Fast and Efficient Nitration of Salicylic Acid and Some Other Aromatic Compounds over H_3PO_4/TiO_2-ZrO_2 Using Nitric Acid

Kalbasi, Roozbeh Javad*,[a,b]   Massah, Ahmad Reza*,[a,b]
Zamani, Farzad[a]   Javaherian Naghash, Hamid[b]

[a] *Department of Chemistry, Islamic Azad University, Shahreza Branch, 311-86145, Shahreza, Isfahan, Iran*
[b] *Razi Chemistry Research Center, Islamic Azad University, Shahreza Branch, Shahreza, Isfahan, Iran*

TiO_2-ZrO_2 (1/1)-surf with Ti and Zr molar ratio of 1/1 was prepared with surfactant through a sol-gel method. The optimum experimental condition was investigated for nitration of salicylic acid. Then, a number of nitration reactions were carried out with a variety of aromatic compounds in the optimum condition. The 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst showed good selectivity and yield in a short time for the nitration of salicylic acid and some other aromatic compounds.

Keywords nitration, H_3PO_4/TiO_2-ZrO_2, nitric acid, salicylic acid, aromatic compound

Introduction

Nitration of organic compounds is one of the very important processes in chemical industries. Nitro aromatic compounds are utilized extensively as chemical feed stocks for a wide range of useful materials. Among the aromatic nitro compounds, 5-nitrosalicylic acid is a very important intermediate for the pharmaceutical industry. The derived amine (mesalazine) has been selected as a drug for ulcerative colitis for many years.[1] The 5-nitrosalicylic acid is currently obtained through nitration processes of salicylic acid by means of different nitrating systems such as mixed acid (nitric acid/sulfuric acid, molar ratio＝3) or 70% nitric acid solutions.[2,3] In a previous investigation,[4] the authors have shown that runaway phenomena can occur during the nitration process of salicylic acid by means of nitric acid/acetic acid mixtures as a result of polynitration reactions, which take place when the thermal control of the process is lost. In particular, successive nitration of 5-nitrosalicylic acid and by-product (3-nitrosalicylic acid) leads to the formation of explosive picric acid.[5]

A major problem associated with the industrial nitration technology is that the usage of corrosive liquid phase including nitric acid-sulfuric acid mixture generates large amounts of waste that is very costly to treat. Over-nitration, oxidation of by-products and poor selectivity are other problems.[6] To overcome these problems, a considerable effort has been put into developing heterogeneously catalyzed reactions for the liquid and vapor phase nitration using solid acid catalysts. In this contest, a lot of attempts have been made to find an efficient catalyst for the nitration of aromatics and substituted aromatics. Many reagents and catalysts have been introduced for the nitration of aromatic compounds such as acetyl nitrate, benzoyl nitrate, trimethylsilyl nitrate,[7] *N*-nitropyridinium salts, nitrogen oxide,[8] $NaHSO_4 \cdot H_2O$, $Mg(HSO_4)_2$, and oxone,[9,10] sulfonated polyorganosiloxanes[11,12] and acidic resins.[13]

Phosphate-based solid acids have already been quite efficacious in several industrially important acid-demanding reactions.[14,15] In addition, phosphate seems to enhance catalytic properties, to stabilize surface area and crystal phase, to improve the surface acidity and to make the impregnated material porous.[16]

Recently, it has been observed that H_3PO_4/TiO_2-ZrO_2 (1/1)-surf showed high thermal stability, low catalytic deactivation and very good selectivity for Beckmann rearrangement,[17] acylation of phenol[18] and Fries rearrangement.[19] These data showed that H_3PO_4/TiO_2-ZrO_2 (1/1)-surf had a good activity and selectivity for the acid catalyzed reactions.

In this paper, the efficacy of the H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst is presented for the nitration of salicylic acid to 5-nitrosalicylic acid. The activity and regio selectivity of this catalyst for the nitration of some other aromatic compounds are also reported.

Experimental

Preparation of the catalyst

TiO_2-ZrO_2 (1/1)-surf was used as the support, which was prepared by a sol-gel method[20,21] and is denoted as TiO_2-ZrO_2 (1/1)-surf.[17] A series of catalysts with varying H_3PO_4 contents were prepared by impregnating calculated amounts of H_3PO_4 dissolved in deionized water on the TiO_2-ZrO_2 (1/1)-surf support. The impreg-

---

* E-mail: rkalbasi@iaush.ac.ir, massahar@iaush.ac.ir; Fax: 0098-321-3293095; Tel.: 0098-321-3292072
Received May 26, 2009; revised October 19, 2009; accepted November 19, 2009.

nated catalysts were dried at 110 ℃ for 12 h and then calcined in air at 500 ℃ for 6 h.[17]

Typical procedure for the synthesis of nitro aromatic compounds

To a round-bottomed flask containing a mixture of 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst (0.07 g, 0.23 mmol), nitric acid (65%, 1 mmol), dichloromethane (5 mL) and salicylic acid (1 mmol) was added, and the resulting mixture stirred at reflux temperature. The progress of the reaction was monitored by GC (Varian CP3800). At the end of the reaction, the catalyst was separated by filtration and washed with ethyl acetate (10 mL×2). The filtrate was washed sequentially with 5% aqueous solution of sodium bicarbonate (2.5 mL), and water (5 mL), and then dried with anhydrous $MgSO_4$. The evaporation of solvent, followed by column chromatography of the crude mixture on silica gel using *n*-hexane and ethyl acetate as eluent, afforded 3-nitrosalicylic acid and 5-nitrosalicylic acid in a 26∶74 ratio in pure form. The overall yield was 83%. The conditions of nitration reaction were optimized for salicylic acid, and consequently the nitration of some other aromatic compounds was performed in the optimum conditions.

Results and discussion

Catalyst characterization

The catalyst was characterized using a variety of physical methods, including FT-IR (Fourier transform infrared), XRD (X-ray diffraction), XRF (X-ray fluorescence) and BET (Brunauer-Emmett-Teller) surface area measurements.[17] The acidity of the catalyst was determined using pyridine adsorption-desorption.[18] In order to verify the presence of minor phases, SEM (scanning electron microscopy) and EDS (energy dispersive spectrum) analyses were carried out on TiO_2-ZrO_2 (1/1)-surf before and after the loading of H_3PO_4 (by SERON, AIS-2100). The EDS data of the calcined TiO_2-ZrO_2 (1/1)-surf and 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf are presented in Figure 1. As can be seen, Ti/Zr ratio obtained from the corresponding EDS data for the TiO_2-ZrO_2 (1/1)-surf and 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf samples were approximately similar as expected. Moreover, the results from EDS analyses are presented in Table 1. The percentage of P in the loaded catalyst was 7.27 wt%, which was close to the value set in the catalyst design.

Table 1 EDS results of TiO_2-ZrO_2 (1/1)-surf before and after the loading of H_3PO_4

Sample	Ti	Zr	O	P
TiO_2-ZrO_2 (1/1)-surf	41.07%	49.62%	8.7%	—
25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf	31.79%	40.08%	20.48%	7.27%

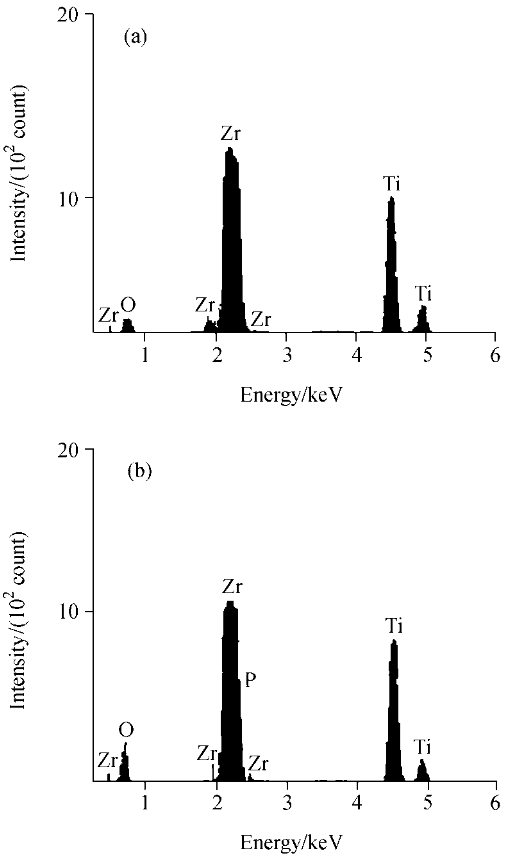


Figure 1 EDS diagrams of catalyst before and after the loading of H_3PO_4: (a) TiO_2-ZrO_2 (1/1)-surf and (b) 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf.

In addition, SEM images show the external morphology of the calcined catalyst before (Figures 2a, 2b) and after the loading of phosphoric acid (Figures 2c, 2d), from which the phosphoric acid layer on TiO_2-ZrO_2 (1/1)-surf can be seen (Figures 2c, 2d).

XRD patterns for calcined samples at 500 ℃ after loading of H_3PO_4 with different concentrations are shown in Figure 3 (by Bruker D8ADVANCE, Cu Kα radiation). TiO_2-ZrO_2 (1/1)-surf before loading H_3PO_4 shows an amorphous form, but after this loading the peaks corresponding to the crystalline TiO_2 phase and crystalline ZrO_2 phase are observed. In the TiO_2 spectrum, the peak at $2\theta = 25.5°$ corresponds to the anatase crystalline phase and in the ZrO_2 spectrum the peak at $2\theta = 30.0°$ corresponds to the tetragonal crystalline phase.[22-25]

Catalytic activity

One of our major concerns was to examine the activity and the regio selectivity of this catalyst for the nitration of salicylic acid and some other aromatic compounds. Accordingly, a number of reactions were carried out with a variety of aromatic compounds, after ascertaining the optimum experimental conditions. The results are summarized in Table 2. The catalyst was very effective towards activated aromatic compounds (Entries 2—5, Table 2) and the corresponding

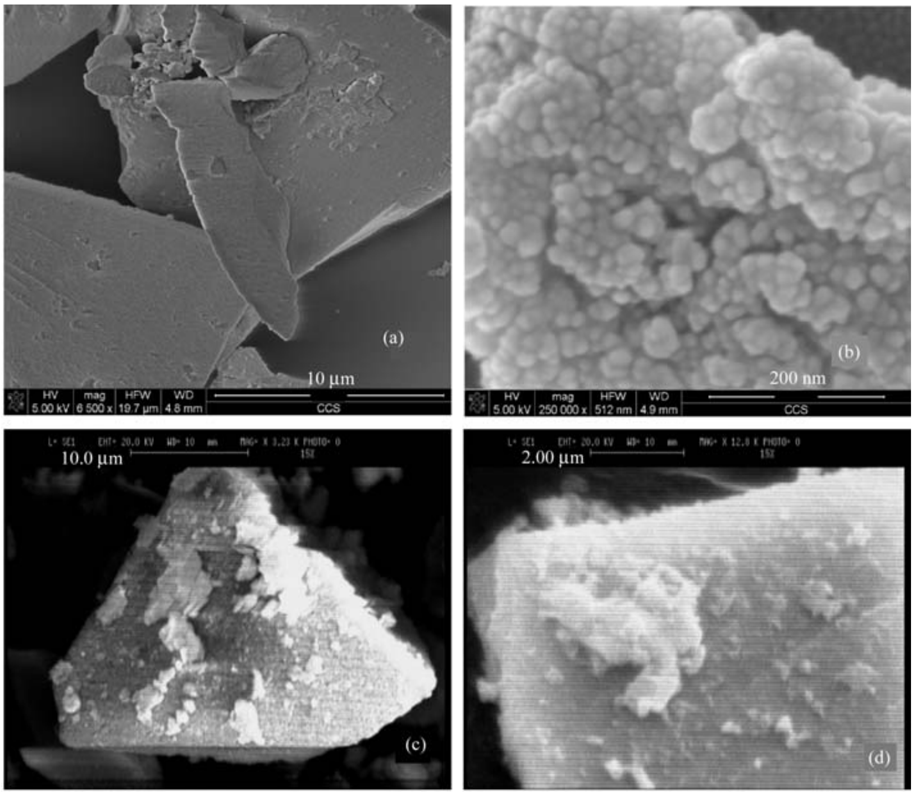


Figure 2 SEM images of samples at different magnifications: (a) TiO_2-ZrO_2 (1/1)-surf, (b) TiO_2-ZrO_2 (1/1)-surf, (c) 15 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf, (d) 15 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf.

Table 2 Mono-nitration of aromatic compounds

Entry	Substrate	Product[b]	Total yield[a]/ %	Time/min	Molar ratio (aromatic compound ∶ nitric acid)
1	Benzene	Nitrobenzene	98	25	1∶1.5
2	Phenol	(a) 4-Nitrophenol (90%), (b) 2-Nitrophenol (10%)	96	1	1∶1
3	*p*-Cresol	(a) 2-Nitro-*p*-cresol (95%), (b) 3-Nitro-*p*-cresol (5%)	90	Immediately	1∶1
4	1-Naphthol	4-Nitro-1-naphthol	75	1	1∶1.5
5	2-Naphthol	1-Nitro-2-naphthol	65	1	1∶1.5
6	Anthracene	9-Nitroanthracene	70	5	1∶1.5
7	Biphenyl	4-Nitrobiphenyl	43	15	1∶1.5
8	Benzoic acid	3-Nitrobenzoic acid	30	30	1∶2.8
9	Benzonitrile	3-Nitrobenzonitrile	28	30	1∶2.8
10	Nitrobenzene	1,3-Dinitrobenzene	25	30	1∶2.8
11	Benzophenone	3-Nitrobenzophenone	36	25	1∶2.8
12	Bromobenzene	(a) 1-Bromo-4-nitrobenzene (90%), (b) 1-Bromo-2-nitrobenzene (10%)	70	15	1∶2.8
13	Chlorobenzene	(a) 1-Chloro-4-nitrobenzene (90%), (b) 1-Chloro-2-nitrobenzene (10%)	70	15	1∶2.8
14	Salicylic acid	(a) 5-Nitrosalicylic acid (74%), (a) 3-Nitrosalicylic acid (26%)	83	5	1∶1

[a] Isolated yield. [b] Isomeric ratio was estimated using ^{1}H NMR and ^{13}C NMR spectra of the crude products [Reaction conditions: catalyst (0.07 g), dichloromethane (5 mL), reflux temperature].

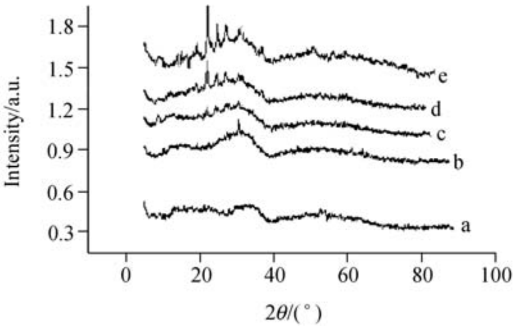


Figure 3 XRD patterns for the calcinated catalysts: (a) TiO_2-ZrO_2 (1/1)-surf, (b) 5 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf, (c) 15 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf, (d) 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf and (e) 35 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf.

nitro products were readily obtained in good to excellent yields (65%—96%). Moderately activated aromatic compounds also underwent nitration in good yields (Entries 12—14, Table 2). It is notable that poly aromatic hydrocarbons, *viz.*, anthracene (Entry 6, Table 2) and biphenyl (Entry 7, Table 2) underwent regioselective nitration under the same reaction conditions. Moreover, the catalyst was effective towards inactivated compounds. Interestingly, for a substrate amenable to facile oxidation, there were not any oxidation products. Thus, the reaction of *p*-cresol (Entry 3, Table 2) led only to nitration products. It is considerable that these reactions were carried out in a short time in comparison with other reported procedures. A preparative scale reaction was performed using 3 g of salicylic acid, and the reaction worked well with an isolable yield of 83% (Entry 14, Table 2).

The influence of various reaction parameters such as solvent, reaction temperature, amount of loaded H_3PO_4 and catalyst, feed ratio of salicylic acid to nitric acid and recyclability of the catalyst has been studied to optimize reaction conditions.

Improvement of H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalytic activity was made by optimizing the amount of loaded H_3PO_4. The variation of loaded H_3PO_4 (15—35 wt%) has different effects on the yield and selectivity of the catalyst (see Figure 4). In the presence of the optimized catalyst (25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf), over 70% selectivity and about 85% yield were observed. In order to decrease the amount of by-products caused by oxidation, H_3PO_4 was used for treating TiO_2-ZrO_2 (1/1)-surf. The acidity of H_3PO_4 is lower than H_2SO_4 which has been used in other researches.[26,27]

In general, the most important role of H_3PO_4 in this new catalyst is to destroy the strong Brønsted acid sites and substitute them with weak Brønsted sites. In this condition, the weak Brønsted acid sites were increased. Therefore, it could be expected that we had a milder catalyst, which shows good yield and selectivity for the nitration reaction without producing any polynitration and oxidation products. According to Tanabe's hypothesis,[28] the surface structure of TiO_2-ZrO_2 can be represented as I and II in Scheme 1. Both structures (I) and (II) contain Lewis acidic and basic sites. So it can be seen that TiO_2-ZrO_2 and TiO_2-ZrO_2-surf just show Lewis acid sites and Brønsted acid sites are not available. On the other hand, with loading H_3PO_4 on these supports two things happened: Some of loaded H_3PO_4 removes the adsorbed water on the Lewis sites (structures I and II), which leads to increasing Lewis acid sites of the obtained catalyst (Zr^{4+} and Ti^{4+}).[16] Some other H_3PO_4 that loaded by esterification of remaining M-OH groups on the support produces weak Brønsted acid sites (P-OH) (Schemes 1 and 2). As a result, the 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst has the maximum yield and the best selectivity for 5-nitrosalicylic acid in this condition.

In order to investigate effect of the support [TiO_2-ZrO_2 (1/1)-surf] on the nitration reaction, we used H_3PO_4 (with the same ratio of the optimized catalyst) without any support as catalyst in the nitration of salicylic acid by keeping other parameters constant. After 35 min, 60% selectivity and about 65% yield were observed. Therefore, TiO_2-ZrO_2 (1/1)-surf as a support is very useful for the nitration reaction.

The effect of temperature on the nitration of salicylic acid was also studied. The reaction was carried out in the presence of 0.07 g of 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf using salicylic acid∶nitric acid molar ratio 1∶1 and the reaction temperatures were varied from room temperature (25 ℃) to 40 ℃. The results are presented in Table 3. It was observed that with increase of the reaction temperature from 25 to 40 ℃, the salicylic acid yield was increased from 75% to 83%. In addition, the selectivity was also raised with increasing temperature. In general, when the reaction is carried out at lower temperature, the conversion decreases. We believe that increasing the temperature is apparently favorable for accelerating the reaction.

Table 3 Effect of temperature

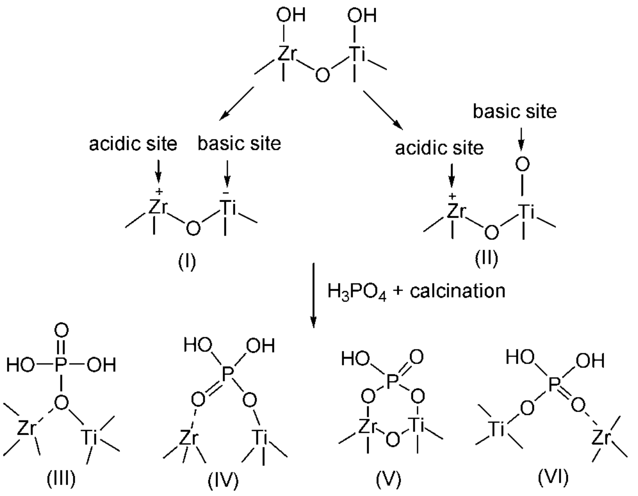
Temperature/℃	Yield/%	Selectivity/%		Time/min
		para	*ortho*	
Room temperature	75	70	30	60
40	83	74	26	5

Reaction conditions: dichloromethane (5 mL), *n*(salicylic acid)∶*n*(nitric acid)=1∶1, catalyst (0.07 g).

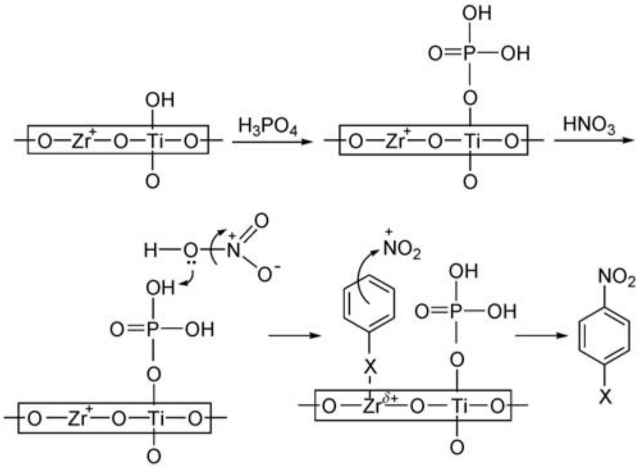
The effect of the amount of 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf on salicylic acid conversion and product selectivity was studied in the range of 0.02 to 0.15 g at 40 ℃ in dichloromethane. The results are presented in Figure 5, which shows that the yield increases with raising the amount of catalyst up to 0.07 g. But a further increase leads to a drop in overall yield. 0.07 g catalyst was selected for further experimental studies due to its optimum performance.

The effect of the feed ratio of salicylic acid to nitric yield and product selectivity was studied from 1∶1 to

Scheme 1 TiO_2-ZrO_2 structures and interaction with H_3PO_4



Scheme 2 Mechanism for the nitration of aromatic compounds over H_3PO_4/TiO_2-ZrO_2



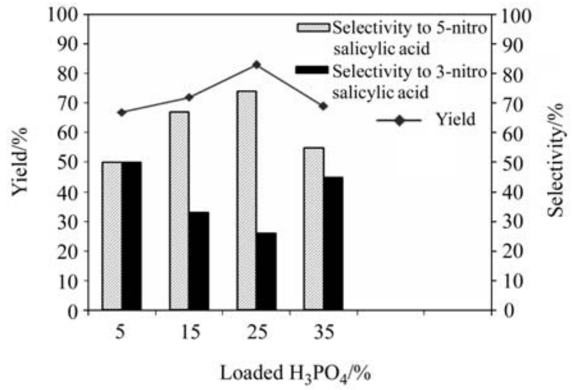


Figure 4 Effect of loaded H_3PO_4. Reaction conditions: reflux temperature, dichloromethane (5 mL), *n*(salicylic acid)∶*n*(nitric acid)=1∶1, catalyst 0.07 g.

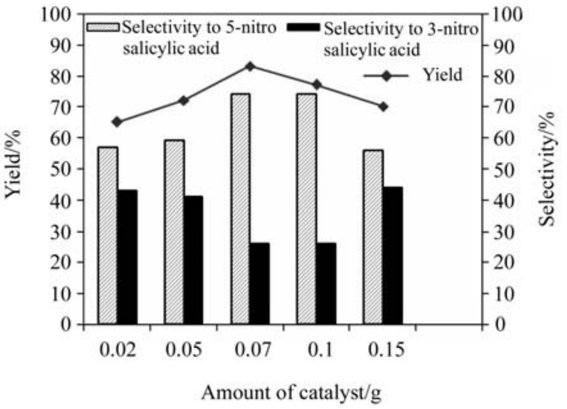


Figure 5 Effect of the catalyst amount. Reaction conditions: reflux temperature, dichloromethane (5 mL), *n*(salicylic acid)∶*n*(nitric acid)=1∶1.

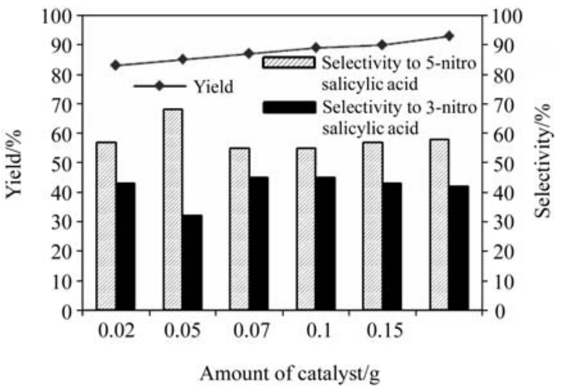


Figure 6 Effect of salicylic acid∶nitric acid molar ratio. Reaction conditions: catalyst (0.07 g), reflux temperature, dichloromethane (5 mL).

1∶2.8 at 40 ℃ over 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf. The results are presented in Figure 6. At the 1∶2.8 feed ratio, the yield was about 95%, however, the 5-nitrosalicylic acid selectivity was about 58%. This reveals that at a low feed ratio (1∶1 or 1∶1.2), salicylic acid is more highly adsorbed than nitric acid on the acid sites of the catalyst. Therefore, the yield was decreased but the selectivity was increased. Moreover, at high feed ratios (high percentage of nitric acid), multi-nitration predominantly occurred. The maximum selectivity to 5-nitrosalicylic acid was observed for the 1∶1 feed ratio.

The nitration of salicylic acid at reflux temperature was carried out using various common solvents such as CH_2Cl_2, CH_3CN, CH_3OH and $CHCl_3$. The results are shown in Table 4. Using 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf, the highest yield and selectivity for the nitration of salicylic acid were obtained when the reaction was carried out in CH_2Cl_2 as solvent. As can be expected, the protic solvents such as methanol were not appropriate for the nitration reaction, because it may block the active sites of the catalyst. Consequently, the yield and selectivity were decreased because of the decreasing of salicylic acid interaction with the active surface of catalyst.

Our investigations indicate that polar aprotic solvent, such as dichloromethane, leads to higher selectivity to 5-nitrosalicylic acid than other aprotic solvents. The most likely reason for this, is that the polar solvents in-

Table 4 Influence of solvent[a]

Solvent	Yield/%	Selectivity/%		Time/min
		para	*ortho*	
CH_2Cl_2	83	74	26	5
$CHCl_3$	70	70	30	5
CH_3CN	72	67	33	5
CH_3OH	No reaction	No reaction		270
Solvent free	69	65	35	15

[a] Reaction conditions: catalyst (0.07 g), reflux temperature, *n*(salicylic acid)∶*n*(nitric acid)＝1∶1.

crease the desorption rate of product. Accordingly, its contact time on the catalyst surface was decreased, and less poly nitration precursors were obtained. Furthermore, the polarity of dichloromethane may cause the intermediate species such as nitronium ion to become more stable.

Upon completion of reaction, reusability of the catalyst was examined using 0.07 g of 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf. In order to regenerate the catalyst after 5 min reaction time, it was separated by filtration, washed with ethyl acetate, calcined at 540 ℃ for 6 h and reused in the nitration reaction with a fresh reaction mixture. It was observed that with increase in the number of usage times of the catalyst, its catalytic activity was decreased, which could probably be due to the leaching of the catalyst (Table 5).

Table 5 Recyclability of the catalyst

Reaction cycle	Yield/%	Selectivity/%		Time/min
		para	*ortho*	
1	83	74	26	5
2	77	74	26	5
3	72	74	26	5

Table 6 shows the comparison between the catalysts used in the present study and other solid catalysts reported in the literature for the nitration of salicylic acid and other aromatic compounds. As can be seen, the 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst shows good selectivity and reasonable yield for the nitration of salicylic acid and some other aromatic compounds in a short time.

Conclusion

A heterogeneous solid acid catalyst has been developed by impregnation of phosphate over TiO_2-ZrO_2 (1/1)-surf for the nitration of salicylic acid and some other aromatic compounds using nitric acid. The 25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf catalyst showed good selectivity and yield at short run for the nitration of activated, moderately activated and inactivated aromatic compounds without producing poly nitration and oxidation by-products. In addition to the short reaction time, this catalyst showed good activity after the third cycle of the reaction.

Table 6 Comparison with other solid acid catalysts

Catalyst	Substrate	Reagent	Conversion/%	Selectivity/%		Time/min	Reference
				para	*ortho*		
Phosphate/titania	Phenol	Nitric acid	90[a]	58	42	2	29
Sulfate/titania	Phenol	Nitric acid	93	8	90	120	30
ZSTA-15	Phenol	Nitric acid	95	8	91	60	31
Sulfate/titania	Phenol	Nitric acid	85.6	3.9	92.4	120	32
Nickel(II) nitrate	Phenol	ρ-Toluenesulfonic acid	85[a]	—	85	30	33
25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf	Phenol	Nitric acid	96[a]	90	10	1	This work
$Yb(N(SO_2C_4F_9)_2)_3$/MCM-41	Chlorobenzene	Nitric acid	97.2	56.3	43.2	1440	34
ZSTA-15	Chlorobenzene	Nitric acid	32	52	28	60	31
25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf	Chlorobenzene	Nitric acid	70[a]	90	10	15	This work
Phosphate/titania	Bromobenzene	Nitric acid	70[a]	75	25	90	29
$Yb(N(SO_2C_4F_9)_2)_3$/MCM-41	Bromobenzene	Nitric acid	97.2	56.2	43.2	1440	34
25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf	Bromobenzene	Nitric acid	70[a]	90	10	15	This work
Phosphate/titania	Benzene	Nitric acid	86[a]	—	—	5	29
$Yb(N(SO_2C_4F_9)_2)_3$/MCM-41	Benzene	Nitric acid	64.3[a]	—	—	480	34
25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf	Benzene	Nitric acid	98[a]	—	—	25	This work
Benzyltriphenylphosphonium peroxodisulfate	Salicylic acid	$NaNO_3$	—	70	—	390	35
25 wt% H_3PO_4/TiO_2-ZrO_2 (1/1)-surf	Salicylic acid	Nitric acid	83[a]	74	26	5	This work

[a] Yield.

Acknowledgements

Special thanks from the authors are given to Islamic Azad University, Shahreza Branch (IAUSH) Research Council and Center of Excellence in Chemistry (IAUSH) to support this work.

References

1 Forbes, A.; Cartwright, A.; Marchant, S.; McIntyre, P. *Aliment. Pharmacol. Therapeut*. **2003**, *17*, 1207.

2 Tan, Z. Y.; Liu, T. S.; Zou, G. X.; Lu, Z. F.; Xu, X. B.; Xie, L. F.; Lin, B. *Guangzhou Chem. Indust. Technol*. **2003**, *31*, 37 (in Chinese).

3 Mayo, D. W.; Pike, R. M.; Trumper, P. K. *Microscale Organic Laboratory*, John Wiley and Sons, Inc., New York, **1994**, p. 383.

4 Andreozzi, R.; Caprio, V.; Di Somma, I.; Sanchirico, R. *J. Hazard. Mater*. **2006**, *134*, 1.

5 Bretherick, L. *Handbook of Reactive Chemical Hazards*, Butterworths, London, **1990**.

6 Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration: Method and Mechanism*, VCH, New York, **1989**, p. 51.

7 Iranpoor, N.; Firouzabadi, H.; Heydari, R. *Synth. Commun*. **1999**, *29*, 3295.

8 Radoslaw, R. B.; Andrew, J. S. *Tetrahedron Lett*. **2001**, *42*, 6767.

9 Zolfigol, M. A.; Bagherzadeh, M.; Madrakian, E.; Ghaemi, E.; Taqian-nasab, A. *J. Chem. Res*. (*S*) **2001**, 140.

10 Zolfigol, M. A.; Madrakian, E.; Ghaemi, E. *Indian J. Chem*. **2001**, *40B*, 1191.

11 Suzuki, S.; Tohmori, K.; Ono, Y. *Chem. Lett*. **1986**, *5*, 747.

12 Suzuki, S.; Tohmori, K.; Ono, Y. *J. Mol. Catal*. **1987**, *43*, 41.

13 Olah, G. A.; Krishnamurthy, V. V.; Narang, S. C. *J. Org. Chem*. **1982**, *47*, 596.

14 Samantaray, S. K.; Mishra, T.; Parida, K. M. *J. Mol. Catal. A: Chem*. **2000**, *156*, 267.

15 Kalbasi, R. J.; Ghiaci, M.; Massah, A. R. *Appl. Catal. A: Gen*. **2009**, *353*, 1.

16 Beltrame, P.; Beltrame, P. L.; Carniti, P.; Castelli, A.; Forni, L. *Appl. Catal*. **1987**, *29*, 327.

17 Ghiaci, M.; Abbaspur, A.; Kalbasi, R. J. *Appl Catal. A: Gen*. **2005**, *287*, 83.

18 Ghiaci, M.; Kalbasi, R. J.; Mollahasani, M.; Aghaei, H. *Appl. Catal. A: Gen*. **2007**, *320*, 35.

19 Ghiaci, M.; Kalbasi, R. J.; Aghaei, H. *Catal. Commun*. **2007**, *8*, 1843.

20 Miller, J. M.; Lakshmi, L. J. *J. Phys. Chem*. **1998**, *102B*, 6465.

21 Miller, J. M.; Wails, D.; Belelie, J. S. *J. Chem. Soc., Faraday Trans*. **1998**, *94*, 789.

22 Matsuhashi, H.; Hinio, M.; Arata, K. *Appl. Catal*. **1990**, *59*, 203.

23 Das, D.; Mishra, H. K.; Dalai, A. K.; Parida, K. M. *Appl. Catal. A: Gen*. **2003**, *243*, 271.

24 Manriquez, M. E.; López, T.; Aguilar, D. H.; Quintana, P. In *Emerging Fields in Sol-Gel Science and Technology Materials*, Eds.: López, T.; Avnir, D.; Aegerter, M., Kluwer Academic Publishers, Gujarat, India, **2003**, p. 254.

25 Wang, J. A.; Novaro, O.; Bokhimi, X.; López, T.; Gómez, R. *J. Phys. Chem*. **2001**, *105B*, 9692.

26 Riego, J. M.; Sedin, Z.; Zaldivar, J. M.; Marziano, N. C.; Toratato, C. *Tetrahedron Lett*. **1996**, *37*, 513.

27 Vassena, D.; Kogelbauer, A.; Prins, R. *Catal. Today* **2000**, *60*, 275.

28 Tanabe, K.; Sumiyoshi, T.; Shibata, K. *Bull. Chem. Soc. Jpn*. **1974**, *47*, 1064.

29 Bharadwaj, S. K.; Hussain, S.; Kar, M.; Chaudhuri, M. K. *Appl. Catal. A: Gen*. **2008**, *343*, 62.

30 Parida, K. M.; Rath, D. *J. Mol. Catal. A: Chem*. **2006**, *258*, 381.

31 Mallick, S.; Parida, K. M. *Catal. Commun*. **2007**, *8*, 1487.

32 Sunajadevi, K. R.; Sugunan, S. *Mater. Lett*. **2006**, *60*, 3813.

33 Anuradha, V.; Srinivas, P. V.; Aparna, P.; Madhusudana, R. J. *Tetrahedron Lett*. **2006**, *47*, 4933.

34 Yuan, Y.; Nie, J.; Zhang, Z.; Wang, S. *Appl. Catal. A: Gen*. **2005**, *295*, 170.

35 Tajik, H.; Zolfigol, M. A.; Albadi, J.; Eslami, R. *Synth. Commun*. **2007**, *37*, 2771.

(E0905263 Sun, H.; Dong, H.)