

Nitration of phenolic compounds by metal-modified montmorillonite KSF

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Abstract—The nitration of phenolic compounds with 60% nitric acid (1.2 equiv) has been carried out in the presence of metal-modified montmorillonite KSF, prepared from different metals (V, Mo, W; Sc, La, Yb, Eu, In, Bi, Ti, Zr, Hf) and KSF or nitric acid treated HKSF, as catalysts. These catalysts showed good stabilities and high catalytic activities in nitration process. In addition, these catalysts can be recovered easily and reused for many times in nitration. This process is an eco-safer and environment-benign way for clean synthesis of nitrated phenolic compounds.

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1. Introduction

The replacement of current chemical processing with more environmentally benign alternatives is an increasingly attractive subject.¹ Nitration of aromatic compounds is one of the most important industrial processes^{2–9} and is the subject of a large body of literature.^{10–13} Especially, nitrated phenolic compounds are very useful intermediates in the preparation of fine chemicals.^{13–16} In general, nitration of aromatic compounds typically requires a mixture of concentrated or fuming nitric acid with sulfuric acids leading to excessive acid waste streams and added expense.¹⁷ The obvious disadvantages of the commercial manufacturing process currently used has led to a substantial effort to develop viable alternatives, by using solid acid catalysts, other sources of NO_2^+ , organic nitrating agents, other acids replacing sulfuric acid, etc.^{18,19} But, none of them thus far have practical value in industrial use. Recently, it was found that metal salts or metal complexes could be used as catalysts for the nitration of phenolic compounds, although the loss of catalyst occurred during the recovery of the employed catalyst in above nitration processes.^{20–23} Enlightened by these findings, we attempted to seek out a more practical process for the nitration of phenolic compounds using stoichiometric or a small excess of nitric acid under mild conditions because the development of environmentally friendly practical procedures for

the nitration of aromatic compounds is highly desirable. So far, we have reported that $\text{Ln}(\text{OPf})_3$ ($\text{Ln} = \text{Sc}, \text{Yb}, \text{La}$, $\text{Pf} = \text{C}_8\text{F}_{17}\text{SO}_3$), $\text{Bi}(\text{NO}_3)_3/\text{montmorillonite KSF}$ and Zr or Hf oxychloride complex/montmorillonite KSF are effective catalysts for nitration of aromatic or phenolic compounds with a small excess of 60–65% nitric acid under mild conditions.^{24–28} However, in these nitration processes, 500 mg of KSF for 1.0 mmol of phenolic compounds are required to give the nitrated products in good yields. Obviously, the large amount of KSF will cause the inconvenience for the practical nitration process. Therefore, we attempted to reduce the amount of KSF in this nitration process. The problem is that if the nitration is carried out with less amount of KSF, the loss of active components in KSF will hamper the catalytic ability of these catalysts because the nitration was carried out in a strong nitric acid solution. Therefore, the modification of KSF to achieve higher catalytic ability is desirable.

In fact, considerable attention has been given to the development of new functionally active supports, and a new class of catalysts based on layered aluminosilicates modified by the introduction of the hydroxo complexes of polyvalent metals into the interlayer space has been reported.^{29–31} These materials possess unique structural and catalytic properties, which depend on both the chemical properties of the introduced compounds and modification procedures and conditions.^{32,33} Montmorillonites are silicates of aluminum with layered structure that present a wide use in organic synthesis³³ and exhibit specific features.³⁴ In the recent years, metal-modified

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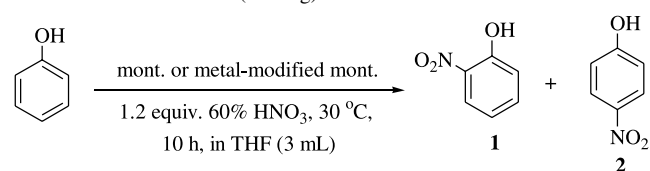
montmorillonites were reported widely, and many metals, such as Zn, Mn, Fe, Cu, Cr, V, Mo Ti, etc.,^{35–39} were commonly used to improve the catalytic abilities of montmorillonites. In these catalysts, the metal complexes are doped into the layered structure of montmorillonites and exist in more stable states. In any sense, these catalysts could keep excellent catalytic activity even after recycling and can be reused for many times. We thought that these metal-modified montmorillonite catalysts might be more efficient for the catalytic nitration of phenolic compounds in a similar way. Moreover, by adopting metals to modify montmorillonite, the montmorillonite's catalytic ability can be improved and the employed amount of KSF in these catalysts could be reduced to some extent. Herein, we wish to report a new catalytic system for the nitration of phenolic compounds to give the corresponding nitrated products in good yields in a heterogeneous phase under mild conditions. By this protocol, the amount of KSF in the corresponding mixed catalyst was reduced to 250 mg for 1.0 mmol of phenolic compounds, and the catalysts could be recycled and reused easily.

2. Results and discussion

Montmorillonite K10, montmorillonite KSF and nitric acid treated montmorillonite KSF (denoted as HKSF) were used as base catalysts and carriers. The preparation of metal-modified montmorillonite catalysts was carried out by the similar methods as those described in previous literature.^{35–39} The procedure is shown below. Single-metal-modified montmorillonite catalysts were first prepared by wet impregnation method. Montmorillonite was impregnated with V, Mo, W, respectively, by mixing calculated amounts (10 wt% calculated by metal oxides) of the ammonium salt of V, Mo and W with the clay and refluxing either in acetone or in the mixed solvent of acetone and water with magnetic stirring. Acetone was dried off from the catalyst sample at room temperature. The resulting catalyst sample was further dried at 120 °C by an oven for 2 h and calcined by muffle furnace at 600 °C for 4 h. The catalyst samples prepared are denoted either as M₁-HKSF or as M₁-KSF in which M₁ represents the first incorporated metal. These M₁-HKSF and M₁-KSF sample were used as carriers and then modified with second metal such as In, Bi, Ti, Zr, Hf, Sc, Yb, Eu by the similar method. The resulting sample was dried at 120 °C by an oven for 2 h and calcined by muffle furnace at 400 °C for 4 h. The catalyst samples prepared are denoted as M₂-M₁-HKSF or M₂-M₁-KSF where M₁ and M₂ are the incorporated metals.

We examined montmorillonite clays (250 mg) and single-metal-modified KSF (250 mg) in the nitration of phenol (1.0 mmol) with 1.2 equiv of 60% nitric acid in THF (3 mL). The results are summarized in Table 1. Montmorillonite K10 and montmorillonite KSF (250 mg) could be used as nitration catalysts of phenol in 3 mL of THF (Table 1, entries 1 and 2). However, when KSF was washed by water (denoted as HKSF) or by nitric acid, or was calcined at 600 °C by a muffle furnace (denoted as CKSF) for 4 h, no reaction occurred under the same conditions (Table 1, entries 3–5). These results suggest that when the employed amount of KSF was reduced to 250 mg for 1.0 mmol of phenol, the loss of active component by nitric acid solution

Table 1. Nitration of phenol catalyzed by montmorillonite or metal-modified montmorillonite (250 mg)



Entry	Catalyst	Yield (%) ^a	
		1	2
1	Mont. K10	38	42
2	Mont. KSF	39	45
3	CKSF ^b	nr	
4	WKSF ^c	nr	
5	HKSF ^d	nr	
6	Mo-HKSF ^e	39	47
7	Mo-KSF ^f	37	45
8	V-HKSF ^f	35	45
9	V-KSF ^f	39	46
10	W-HKSF ^g	nr	
11	W-KSF ^g	nr	

^a Isolated yield.

^b KSF was calcined at 600 °C for 4 h.

^c KSF was washed by water.

^d KSF was washed by 10% HNO₃.

^e Metal Mo modified KSF or HKSF.

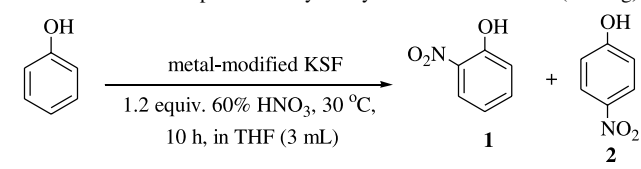
^f Metal V modified KSF or HKSF.

^g Metal W modified KSF or HKSF.

will cause serious deactivation of the catalyst in nitration process. Metal Mo and V modified HKSF or KSF gave the good results in the nitration of phenol although metal W modified HKSF or KSF did not catalyze the nitration of phenolic compounds under the same conditions (Table 1, entries 6–11). These results suggest that Mo and V modified HKSF or KSF can be used in nitration even with reduced amount of KSF.

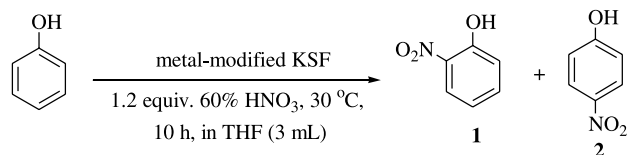
Next using these double-metal-modified KSF catalysts (M₂-M₁-HKSF or M₂-M₁-KSF), in which the second doped metal is In (M₂=In, M₁=Mo, V, W), we examined their catalytic abilities in this nitration reaction. The results are summarized in Table 2. We found that metal W modified KSF did not have the catalytic ability in this nitration either even doped with second metal In and the metal V or Mo modified KSF with second metal In gave the good results in the same reaction (Table 2, entries 1–6). Thus, metal V and

Table 2. Nitration of phenol catalyzed by metal-modified KSF (250 mg)



Entry	Catalyst	Yield (%) ^a	
		1	2
1	In-Mo-KSF	41	47
2	In-Mo-HKSF	43	44
3	In-V-KSF	41	47
4	In-V-HKSF	37	48
5	In-W-KSF	nr	
6	In-W-HKSF	nr	

^a Isolated yield.

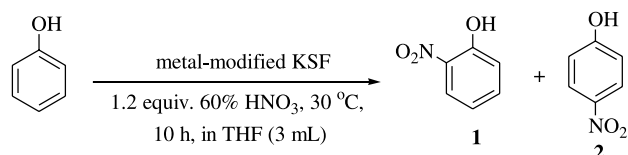
Table 3. Nitration of phenol catalyzed by metal-modified KSF (250 mg)

Entry	Catalyst	Yield (%) ^a	
		1	2
1	Ti–Mo–HKSF	nr	
2	Zr–Mo–HKSF	38	45
3	Hf–Mo–HKSF	41	48
4	Sc–Mo–HKSF	41	46
5	La–Mo–HKSF	41	44
6	Yb–Mo–HKSF	42	45
7	Eu–Mo–HKSF	37	43
8	Bi–Mo–HKSF	39	42
9	Zr–Mo–KSF	39	43
10	Eu–Mo–KSF	37	45

^a Isolated yield.

Mo modified KSF are suitable for the doping of the second metal.

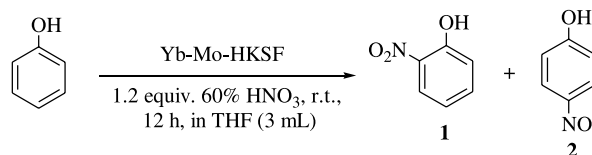
Therefore, metal V and Mo modified KSF were utilized as carriers, respectively, and were modified with other metal salts such as TiCl₄, ZrCl₄, HfCl₄, Sc(NO₃)₃, La(NO₃)₃, Yb(NO₃)₃, Eu(NO₃)₃, and Bi(NO₃)₃ in a similar way as that described above. We examined these catalysts in the nitration reaction and the results are summarized in Tables 3 and 4, respectively. Except metal Ti modified catalysts (Ti–Mo–HKSF and Ti–V–HKSF) all these catalysts gave good results in this nitration under the same conditions (Table 3, entries 1–10 and Table 4, entries 1–8). It should be noted that when M₂–V–KSF or M₂–V–HKSF was used as the catalyst, the corresponding nitrated products 1 and 2 were obtained as slightly red colorized solid presumably due to the oxidation ability of metal V.

Table 4. Nitration of phenol catalyzed by metal-modified KSF (250 mg)

Entry	Catalyst	Yield (%) ^a	
		1	2
1	Ti–V–HKSF	nr	
2	Zr–V–HKSF	38	45
3	Hf–V–HKSF	41	48
4	Sc–V–HKSF	41	46
5	La–V–HKSF	41	44
6	Yb–V–HKSF	42	45
7	Eu–V–HKSF	37	43
8	Bi–V–HKSF	39	42

^a Isolated yield.

Moreover, it should be emphasized here that this catalytic nitration is a heterogeneous catalytic process and these catalysts could be easily recovered from reaction mixture just by filtration. These catalysts can be reused for many times without degradation after them have been reactivated by heating at 120 °C with an oven. In our experiment, we

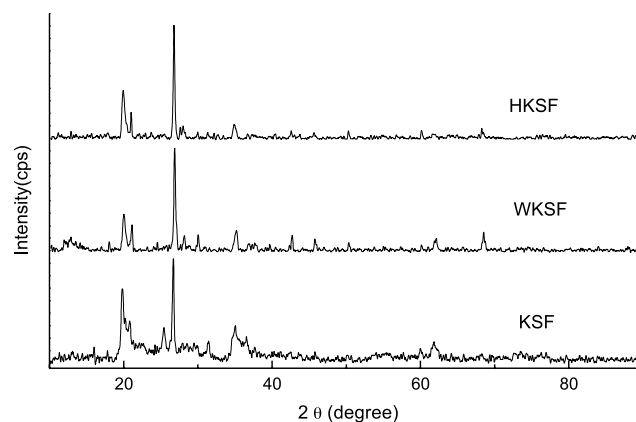
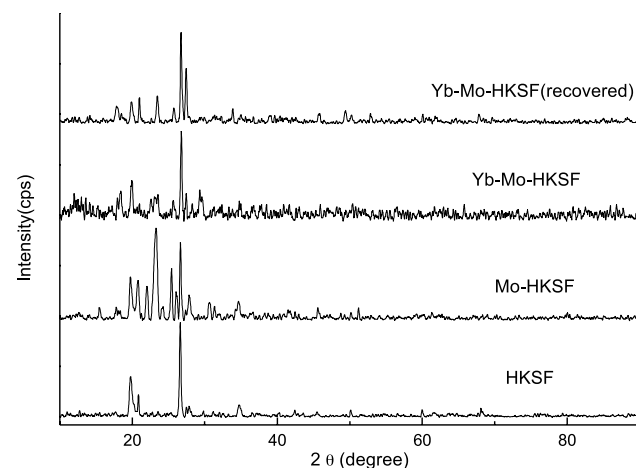
Table 5. Nitration of phenol catalyzed by recovered catalyst

Run	Mass of catalyst/mg recovered catalyst ^a	Yield (%) ^b	
		1	2
1	286 ^c	45	46
2	276 (96)	40	45
3	270 (94)	42	44
4	249 (87)	40	50
5	228 (80)	41	50
6	209 (73)	43	47

^a Mass of catalyst recovered from each run and the data in parantheses indicate the percentage of recovery.^b Isolated yield.^c Recovered catalyst was used.

chose one of these catalysts, and reused this catalyst for six times and it still has good catalytic activity. The results are summarized in Table 5.

All these carriers and catalysts were characterized by powder X-ray diffraction (XRD). XRD patterns of KSF,

**Figure 1.** XRD patterns of KSF, KSF washed by water and KSF washed by 10% HNO₃.**Figure 2.** XRD patterns of HKSF, metal modified HKSF catalysts and recycled catalyst.

WKSF (washed by water) and HKSF (washed by 10% HNO₃) are presented in Figure 1. All these clays showed intense lines in their fine structure. As it has been pointed out, when KSF was washed by nitric acid solution, the active components lost into water. The XRD pattern has indeed showed some changes in fine structure although the basal structure of KSF was kept. XRD patterns of HKSF and its metal modified structure are presented in Figures 2 and 3, respectively. When HKSF was modified by metal Mo or by double metals Yb–Mo, the composition of the clays was changed and these differences have been indicated in their XRD which lead to different catalytic activities in nitration. The doping of metal did not effect the basal supporting structure of HKSF as shown in Figures 2 and 3. The XRD analysis of the recovered catalyst indicated no alteration with the original catalyst even Yb–Mo–HKSF catalyst was reused for six times. Metal V or double metals Yb–V modified catalysts showed similar characters as with that of metal Mo or double metals Yb–Mo modified catalysts.

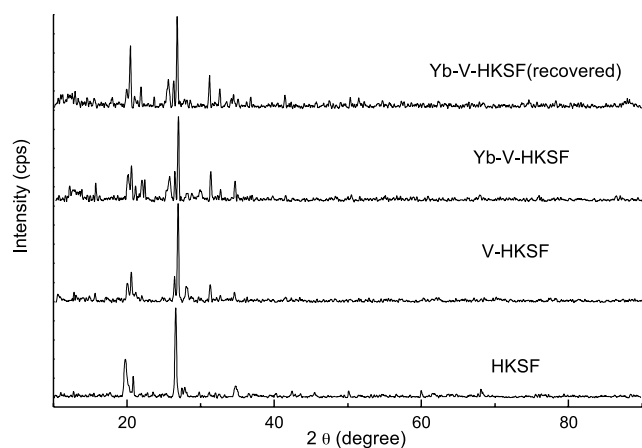


Figure 3. XRD patterns of HKSF, metal modified HKSF catalysts and recycled catalyst.

These catalytic systems were more effective and reusable in the nitration of phenolic compounds because of its stability against strong hydrolytic reaction conditions in nitration.

Based on above investigation, we turned out to use Yb–Mo–HKSF or Eu–Mo–HKSF as catalysts to nitrate a variety of other phenolic substrates with 1.2 equiv of 60% nitric acid in THF. This electrophilic aromatic nitration reaction proceeded smoothly for many phenolic substrates. The results are shown in Table 6. 4-Fluorophenol, 4-chlorophenol, 4-isopropylphenol, 4-*tert*-butylphenol, reacted smoothly to afford a mono-nitrated product in excellent yields (Table 6, entries 1, 2, 4, and 5). 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 6, entry 3 and Fig. 4). This nitration behavior has been described in previous literature.⁴⁰ In the case of the activated phenolic aromatic compound, 4-methoxyphenol, mono-nitrated product and dinitrated product were obtained in total 76% yield (mono/di = 66:34, when 1.2 equiv HNO₃ was used) or in total 66% yield (mono/di = 6:94, when 2.0 equiv HNO₃ was used) (Table 6, entries 6 and 7).

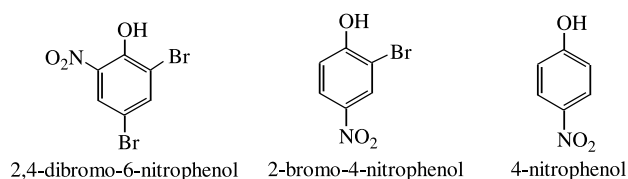


Figure 4.

In addition, we also examined the nitration reaction of 2-cresol, 3-cresol and 4-cresol by 1.2 equiv of 60% nitric acid in the presence of Yb–Mo–HKSF or Eu–Mo–HKSF. In the case of 3-cresol, three mono-nitrated phenolic products were obtained in total 91% yield (Table 7, entry 2). However, in the nitration of 4-cresol and 2-cresol, both mono-nitrated and dinitrated products were obtained in good total yields, respectively, at the same time under identical conditions (Table 7, entries 1 and 3).

We further investigated the nitration of 2-chlorophenol, 1,2-diethoxybenzene, 2-ethoxyphenol and resorcinol with

Table 6. Nitration of phenolic compounds catalyzed by Yb–Mo–HKSF or Eu–Mo–HKSF (250 mg)

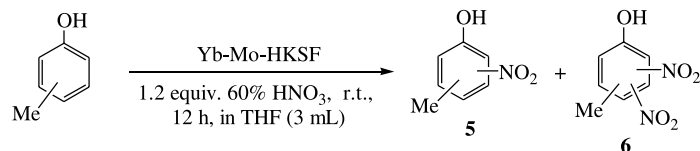
Entry	R	Time (h)	Yield (%) ^a	
			3	4
1	F	12	87 (90) ^b	—
2	Cl	4	88 (78) ^b	—
3	Br	4	63 (65) ^b , other products 36 (29) ^{b,c}	—
4	<i>i</i> -Pr	12	74 (87) ^b	—
5	<i>t</i> -Bu	12	88 (93) ^b	—
6	OMe	4	50 (48) ^b	26 (24) ^b
7 ^d	OMe	1	4 (4) ^b	62 (63) ^b

^a Isolated yields.

^b Eu–Mo–HKSF was used as catalyst.

^c The products include 2,4-dibromo-6-nitrophenol, 2-bromo-4-nitrophenol and 4-nitrophenol (Fig. 4).

^d The quantity of nitric acid is 2.0 equiv.

Table 7. Nitration of cresol catalyzed by Yb–Mo–HKSF or Eu–Mo–HKSF (250 mg)

Entry	Cresol	Yield (%) ^a	
		5	6
1	4-MeC ₆ H ₄ OH	 88 (86) ^b	 3 (3) ^b
2	3-MeC ₆ H ₄ OH	 13 (9) ^b , 26 (25) ^b , 52 (53) ^b	
3	2-MeC ₆ H ₄ OH	 39 (40) ^b , 45 (42) ^b	 9 (9) ^b

^a Isolated yields.^b Eu–Mo–KHSF was used as the catalyst.

60% HNO₃ (1.2 equiv) in the presence of Yb–Mo–HKSF or Eu–Mo–HKSF under identical conditions. The results are summarized in Table 8. We found that nitration of 2-chlorophenol proceeded smoothly within 4 h to give the mono-nitrated products in high yields (Table 8, entry 1). For 2-ethoxyphenol, a similar good result was obtained under identical conditions (Table 8, entry 2). For nitration of 1,2-diethoxybenzene, mono-nitrated product was obtained in 66% yield with 60% HNO₃ (1.2 equiv) at 60 °C (Table 8, entry 3). For resorcinol, mono-nitrated product was obtained in 66% yield under identical conditions (Table 8, entry 4).

In conclusion, we have found an environmentally conscious practical procedure for the nitration of phenolic compounds under mild conditions. In the presence of metal-modified montmorillonite catalysts, less amount of catalysts (250 mg catalyst for 1.0 mmol of phenolic substrate) and 1.2 equiv, of 60% nitric acid can be used in nitration of a variety of phenolic compounds to give the nitrated products in good to high yields. The use of a large excess amount of concentrated or fumed nitric acid can be avoided by this catalytic system. Moreover, these catalysts can be easily recovered from the reaction mixture and can be reused for many times. This nitration method was carried out in THF, an environmentally safer solvent without sulfuric acids. Overall, this method is an eco-safer and environment-benign way for nitration of phenolic compounds.

3. Experimental

3.1. General remarks

MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in CDCl₃ 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⁺ mass spectrometer. The XRD patterns of the catalyst samples oriented on glass slides were recorded on a Philips semiautomatic diffractometer with Ni-filtered Cu Kα radiation (λ = 1.54178 Å). A scan rate of 0.02° min⁻¹ was used on the samples over the 2θ range of 10–90°. Organic solvents were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All 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 previous literature.^{26,27}

3.2. 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 h at room temperature. Then, the mixture was filtrated and washed by water until the filtrate showed pH ≈ 7. The residue was dried at 120 °C by an oven for 2 h, which was used as carrier (HKSF).

Preparation of single-metal-modified catalysts (Mo–HKSF): (NH₄)₆Mo₇O₂₄·4H₂O (1.83 g) was dissolved in 20 mL of mixed solution of acetone and water (3:1), then the above 13.5 g of HKSF was added into the solution and the resulting mixtures were refluxed with magnetic stirring for 2 h. 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 h and then calcined by a muffle furnace at 600 °C for 4 h to obtain the single metal Mo modified catalyst (Mo–HKSF). In addition, V–HKSF and W–HKSF were prepared in the similar procedure.

Table 8. Nitration aromatic compounds catalyzed by Yb–Mo–HKSF or Eu–Mo–HKSF (250 mg)

Entry	R ¹	R ²	Time (h)	Yield (%) ^a	
				7	8
1	OH	Cl	4	43 (48) ^b	54 (44) ^b
2	OH	OE <i>t</i>	4	35 (33) ^b	54 (53) ^b
3 ^c	OE <i>t</i>	OE <i>t</i>	24	—	66 (64) ^b
4			1		67 (69) ^b

^a Isolated yield.^b Eu–Mo–HKSF was used as the catalyst.^c The reaction temperature is 60 °C.

Preparation of double-metals-modified catalysts (Yb–Mo–HKSF)/ 1.82 g of Yb(NO₃)₃ was dissolved in 20 mL of mixed solution of acetone and water (3:1), then 9.0 g of Mo–HKSF was added into the solution and the mixtures were refluxed with magnetic stirring for 2 h. 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 h and then calcined by a muffle furnace at 400 °C for 4 h to obtain the double-metals Yb–Mo modified catalyst (Yb–Mo–HKSF). In addition, M–Mo–HKSF, M–V–HKSF and M–W–HKSF (M=In, Bi, Ti, Zr, Hf, Sc, Yb, Eu, herein, TiCl₄, ZrCl₄, HfCl₄, Sc(NO₃)₃, La(NO₃)₃, Yb(NO₃)₃, Eu(NO₃)₃, In(NO₃)₃ and Bi(NO₃)₃ were used as mental salts) were prepared in the similar procedures as those described above.

3.3. General procedure for the nitration of phenolic compounds

Catalyst (250 mg) was put into a glass vessel, and then phenol (94 mg, 1.0 mmol) and THF (3 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 h at room temperature. The catalyst was recovered by filtration, and the filtrate was extracted with dichloromethane (CH₂Cl₂). 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 2-nitrophenol (59 mg) and 4-nitrophenol (62 mg) in total 87% yield.

3.4. The recovery of the catalysts and the reusing procedure

The catalyst can be easily recovered from the reaction mixture just by filtration and reused for many times after it is activated by heating in an oven at 120 °C for 2 h. The recycled catalyst was used for the nitration of phenol. After filtration, the catalyst was recovered and the reaction mixture was extracted with dichloromethane (CH₂Cl₂). 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 2-nitrophenol (62 mg) and 4-nitrophenol (63 mg), total yield 90%.

3.4.1. 2,4-Dibromo-6-nitrophenol. A yellow solid: 26 mg, yield 9%, mp 114–116 °C, IR (KBr) ν 1531, 1392 cm⁻¹ (NO₂), 3070, 1242 cm⁻¹ (OH); ¹H NMR (CDCl₃, 300 MHz, TMS) δ 8.00 (1H, d, *J*=2.4 Hz, Ar), 8.25 (1H, d, *J*=2.4 Hz, Ar), 11.05 (1H, s, ArOH); MS (EI) *m/z* 297 (M⁺, 100), 267 (M⁺–30, 18.37), 239 (M⁺–58, 19.23), 223 (M⁺–74, 12.92). Anal. Calcd for C₆H₃Br₂NO₃ (%): requires C, 24.27; H, 1.02; N, 4.72%. Found: C, 24.55; H, 1.11; N, 4.54%.

3.4.2. 2-Bromo-4-nitrophenol. A yellow solid: 17 mg, yield 8%, mp 115–118 °C, IR (KBr) ν 1515, 1337 cm⁻¹ (NO₂), 3390, 1249 cm⁻¹ (OH); ¹H NMR (CDCl₃, 300 MHz, TMS) δ 6.21 (1H, s, ArOH), 7.13 (1H, d, *J*=9.0 Hz, Ar), 8.16 (1H, dd, *J*=9.0, 3.0 Hz, Ar), 8.44 (1H, d, *J*=3.0 Hz, Ar); MS (EI) *m/z* 219 (M⁺, 100), 189 (M⁺–30, 85.62), 171 (M⁺–46, 12.50), 145 (M⁺–74, 31.51), 119 (M⁺–100, 8.76). Anal. Calcd for C₆H₄BrNO₃ (%): requires C, 33.06; H, 1.85; N, 6.42%. Found: C, 33.09; H, 1.92; N, 6.6 8%.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.09.027

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