Catal Lett (2011) 141:1814–1820
DOI 10.1007/s10562-011-0721-0

An Efficient and Eco-friendly MoO_3–SiO_2 Solid Acid Catalyst for Electrophilic Aromatic Nitration with N_2O_5

**Xiaoming Ma · Bindong Li · Chunxu Lv ·
Ming Lu · Jian Wu · Linjie Liang**

Received: 27 June 2011 / Accepted: 5 October 2011 /

Abstract Electrophilic aromatic nitration using N_2O_5 as a green nitrating agent catalyzed by MoO_3–SiO_2 under mild conditions has been described. A series of MoO_3–SiO_2 catalysts with varying MoO_3 loadings (5–20 mol%) were prepared by sol–gel technique and characterized using FTIR, XRD, SEM, BET and NH_3–TPD to study its surface properties. MoO_3–SiO_2 shows good catalytic activity and reusability for the nitration of alkyl and halogen aromatics giving high conversions, but less efficiency for the deactivated aromatics. Reactions conducted under non-acidic conditions using N_2O_5 makes the process safe and environmentally friendly.

Keywords Nitration · Solid acid catalyst · N_2O_5 · Catalysis

1 Introduction

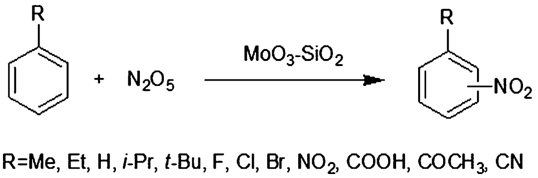
Nitration of aromatic compound is widely used in organic syntheses and industrial application. Many nitro-aromatic compounds are important intermediates as they are greatly utilizable in synthesis of drugs, pharmaceuticals, dyestuff, perfumes, plastics and explosives [1, 2]. The traditional method for nitration, involving use of a mixture of nitric and sulfuric acids, though still in widespread commercial use, suffers from many disadvantages, including the generation of large quantities of corrosive waste and in many cases the production of mixtures of isomers in which the most desirable one is not in high yield.

Therefore many efforts have been directed towards the development of environmentally friendly and reusable alternatives in recent years for using solid acids [3–5] and heteropoly acids. Different catalysts tested so far include H_3PO_4/ZSM-5 [6] sulfated zirconia [7, 8], WO_3/ZrO_2 [9] sulfated titania [10], SO_4^{2-}/TiO_2 doped with CeO_2 [11], sulfonated ion exchange resins (polystyrenesulfonic acid) [12] perfluorinated rare earth metal salts [13, 14], lithium, molybdenum, ytterbium on silica gel [15], $H_5PMo_{10}V_2O_{40}$ [16], $H_3PW_{12}O_{40}/SiO_2$ [17]. These catalysts effectively play the role of sulfuric acid in the reaction, assisting the formation of nitronium species. Despite this, a high concentration of nitric acid as nitrating agent is still required, and the need to be carried out at high temperatures for long times [13–15], for aromatics nitration whether liquid acid or solid acid as catalysts.

In recent years, various clean nitration approaches have been explored which involve nitrogen oxides such as NO_2 [18–22], N_2O_4 [23], and N_2O_5 [24] under "neutral" conditions. The non-acid method for aromatic nitration using NO_2–O_3 gives excellent conversion of a wide variety of aromatic compounds under mild conditions (Kyodai nitration) [19, 20]. However use of ozone adds to the cost of the process. Fe(III)-catalyzed nitration using NO_2–O_2 system requires a long reaction time (12–36 h) and large amount of nitrogen dioxide and catalyst [22]. N_2O_5 [25], as this is known to be a highly active nitrating agent, was first prepared over 150 years ago. Smallridge and co-workers [24] have recently developed a simple, fast and mild method for the nitration of aromatic rings, by using N_2O_5 catalyzed with $Fe(acac)_3$. The reaction is tolerant of a range of functional groups and gives almost quantitative yields.

In our efforts to develop a new, efficient and eco-friendly process for electrophilic aromatic nitration, we have prepared an eco-friendly solid acid catalyst of MoO_3–SiO_2

X. Ma · B. Li (✉) · C. Lv · M. Lu · J. Wu · L. Liang
Chemical Engineering College, Nanjing University of Science and Technology, Nanjing 210094, China
e-mail: libindong@mail.njust.edu.cn



Scheme 1

composites by sol–gel method, and applied in nitration of simple aromatic compounds using N_2O_5 as a green nitrating agent (Scheme 1). The results are presented in this paper.

2 Experimental

All chemicals were purchased from commercial sources and used for the reaction without further purification. All the products reported here are known compounds and their identity was determined by comparing their GC data with those of the authentic samples. Mass spectra were obtained with an automated FININIGAN Trace Ultra-Trace DSQ GC/MS spectrometer or a FININIGAN TSQ QUANTUM ULTRAAM (Thermal) LC/MS spectrometer. Conversions of substrates and product selectivities were calculated based on the GC analysis. The compositions of the nitration products were analyzed using a gas chromatograph (Agilent GC-6820) equipped with a 30 m × 0.32 mm × 0.5 mm HP-Innowax capillary column and a flame ionization detector.

2.1 Preparation of N_2O_5 [24]

Freshly distilled nitric acid (100%) was added slowly to a distillation flask containing P_2O_5. Slow distillation affords N_2O_5 with liberation of nitrogen oxides. The collected N_2O_5 is placed in a freezer until a solid is formed, the product is then warmed slowly to 10°C at which time any liquid nitrogen oxides are discarded, to leave a white/yellow solid. It is important that the N_2O_5 used is free of nitrogen oxide(s). Caution: N_2O_5 is highly corrosive and liberates toxic nitrogen oxides. Small amounts can be quickly neutralized with copious amounts of water.

2.2 Catalyst Preparation

A series of MoO_3–SiO_2 catalysts with varying molybdenum concentrations (5–20 mol%) were prepared by modification of sol–gel technique following the literature reported method [26]. Ammonium heptamolybdate (AHM) and tetraethyl orthosilicate (TEOS) were used as molybdenum and silica sources, respectively. In a typical procedure 20 mol% MoO_3/SiO_2 catalyst was synthesized by dissolving 14.11 g AHM in 40 mL distilled water at 80°C. This hot solution was added drop wise to the dry isopropyl alcohol solution of TEOS (48.0 g) with constant stirring. The resultant transparent greenish gel was aged at 120°C for 12 h and calcined at 500°C in air in a muffle furnace for 12 h. Similarly catalysts with 5, 10, 15 mol% Mo loadings were also prepared. Pure high surface area silica catalyst was prepared for comparison by adding 52 g TEOS to 30 g dry isopropyl alcohol; to this mixture 0.02 g ammonia solution (25%) was slowly added with constant stirring. The transparent white gel thus obtained was air dried and calcined in a muffle furnace at 500°C for 12 h.

2.3 Catalyst Characterization

XRD analysis was carried out with BRUKER AXS German, XRD system, D8ADVANCE using Cu-Kα ($\lambda = 1.542$ Å) radiation, the diffractograms were recorded in 10–80° range of 2θ. Temperature programmed desorption of ammonia (NH_3–TPD) was carried out using Micromeritics Autochem 2920 instrument. BET surface area and pore size was estimated by NOVA 1200 Quanta chrome. The FTIR spectra were recorded on Perkin-Elmer 1720 single beam spectrometer using KBr disks. SEM images were recorded using a Tungsten source on JEOL JSM-6380LV instrument.

2.4 Nitration of Aromatic Compounds: Typical Procedure

To a cooled (0°C) vigorously stirred mixture of the MoO_3–SiO_2 (20 wt% of substrate) and toluene (5 mmol) was added a solution of N_2O_5 (5 mmol) and CH_2Cl_2 (5 mL). The reaction was carried out at 0°C for 1 h, and then the catalyst was filtered off and washed with some CH_2Cl_2, which was added to the filtrate. The CH_2Cl_2 solution was washed with a few portions of saturated $NaHCO_3$ solution, then several times with water, dried with $MgSO_4$, and examined by GC.

3 Results and Discussion

3.1 Catalyst Characterization

The specific surface areas and acidity of all the catalysts are listed in Table 1. A very high surface area of 630 m^2/g was observed in the case of pure silica. It is evident from the BET data of the samples that the specific surface area decreased when increasing the MoO_3 loading from 5 to 20 mol%. The decrease in the specific surface area can be explained by the different distribution of MoO_3 on the SiO_2 surface, which has a low surface area. The surface area decreases at higher coverages since the pores are partially

Table 1 Surface area and acidity of the MoO_3–SiO_2

Catalyst	Surface area (m^2/g)	Average pore diameter (Å)	Pore Volume (cc/g)	NH_3 desorbed (mmol/g)
Silica	630	18.42	0.45	0.04
5 mol% MoO_3–SiO_2	565	20.62	0.58	0.38
10 mol% MoO_3–SiO_2	372	47.66	0.88	0.86
15 mol% MoO_3–SiO_2	270	52.85	0.71	1.21
20 mol% MoO_3–SiO_2	150	37.93	0.28	1.14

blocked. At even higher coverages, crystallization of MoO_3 takes place, filling the pores of the support. NH_3–TPD experiments were performed to determine the strength of acid sites present on the catalyst surface, together with total acidity. The results are given in Table 1. The ammonia thermodesorption results give clear evidence for the truth that the acidity and acid strength of the catalyst are majorly due to Mo species. It was observed that the acidity of SiO_2 was very low (0.04 mmol/g), and the catalyst acidity and acid strength were increased as the percentage of Mo loading was increased. The catalyst with 15 mol% Mo loading shows the best result (1.21 mmol/g) although the 20 mol% Mo loading catalyst also has higher acidity (1.14 mmol/g). The development of acid sites was related to the coordinatively unsaturated Mo^{6+} species on the surface (Lewis acid sites) [27] and to the hydroxyl groups formed by protonating the bridging Si=O=Mo or terminal Mo=O bonds on the surface (Brønsted acid sites) of catalysts [28, 29]. The decrease in the acidity at high loading could be due to the formation of bulk Molybdenum oxide.

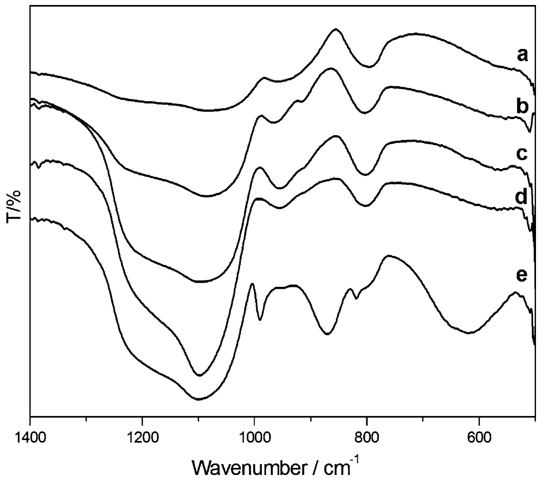


Fig. 1 FTIR spectra of **a** SiO_2, **b** 5 mol% MoO_3–SiO_2, **c** 10 mol% MoO_3–SiO_2, **d** 15 mol% MoO_3–SiO_2, **e** 20 mol% MoO_3–SiO_2

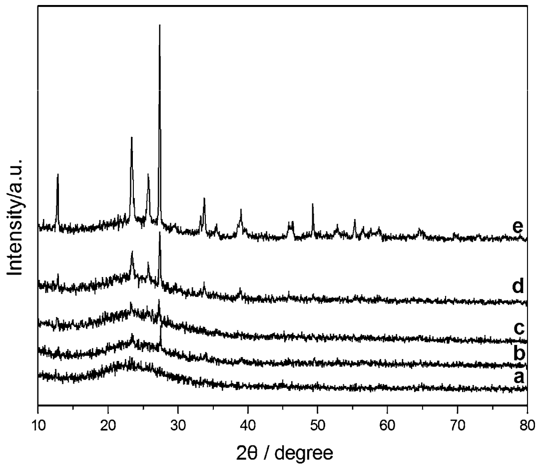


Fig. 2 XRD patterns of **a** SiO_2, **b** 5 mol% MoO_3–SiO_2, **c** 10 mol% MoO_3–SiO_2, **d** 15 mol% MoO_3–SiO_2, **e** 20 mol% MoO_3–SiO_2

The FTIR spectra of all the catalyst samples prepared by sol–gel technique are presented in Fig. 1. The intensive bands at around 1300–1000 cm^{-1} and 800 cm^{-1} due to asymmetric stretching, symmetric stretching and bending modes of Si–O. The band at 990 cm^{-1} and 870 cm^{-1}, which appeared in the case of higher loading of Mo, indicated the formation of the α-MoO_3. The broad band at around 960 cm^{-1} with a shoulder at about 910 cm^{-1} for all the samples is the sign of supported molybdenum species [30], however the spectra of the low loading samples mainly show the bands of the SiO_2 (Fig. 1b–e).

The XRD patterns of the pure silica and 5–20 mol% MoO_3–SiO_2 catalysts prepared by sol–gel method are depicted in Fig. 2. No apparent diffraction peaks associated with the bulk MoO_3 phase were detected at low Mo loading (Fig. 2b, c), the patterns show the amorphous nature just like pure silica (Fig. 2a). Catalysts with 15 and 20 mol% Mo (Fig. 2d, e) loading showed highly crystalline nature with intense peaks at $2\theta = 12.7°$, 23.4°, 25.7° and 27.3° corresponding to the α-MoO_3 in the orthorhombic phase [31]. It is evident from the XRD patterns of the catalysts there is a uniform distribution of amorphous molybdenum oxo species on the amorphous silica up to 10 mol% Mo loading, nevertheless crystalline MoO_3 is formed on amorphous silica support at higher Mo loading.

Figure 3 represents the results of scanning electron micrograms (SEM) recorded in order to demonstrate the morphology and particle size of the catalysts. As can be seen, the surface of SiO_2 is very smooth, however images for MoO_3–SiO_2 clearly shows distinct difference in the morphology from that of SiO_2. The differences in SEM images thus, illustrate that incorporation of MoO_3 changes the morphological structure of SiO_2 surface considerably, and provide the back up to the result observed by XRD analysis.

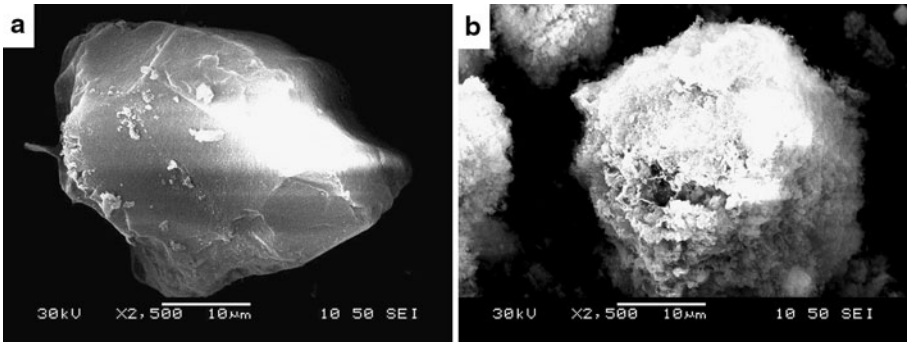


Fig. 3 SEM images of **a** SiO_2, **b** 15 mol% MoO_3–SiO_2

3.2 Catalytic Activity

3.2.1 *Influence of MoO_3–SiO_2 with Different Mo Loading*

In order to study various reaction parameters for aromatic compounds, we chose toluene as a model substrate. Nitration of toluene with N_2O_5 was carried out using series of MoO_3–SiO_2 catalysts with different Mo loadings on silica to optimize the reaction conditions and the results are given in Table 2 and Fig. 4.

The effect of different Mo loading over SiO_2 on the nitration reaction in the presence of 9.2 mg (20 wt% to toluene) MoO_3–SiO_2 at 0°C, using toluene: N_2O_5 molar ratio 1:1 was investigated. The results are also compared with blank reaction (without catalyst) and pure silica (Table 2, entry 1, 2). As expected SiO_2 showed little catalytic activity (65% toluene conversion), however the reaction catalyzed by MoO_3–SiO_2 with different Mo loadings proceeded well and a remarkable increase in toluene conversion from 72 to 94% was obtained. It was observed that as Mo loading increased the conversion of toluene also increased, and got a maximum toluene conversion of 94% when used 15 mol% MoO_3–SiO_2, although increasing the Mo loading to 20 mol% no marked change in toluene conversion and product distribution were observed. Thus 15 mol% MoO_3–SiO_2 was used as the preferred catalyst for further studies.

The effect of catalyst amount on the given reaction protocol was investigated. It was found that the toluene conversion was increased with the amount of 15 mol% MoO_3–SiO_2 increased from 5 to 20 wt% (Table 2, entries 5, 7–10). On further investigation increasing the amount to 25 wt% little change in toluene conversion and selectivity were observed and hence 20 wt% MoO_3–SiO_2 catalyst was chosen as the optimum amount.

The nitration of toluene was followed at different times in the presence of 9.2 mg (20 wt% to toluene) of 15 mol% MoO_3–SiO_2 at 0°C, using toluene: N_2O_5 molar ratio 1:1. The results are shown in Fig. 4. From Fig. 4, it was observed that there was gradual increase of the toluene

Table 2 Influence of MoO_3–SiO_2 on toluene nitration

Entry	Catalyst	Catalyst amount (wt%)[a]	Conversion (%)[b]	Product distribution (%)[b]			*o*/*p* Ratio[b]
				Orhto	Meta	Para	
Effect of Mo loading							
1	Blank	–	64	56.4	3.0	40.6	1.38
2	SiO_2	20	65	57.8	2.7	39.5	1.46
3	5 mol% MoO_3–SiO_2	20	72	56.1	2.2	41.7	1.34
4	10 mol% MoO_3–SiO_2	20	80	54.2	2.7	43.1	1.25
5	15 mol% MoO_3–SiO_2	20	94	54.9	2.3	42.8	1.28
6	20 mol% MoO_3–SiO_2	20	92	55.9	2.5	41.6	1.34
Effect of catalyst loading							
7	15 mol% MoO_3–SiO_2	5	70	53.9	2.9	43.2	1.25
8	15 mol% MoO_3–SiO_2	10	82	54.2	3.1	42.7	1.27
9	15 mol% MoO_3–SiO_2	15	89	53.8	2.4	43.8	1.23
10	15 mol% MoO_3–SiO_2	25	91	55.3	2.7	42.0	1.32

Reaction conditions: toluene (5 mmol), N_2O_5 (5 mmol), CH_2Cl_2 (5 mL), 1 h at 0°C

[a] Catalyst amount: Weight ratio to toluene (46 mg, 5 mmol)

[b] Calculated from original GC data

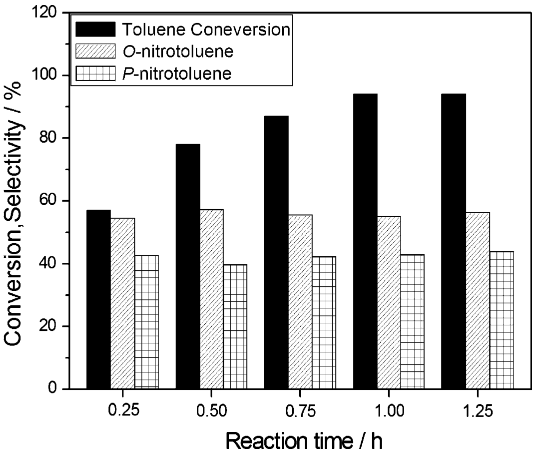


Fig. 4 Effects of reaction time on toluene nitration. Reaction conditons: toluene (5 mmol), N_2O_5 (5 mmol), CH_2Cl_2 (5 mL), 15 mol% MoO_3–SiO_2 (9.2 mg, 20 wt% to toluene), 0°C

conversion up to 1 h (the conversion was 94%) and thereafter no notable increase of the conversion is noticed, suggesting the influence of time on conversion. With increasing the time, more number of nitronium ions (NO_2^+) are formed which indeed increase the conversion of toluene. In addition, the product distribution does not affect significantly.

Numerous papers have reported that strong acidic catalysts can promote the formation of electrophilic nitronium ions (NO_2^+) from N_2O_5 [32, 33]. This reaction was related to a normal electrophilic aromatic substitution mechanism involving the nitronium ion (NO_2^+) via N_2O_5 over solid acid catalyst [24, 34]. The results given in Table 2 suggested clearly that, the progressive increase of activity was attributed to an enhancement of the extent of MoO_3 present and express the progressive increase of the concentration of active sites involved in the catalyzed reaction. The observed catalytic activities appear to be consistent with the acidic property of catalysts, indicating that the high nitration conversion can be obtained with strong acidic catalyst. In the present work the increase of surface acidity could be responsible for the increase of catalytic activity. The maximum catalytic activity of 15 mol% MoO_3–SiO_2 is attributed to the higher acidity of the catalyst (1.21 mmol/g).

Compared to the 1.79 ratio of *o*/*p* of the nitration of toluene in HNO_3/H_2SO_4 [35], the nitration with N_2O_5 catalyzed by MoO_3–SiO_2 has regioselectivity about 1.3, and no marked change of the selectivity was observed when nitration was done using catalysts with various Mo loading. This is due to occurrence of the reaction inside the larger pores of the catalyst in the same manner as in the bulk phase.

3.2.2 Nitration of Different Aromatic Substrates

Successful catalytic nitration of toluene with N_2O_5 has promoted us to test the general scope and versatility of this procedure. A variety of simple aromatic compounds were subjected to the nitration reaction and results are presented in Table 3. The electrophilic aromatic nitration proceeded very well for alkyl and halogen aromatic substrates, but less efficiency for some deactivated aromatics (such as nitrobenzene, benzoic acid, acetophenone and benzonitrile). For the nitration of benzene, fluorobenzene, chlorobenzene and bromobenzene, moderate conversions were obtained and only mono-nitro products were detected

Table 3 Nitration of different aromatic substrates

Entry	R	Conversion (%)[c]	Product distribution (%)[c]			*o*/*p* Ratio[c]
			Ortho	Meta	Para	
1[a]	F	76	38	–	62	0.61
2[a]	Cl	72	41.2	0.4	58.4	0.70
3[a]	Br	58	43.6	–	56.4	0.77
4[b]	H	78	–	–	–	–
5	Et	82	44.6	1.7	53.7	0.83
6	*i*-Pr	83	22.3	3.6	74.1	0.30
7	*t*-Bu	87	14.8	5.3	79.9	0.18
8[a]	NO_2	7	–	100	–	–
9[a]	COOH	15	21.2	66.6	12.2	–
10[a]	$COCH_3$	13	35.4	54.2	10.4	–
11[a]	CN	11	11.5	68.2	20.3	–

Reaction conditions: substrate (5 mmol), N_2O_5 (5 mmol), CH_2Cl_2 (5 mL), catalyst amount (20 wt% to substrate), 1 h at 0°C

[a] Reaction carried out at 30°C for 2 h

[b] Reaction carried out at 20°C for 1 h

[c] Calculated from original GC data

Table 4 Reuse of MoO_3–SiO_2 in the nitration of toluene

Entry	Run	Conversion (%)[a]	Product distribution (%)[a]			*o*/*p* Ratio[a]
			Ortho	Meta	Para	
1	Fresh	94	54.9	2.3	42.8	1.28
2	1st run	91	53.5	2.1	44.4	1.20
3	2nd run	90	55.8	3.1	41.1	1.36
4	3rd run	86	55.1	2.6	42.3	1.30
5	4th run	85	54.2	2.0	43.8	1.24

Reaction conditions: toluene (5 mmol), N_2O_5 (5 mmol), CH_2Cl_2 (5 mL), 15 mol% MoO_3–SiO_2 (9.2 mg, 20 wt% to toluene), 1 h at 0°C

[a] Calculated from original GC data

(Table 3, entries 1–4). As seen from the table, nitration of alkyl aromatic compounds gave high conversion, and the product distribution showed *para*-selectivity which mainly due to the steric effect of the substituted group, and no nitration of the side-chain was observed (Table 3, entries 5–7). Attempts to nitrate deactivated aromatic rings, such as nitrobenzene, benzoic acid, acetophenone and benzonitrile, using N_2O_5: substrate molar ratio 1:1 at 30°C for 2 h without any catalyst resulted in recovery of unreacted starting material. Fortunately, the nitration of deactivated substrates showed a positive impact of using the MoO_3–SiO_2 as the catalyst, although this protocol showed less efficiency compared with the application for the alkyl and halogen aromatics nitration.

As is shown in the table (Table 3, entries 8–11), under the reaction conditions employed, the conversion of nitrobenzene, benzoic acid, acetophenone and benzonitrile were respectively 7, 15, 13 and 11%. However, it is interesting to note that nitration of compounds containing a carbonyl group (e.g. benzoic acid and acetophenone) using this methodology, which produce increased amounts of the *o*-isomer. It is known that nitration of such carbonyl compounds under non-acidic conditions using NO_2/O_3 (Kyodai Nitration) afford dramatically different ratio of regioisomers in comparison with e.g. mixed-acid [36], and the active nitrating agent is thought to be N_2O_5 which is formed in situ from NO_2 and O_3. It has been speculated that in the absence of acidic protons the carbonyl group is not protonated leading to *o*-nitration whilst the protonated carbonyl group is *meta* directing.

3.3 Catalyst Reusability

The recycling performance of 15 mol% MoO_3–SiO_2 was investigated by the nitration of toluene with N_2O_5 under the identical conditions (Table 4). In order to regenerate the catalyst after 1 h reaction time, it was separated by filtration, washing with water, acetone and diethyl ether, dried at 120°C for 2 h and reused in next reaction. A marginal decrease in toluene conversion was observed when the catalyst was used during five cycles which could be attributed to the slight leaching of the active species from the surface due to the use of water for the separation of the catalyst from the reaction mixture.

4 Conclusion

In conclusion, MoO_3–SiO_2 catalysts prepared by sol–gel method were used successfully for nitration of simple aromatic compounds, and an enhanced regionselectivity was achieved at the nitration progress. Furthermore, the MoO_3–SiO_2 catalysts could be easily separated from the reaction mixture and reused 5 cycles without significant loss in its activity. In addition, this procedure avoids using mixed-acid making the process environmentally friendly. However, future work on increasing the nitration conversion of deactivated aromatics with this mild reaction system would be further studied.

Acknowledgments We are grateful for the financial support from the National Nature Science Foundation of China-Academy of Engineering Physics (No. 10976014) and Nature Science Foundation of Jiangsu Province (No. BK2011697).

References

1. Schofield K (1980) Aromatic nitration. Cambridge University Press, Cambridge
2. Olah GA, Malhotra R, Narang SC (1989) Nitration: methods and mechanisms. VCH, New York
3. Dagade SP, Waghmode SB, Kadam VS, Dongare MK (2002) Appl Catal A 226:49
4. Dagade SP, Kadam VS, Dongare MK (2002) Catal Commun 3:67
5. Patil PT, Malshe KM, Dagade SP, Dongare MK (2009) Catal Commun 4:429
6. Kalbasi RJ, Ghiaci M, Massah AR (2009) Appl Catal A 353:1
7. Parida KM, Pattnayak PK (1997) Catal Lett 47:255
8. Yadav GD, Nair JJ (1999) Catal Lett 62:49
9. Brei VV, Prudius SV, Melezhyk OV (2003) Appl Catal A 239:11
10. Sunajadevi KR, Sugunan S (2005) Catal Commun 6:611
11. Mao W, Ma H, Wang B (2009) J Hazard Mater 167:707
12. Wright OL, Teipel J, Thoennes D (1965) J Org Chem 30:1301
13. Shi M, Cui SC (2002) J Fluoine Chem 113:207

14. Shi M, Cui SC (2002) Chem Commun 7(9):994
15. Shi M, Cui SC (2003) Adv Synth Catal 345:1329
16. Heravi MM, Bakhtiari K, Benmorad T, Bamoharram FF, Oskooie HA, Tehrani MH (2007) Monatsh Chem 138:449
17. Zhao XQ, Han YT, Sun XL, Wang YJ (2007) Chin J Catal 28:91
18. Sato H, Hirose K (1998) Appl Catal A 174:77
19. Mori T, Suzuki H (1995) Synlett 5:383
20. Peng X, Suzuki H (2001) Org Lett 3:3431
21. Peng X, Suzuki H, Lu C (2001) Tetrahedron Lett 42:4357
22. Suzuki H, Yonezawa S, Nonoyama N, Mori N (1996) J Chem Soc Perkin Trans 1:2385
23. Iranpoor N, Firouzabadi H, Zolfigol MA (1998) Syn Commun 28:2773
24. Bak RR, Smallridge AJ (2001) Tetrahedron Lett 42:6767
25. Agrawal JP, Hodgson RD (2007) Organic chemistry of explosives. Wiley, London
26. Umbarkar SB, Biradar AV, Mathew SM, Shelke SB, Malshe KM, Patil PT, Dagde SP, Niphadkar SP, Dongare MK (2006) Green Chem 8:488
27. Kataoka T, Dumesic JA (1988) J Catal 112:66
28. Vordonis L, Koutsoukos PG, Lycourghiotis A (1986) J Catal 98:296
29. Vordonis L, Koutsoukos PG, Lycourghiotis A (1990) Colloids Surf 50:353
30. Deliche R, Auissi A, Bettahar MM, Launey S, Fournier M (1996) J Catal 164:16
31. Kido A, Iwamoto H, Azuma N, Ueno A (2002) Catal Surv Asia 6:45
32. Kuba MG, Prins R, Pirngruber GD (2007) Appl Catal A 333:78
33. Barletta B, Bolzacchini E, Meinardi S, Oralandi M, Rindone B (2000) Environ Sci Technol 34:2224
34. Suzuki H, Murashima T, Kozai I, Mori T (1993) J Chem Soc Perkin Trans 1:1591
35. Wang PC, Lu M (2011) Tetrahedron Lett 52:1452
36. Suzuki H, Murashima T (1994) J Chem Soc Perkin Trans 1:903