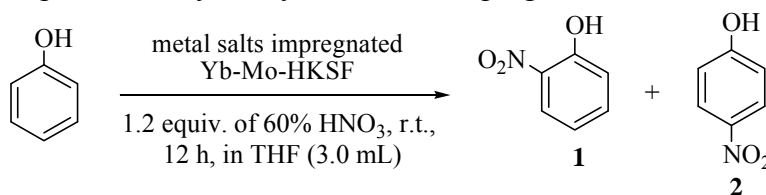
The replacement of current chemical processing techniques with more environmentally benign alternatives is an increasingly attractive subject.<sup>1</sup> Nitration of aromatic compounds is one of the most important industrial processes<sup>2-9</sup> and is the subject of a large body of literature.<sup>10-23</sup> In our laboratory, we have been seeking out a more practical process for the nitration of substituted phenols using stoichiometric or a small excess amount of nitric acid under mild conditions because the development of environmentally friendly practical procedures for the nitration of aromatic compounds is highly desirable.<sup>24-27</sup> However, in our previously reported nitration processes for phenolic compounds, 500 mg of KSF for 1.0 mmol of phenolic compounds must be required to give the nitrated products in good yields.<sup>27</sup> It should be noted that the large amounts of KSF cause the inconvenience for the practical nitration process. Therefore, we attempted to reduce the amount of KSF in this nitration process. Herein we wish to report a new catalytic system of Yb-Mo-HKSF impregnated by other metal salts<sup>28-39</sup> for the nitration of phenolic

compounds to give the corresponding nitrated phenols in good yields in a heterogeneous phase under mild conditions. By this protocol, the amounts of KSF in the corresponding mixed catalysts were reduced to 50 mg for 1.0 mmol of various substituted phenols in 3.0 mL of THF and these catalysts could be recovered and reused easily.

## Results and Discussion

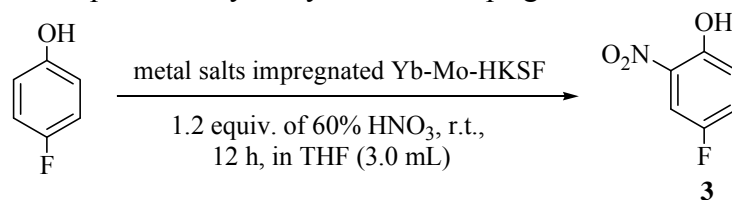
The double-metal-modified Yb-Mo-HKSF catalyst was chosen as a base catalyst because it is the cheapest and most effective double-metal-modified montmorillonite catalyst in nitration of phenolic compounds<sup>40</sup> and impregnated it by various metal salts such as Mn(OAc)<sub>2</sub>, FeCl<sub>3</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, Cu(OAc)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and CuSO<sub>4</sub>. We examined these metal salts impregnated Yb-Mo-HKSF<sup>41</sup> catalysts (50 mg catalyst for 1.0 mmol of phenolic compounds in 3.0 mL of THF) in the nitration of phenol and 4-fluorophenol, respectively under identical conditions. The results are summarized in Table 1 and Table 2, respectively. All these metal salts impregnated Yb-Mo-HKSF catalysts gave good results in the nitration of phenol and 4-fluorophenol under mild conditions. These results suggest that the catalytic abilities of 50 mg of Yb-Mo-HKSF catalyst impregnated with a variety of metal salts are comparable to that of 250 mg of Yb-Mo-HKSF catalyst in the corresponding nitration process under the same conditions.<sup>40</sup> Namely, the catalytic ability of Yb-Mo-HKSF was greatly improved by impregnation with various metal salts.

**Table 1.** Nitration of phenol catalyzed by metal salts impregnated Yb-Mo-HKSF (50 mg)



Entry <sup>a</sup>	Metal salts	Yield/(%) <sup>a</sup>	
		<b>1</b>	<b>2</b>
1	Mn(OAc) <sub>2</sub>	40	45
2	FeCl <sub>3</sub>	42	50
3	CoCl <sub>2</sub>	41	49
4	NiCl <sub>2</sub>	42	47
5	CuCl <sub>2</sub>	40	47
6	ZnCl <sub>2</sub>	42	49
7	Cu(OAc) <sub>2</sub>	43	51
8	Cu(NO <sub>3</sub> ) <sub>2</sub>	43	49
9	CuSO <sub>4</sub>	42	50

<sup>a</sup> Isolated yield.

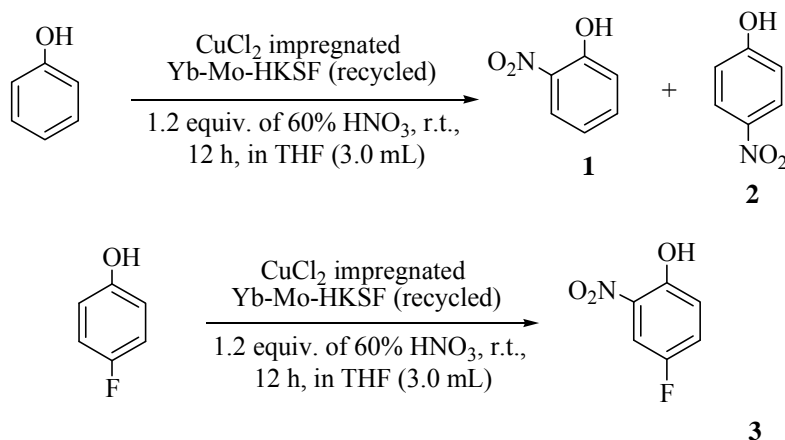
**Table 2.** Nitration of 4-fluorophenol catalyzed by metal salts impregnated Yb-Mo-HKSF (50 mg)

Entry	Metal salts	Yield/(%) <sup>a</sup>
		<b>3</b>
1	Mn(OAc) <sub>2</sub>	86
2	FeCl <sub>3</sub>	87
3	CoCl <sub>2</sub>	89
4	NiCl <sub>2</sub>	88
5	CuCl <sub>2</sub>	86
6	ZnCl <sub>2</sub>	90
7	Cu(OAc) <sub>2</sub>	87
8	Cu(NO <sub>3</sub> ) <sub>2</sub>	89
9	CuSO <sub>4</sub>	88

<sup>a</sup> Isolated yield.

Moreover, it should be emphasized here that this catalytic nitration is a heterogeneous catalytic process and these catalysts can be easily recovered from the reaction mixture by filtration. These catalysts can be reused many times without degradation after being reactivated by heating in an oven at 120 °C. In this catalytic system, we utilized CuCl<sub>2</sub> impregnated Yb-Mo-HKSF catalyst, one of these effective metal salts impregnated Yb-Mo-HKSF catalysts, for the examination of the recovery and reusability in above nitration process. The results are summarized in Table 3. As it can be seen in Table 3, this catalyst can be reused five times under the similar conditions with no loss of catalytic activity. Furthermore, the real heterogeneity of this catalytic system has been examined by a simple test (Sheldon test).<sup>42</sup> The catalyst was filtered after 3 hours at room temperature (reaction temperature), which corresponded to approximately 30% conversion and the filtrate allowed to react further. We found that the reaction completely stopped under identical conditions. This result suggests that this catalytic nitration indeed proceeds in a heterogeneous phase.

On the basis of atomic absorption spectrophotometry to detect the exact leaching amount of Cu<sup>2+</sup> in THF and water solution after nitration, we found that 45% of Cu<sup>2+</sup> indeed leached into the nitrated product, which can be easily removed from the nitrated product by distillation and column chromatography. The control experiment showed that in the presence of CuCl<sub>2</sub> (2.0 mol%) itself, no reaction occurred under identical conditions. This result suggests that this catalytic nitration takes place with the assistance of multi metal ions such as Yb and Mo and in KSF. The leached Cu<sup>2+</sup> itself did not affect the nitration.

**Table 3.** Nitration of phenol and 4-fluorophenol catalyzed by CuCl<sub>2</sub> impregnated Yb-Mo-HKSF (recycled)

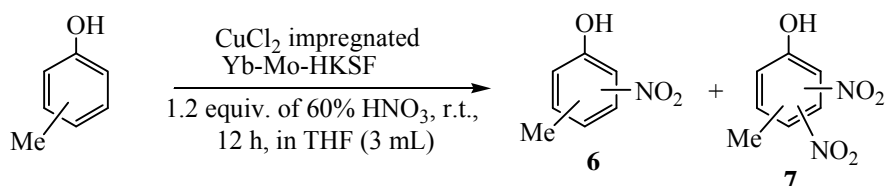
Run	Mass of catalyst/mg <sup>a</sup>	Yield/(%) <sup>b</sup>		Run	Mass of catalyst/mg <sup>a</sup>	Yield/(%) <sup>b</sup>
		1	2			
1 <sup>c</sup>	60	42	50	1 <sup>c</sup>	60	88
2	51	40	47	2	52	89
3	50	43	50	3	50	89
4	45	40	50	4	45	88
5	40	42	47	5	42	88

<sup>a</sup> Mass of catalyst recovered from each run. <sup>b</sup> Isolated yields. <sup>c</sup> recycled catalyst was used.

The catalytic mechanism is not very clear at the present stage and it would be interesting to be investigated in due course.

This catalytic system is more effective and reusable in the nitration of phenolic compounds because of its fair stability against strong hydrolytic reaction conditions in nitration. In addition, HKSF itself can not catalyze the nitration of phenolic compounds under identical conditions and with CuCl<sub>2</sub> impregnated HKSF as a catalyst, 250 mg of catalyst is required for 1.0 mmol of phenolic compounds with 1.2 equiv. of nitric acid.<sup>40</sup> Based on the above investigations, we turned out to use CuCl<sub>2</sub><sup>43</sup> impregnated Yb-Mo-HKSF as a catalyst to nitrate a variety of other phenolic substrates with 1.2 equiv. of 60% nitric acid. These electrophilic aromatic nitration reactions proceeded smoothly for many phenolic substrates. The results are shown in Table 4. The nitration of 4-chlorophenol, 4-isopropylphenol, and 4-*tert*-butylphenol proceeded smoothly to afford the mono-nitrated product in excellent yields (Table 4, entries 1, 3, and 4). For the nitration of 4-bromophenol, four nitrated products, 4-bromo-2-nitrophenol, 2-bromo-4-nitrophenol, 2,4-dibromo-6-nitrophenol and 4-nitrophenol, were obtained in total 99% yield (Table 4, entry 2 and Figure 1). This nitration behavior has been described in literature.<sup>40</sup> In the case of the activated phenolic compound, 4-methoxyphenol, mono-nitrated product and dinitrated product were obtained in total 89% yield (mono : di = 60 : 29, when 1.2 equiv. of HNO<sub>3</sub> was used) or in total 64% yield (mono : di = 3 : 61, when 2.0 equiv. of HNO<sub>3</sub> was used) (Table 4, entries 5 and 6).

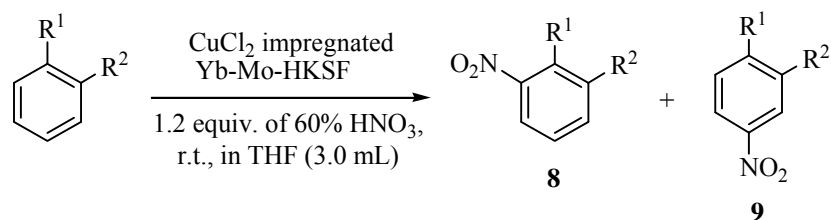


**Table 5.** Nitration of cresol catalyzed by CuCl<sub>2</sub> impregnated Yb-Mo-HKSF (50 mg)

Entry	Cresol	Yield/(%) <sup>a</sup>		
		<b>6</b>	<b>7</b>	
1	4-MeC <sub>6</sub> H <sub>4</sub> OH	 <b>6a</b> , 90	 <b>7a</b> , 2	
2	3-MeC <sub>6</sub> H <sub>4</sub> OH	 <b>6b</b> , 7	 <b>6b'</b> , 25	 <b>6b''</b> , 52
3	2-MeC <sub>6</sub> H <sub>4</sub> OH	 <b>6c</b> , 37	 <b>6c'</b> , 56	 <b>6c''</b> , 1

<sup>a</sup> Isolated yields.

We further investigated the nitration of 2-chlorophenol, 1,2-diethoxybenzene, 2-ethoxyphenol and resorcinol with 60% HNO<sub>3</sub> (1.2 equiv.) in the presence of CuCl<sub>2</sub> impregnated Yb-Mo-HKSF catalyst under the similar conditions. The results are summarized in Table 6. We found that nitration of 2-chlorophenol proceeded smoothly within 4 hours to give the mono-nitrated products in high yields (Table 6, entries 1). For nitration of 2-ethoxyphenol, similar good result was obtained under identical conditions (Table 6, entry 2). For nitration of 1,2-diethoxybenzene, the mono-nitrated product was obtained in 63% yield with 60% HNO<sub>3</sub> (1.2 equiv.) at 60 °C since it is not as reactive as phenol (Table 6, entries 3). For nitration of resorcinol, the mono-nitrated product was obtained in 67% yield under identical conditions (Table 6, entry 4).

**Table 6.** Nitration aromatic compounds catalyzed by CuCl<sub>2</sub> impregnated Yb-Mo-HKSF (50 mg)

Entry	R <sup>1</sup>	R <sup>2</sup>	Time/(h)	Yield/(%) <sup>a</sup>	
				8	9
1	OH	Cl	4	<b>8a</b> , 42	<b>9a</b> , 54
2	OH	OEt	4	<b>8b</b> , 34	<b>9b</b> , 54
3 <sup>b</sup>	OEt	OEt	24	-	<b>9c</b> , 63
4			1		<b>9d</b> , 67

<sup>a</sup> Isolated yield. <sup>b</sup> The reaction temperature is at 60 °C.

In conclusion, we have found an environmentally conscious practical procedure for the nitration of phenolic compounds under mild conditions. In the presence of metal salts impregnated Yb-Mo-HKSF catalyst (50 mg), 1.2 equiv. of 60% nitric acid can be used in nitration of a variety of phenolic compounds (1.0 mmol) in THF (3.0 mL) to give the corresponding nitrated products in good to high yields. The use of a large excess of concentrated or fumed nitric acid and montmorillonite KSF can be avoided with this catalytic system. Moreover, these catalysts can be easily recovered from the reaction mixture and can be reused many times. This nitration process was carried out in THF, an environmentally safer solvent, at room temperature. Overall, this method is an eco-safer and environment-benign way of nitrating phenolic compounds.

## Experimental Section

**General Procedures.** MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in CDCl<sub>3</sub> with tetramethylsilane (TMS) as internal standard; J-values are in Hz. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA<sup>+</sup> mass spectrometer. Organic solvents were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All these

reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. The orientation of nitration was determined by NMR analysis. Flash column chromatography was carried out using 300-400 mesh silica gel. The spectroscopic and analytic data of the most nitrated products have been disclosed in the literature (see Supporting Information).<sup>26,27,40</sup>

### **Preparation of metal catalysts used in the nitration of phenolic compounds**

Preparation of modified carrier: montmorillonite KSF (20 g) and 10% of nitric acid (50 mL) were put into a 250 mL beaker and the mixture was stirred for 12 hours at room temperature. Then, the mixture was filtrated and washed by water until the filtrate showed pH  $\approx$  7. The residue was dried at 120 °C by an oven for 2 hours, which was used as carrier (HKSF).

Preparation of single-metal-modified catalysts (Mo-HKSF):  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (1.83 g) was dissolved in 20 mL of mixed solution of acetone and water (1:1), then the above 13.5 g of HKSF was added into the solution and the resulting mixtures were refluxed with magnetic stirring for 2 hours. Next, the solvent was removed under reduced pressure upon heating at 80 °C and the residue was further dried at 120 °C by an oven for 2 hours and then calcined by a muffle furnace at 600 °C for 4 hours to obtain the single metal Mo modified catalyst (Mo-HKSF).

Preparation of double-metals-modified catalysts (Yb-Mo-HKSF): 1.82 g of  $\text{Yb}(\text{NO}_3)_3$  was dissolved in 20 mL of mixed solution of acetone and water (1:1), then 9.0 g of Mo-HKSF was added into the solution and the mixtures were refluxed with magnetic stirring for 2 hours. Next, the solvent was removed under reduced pressure upon heating at 80 °C and the residue was further dried at 120 °C by an oven for 2 hours and then calcined by a muffle furnace at 400 °C for 4 hours to obtain the double-metals Yb-Mo modified catalyst (Yb-Mo-HKSF).

Preparation of metal salts impregnated Yb-Mo-HKSF: 170 mg of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 10 mL of acetone, then 1.0 g of Yb-Mo-HKSF was added into the solution and the resulting mixtures were refluxed with magnetic stirring for 2 hours. Then, the solvent was removed under reduced pressure upon heating at 80 °C and the residue was further dried at 120 °C by an oven for 2 hours to obtain  $\text{CuCl}_2$  impregnated Yb-Mo-HKSF. Herein,  $\text{Mn}(\text{OAc})_2$ ,  $\text{FeCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{Cu}(\text{OAc})_2$ ,  $\text{Cu}(\text{NO}_3)_2$ , and  $\text{CuSO}_4$  were used as the impregnated metal salts to Yb-Mo-HKSF in the similar procedures.

### **General procedure for the nitration of phenolic compounds**

$\text{CuCl}_2$  impregnated catalyst (50 mg) was put into a glass vessel and then substituted phenol (1.0 mmol) and then THF (3.0 mL) was added into the glass vessel. Nitric acid (60%, 0.095 mL,  $d = 1.3667$ , 1.2 mmol) was added dropwise into the vessel and the mixtures were stirred for 12 hours at room temperature. The catalyst was recovered by filtration, and the filtrate was extracted with ethyl acetate ( $\text{MeCO}_2\text{Et}$ ). The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatograph (eluent: petroleum ether/ $\text{EtOAc} = 10/1$ ) to give the corresponding product. Their yields are presented in Tables 1-6. These nitrated products are all known compounds. Their physical property and spectroscopic data can be found in the literature.<sup>26,27,40</sup>



- 2-Nitrophenol 1.** A yellow solid, m.p. 45-47 °C.<sup>26,27</sup>  
**4-Nitrophenol 2.** A yellow solid, m.p. 117-119 °C.<sup>27</sup>  
**4-Fluoro-2-nitrophenol 3.** A yellow solid, m.p. 75-77 °C.<sup>26,27</sup>  
**4-Chloro-2-nitrophenol 4a.** A yellow solid, m.p. 86-88 °C.<sup>26,27</sup>  
**2-Bromo-4-nitrophenol 4b.** A yellow solid, m.p. 115-118 °C.<sup>40</sup>  
**4-Isopropyl-2-nitrophenol 4c.** A yellow liquid, m.p. 54-56 °C.<sup>26,27</sup>  
**4-tert-Butyl-2-nitrophenol 4d.** A yellow solid, m.p. 70-73 °C.<sup>26,27</sup>  
**4-Methoxy-2-nitrophenol 4e.** A yellow solid, m.p. 80-81 °C.<sup>26,27</sup>  
**4-Methoxy-2,6-dinitrophenol 5e.** A yellow solid, m.p. 77-79 °C.<sup>26,27</sup>  
**4-Methyl-2-nitrophenol 6a.** A yellow solid, m.p. 34-36 °C.<sup>26,27</sup>  
**4-Methyl-2,6-dinitrophenol 7a.** A yellow solid, m.p. 84-86 °C.<sup>26,27</sup>  
**3-Methyl-4-nitrophenol 6b.** A yellow solid, m.p. 128-130 °C.<sup>26,27</sup>  
**5-Methyl-2-nitrophenol 6b'.** A yellow solid, m.p. 56-58 °C.<sup>26,27</sup>  
**3-Methyl-2-nitrophenol 6b''.** A yellow solid, m.p. 39-41 °C.<sup>26,27</sup>  
**2-Methyl-6-nitrophenol 6c.** A yellow solid, m.p. 71-73 °C.<sup>26,27</sup>  
**2-Methyl-4-nitrophenol 6c'.** A yellow solid, m.p. 142-145 °C.<sup>26,27</sup>  
**2-Methyl-4,6-dinitrophenol 7c.** A yellow solid, m.p. 125-128 °C.<sup>26,27</sup>  
**2-Chloro-6-nitrophenol 8a.** A yellow solid, m.p. 70-71 °C.<sup>26,27</sup>  
**2-Chloro-4-nitrophenol 9a.** A yellow solid, m.p. 110-112 °C.<sup>26,27</sup>  
**1,2-Diethoxy-4-nitrobenzene 8b.** A yellow solid, m.p. 75-77 °C.<sup>27</sup>  
**2-Ethoxy-6-nitrophenol 9b.** A yellow solid, m.p. 62-64 °C.<sup>27</sup>  
**2-Ethoxy-4-nitrophenol 9c.** A yellow solid, m.p. 95-97 °C.<sup>27</sup>  
**4-Nitroresorcinol 9d.** A yellow solid, m.p. 117-119 °C.<sup>27</sup>

### The recovery of the employed catalysts and the reusing procedure

The catalyst can be easily recovered from the reaction mixture by filtration and reused many times after it is activated by heating in an oven at 120 °C for 2 hours. After filtration, the catalyst was recovered and the reaction mixture was extracted with ethyl acetate (MeCO<sub>2</sub>Et). The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatograph (eluent: petroleum ether/EtOAc = 10/1) to give the products as yellow solids: 128 mg, total yield: 92%.

### Acknowledgements

We thank the Shanghai Municipal Committee of Science and Technology, Chinese Academy of Sciences (KGCX2-210-01), the Shanghai Municipal Committee of Science and Technology (04JC14083, 06XD14005), and the National Natural Science Foundation of China (20672127, 203900502, and 20732008) for financial support.

## References

1. Clark, J. H. *Green Chem.* **1999**, *1*, 1.
2. Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice* OUP: Oxford, 1999.
3. Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration: Methods and Mechanism*, Feuer, H. Ed., VCH: New York, 1989.
4. Ingold, C. K. *Structure and Mechanism in Organic Chemistry* 2<sup>nd</sup> Edn., Cornell University Press: Ithaca, New York, 1969.
5. Olah, G. A.; Kuhn, S. J. In *Friedel-Crafts and Related Reactions*. Olah, G. A. Ed., Wiley-Interscience: New York, 1964; Vol. 2.
6. Olah, G. A.; Narang, S. C.; Olah, J. A.; Lammertsma, K. *Proc. Nat. Acad. Sci.* **1982**, 4487.
7. Thompson, M. J.; Zeeger, P. J. *Tetrahedron* **1991**, *47*, 8787.
8. Bisarya, S. C.; Joshi, S. K.; Holker, A. G. *Synth. Commun.* **1993**, *8*, 1125.
9. Robrgues, J. A. R.; Oliveira, A. P.; Moran, P. J. S.; Custodio, R. *Tetrahedron* **1999**, *55*, 6733.
10. Olah, G. A. *ACS Symp. Series*, Vol. 22. Albright, F., Ed., ACS: Washington DC, 1967; p.1.
11. Hoggett, J. G.; Moodie, R. B.; Penton, J. R.; Schofield, K. *Nitration and Aromatic Reactivity*, Cambridge University Press: London, 1971.
12. Schofield, K. *Aromatic Nitration*, Cambridge University Press: London, 1980.
13. Malysheva, L. V.; Paukshtis, E. A.; Ione, K. G. *Catal. Rev. Sci. Eng.* **1995**, *37*, 179.
14. Stewart, J. T.; Janicki, C. A. *Anal. Profiles Drug Subst.* **1987**, *16*, 119.
15. Desai, M. N. *Indian J. Appl. Chem.* **1970**, *33*, 277.
16. Mottier, M. *Arch. Sci. Phys. Nat.* **1934**, *16*, 301.
17. Lunar, L.; Sicilia, D.; Rubio, S.; Perez-Bendito, D.; Nickel, U. *Water Res.* **2000**, *34* (6), 1791.
18. Firouzabadi, H.; Iranpoor, N.; Zolfigol, M. A. *Synth. Commun.* **1997**, *19*, 3301.
19. Iranpoor, N.; Firouzabadi, H.; Zolfigol, M. A. *Synth. Commun.* **1993**, *15*, 2773.
20. Ouertani, M.; Girard, P.; Kagan, H. B. *Tetrahedron Lett.* **1982**, *23*, 4315.
21. Cornelis, A.; Laszlo, P.; Pennetreau, P. *Bull. Soc. Chim. Belg.* **1984**, *93*, 961.
22. Cornelis, A.; Laszlo, P. *Synthesis* **1985**, 909.
23. Laszlo, P.; Cornelis, A. *Aldrichmica Acta*, **1988**, 97.
24. Shi, M.; Cui, S. C. *J. Fluoro. Chem.* **2002**, *113*, 207.
25. Shi, M.; Cui, S. C. *Chem. Commun.* **2002**, 994.
26. (a) Cui, S. C.; Shi, M. *Adv. Synth. & Catal.* **2003**, *345*, 1197. (b) Shi, M.; Cui, S.-C.; Yin, W.-P. *Eur. J. Org. Chem.* **2005**, 2379.
27. Shi, M.; Cui, S. C. *Adv. Synth. & Catal.* **2003**, *345*, 1329.
28. Gandia, L. M.; Vicente, M. A.; Gil, A. *Appl. Catal., A*, **2000**, *196*, 281.
29. Prinetto, F.; Tichit, D.; Teissier, R.; Coq, B. *Catal. Today* **2000**, *55*, 103.
30. Pinnavaia, T. J. *Science* **1983**, *220*, 365.
31. Narkynan, S.; Deshpande, K. *Appl. Catal. A*, **2000**, *193*, 17.
32. Varma, R. S. *Tetrahedron* **2002**, *58*, 1235.

33. Vaccari, A. V. *Appl. Clay Sci.* **1999**, *14*, 161.
34. Clark, P. D.; Mesher, S. T. E.; Primak, A. *Phosphorus, Sulfur and Silicon* **1996**, *114*, 99.
35. Clark, P. D.; Mesher, S. T. E.; Primak, A.; Yao, H. *Catal. Lett.* **1997**, *48*, 79.
36. Shinde, A. B.; Shrigadi, N. B.; Samant, S. D. *Appl. Catal. A*, **2004**, *276*, 5.
37. Castillo, H. L.; Gil, A.; Grange, P. *Catal. Lett.* **1997**, *43*, 133.
38. Kurian, M.; Sankaran, S. *React. Kinet. Catal. Lett.* **2004**, *81*, 57.
39. Clewley, R. G.; Fischer, A.; Henderson, G. N. *Can. J. Chem.* **1989**, 1472.
40. Yin, W.-P.; Shi, M. *Tetrahedron* **2005**, *61*, 10861.
41. HKSF is KSF treated by 10% of nitric acid solution. When the employed montmorillonite KSF was washed by water or by 10% (W/W) of nitric acid, we found that some components were washed out into water phase and the washed KSF lost its catalytic ability in the nitration of phenolic compounds. We analyzed the washed KSF and the lost components by emission spectrochemical analysis and we found that the lost components include major amount of Al and Mg, small amount of Fe, and micro amount of Na, Si, Mn, Ni, Cr, Pb, Cu, and Sr (Supporting Information). With HKSF as a base catalyst can increase the reliability and stability of the recovered catalyst in strong acid solution.
42. (a) Lempers, H. E. B.; Sheldon, R. A. *J. Catal.* **1998**, *175*, 62. (b) ten Brink, G. J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *287*, 1636.
43. Copper salt is relatively environmentally safer metal in water phase. (a) McGeer, J. C.; Szebedinszky, C.; McDonald, D. G.; Wood, C. M. *Aquatic Tox.* **2000**, *50*, 231. (b) Almeida, J. A.; Diniz, Y. S.; Marques, S. F. G.; Faine, L. A.; Ribas, B. O.; Bumeiko, R. C.; Novelli, I. L. B. *Environ. Inter.* **2002**, *27*, 673. (c) Zauke, G.-P.; Savinov, V. M.; Ritterhoff, J.; Savinov, T. *The Science of the Total Environment*, **1999**, *227*, 161. (d) Romeo, M.; Siau, Y.; Sidoumou, Z.; Gnassia-Barelli, M. *The Science of the Total Environment*, **1999**, *232*, 169. (e) Granmo, A.; Ekelund, R.; Sneli, J.-A.; Berggren, M.; Svavarsson, J. *Marine Poll. Bull.* **2002**, *44*, 1142. (f) Brouwer, M.; Brouwer, T. H.; A. Syring, R. *Marine Environ. Res.* **2000**, *50*, 103.