
ECSOC 22
The 22nd International Electronic Conference on Synthetic Organic Chemistry
1–30 November 2018
chaired by Dr. Julio A. Seijas Vázquez
molecules MDPI

ZrO_2/g-C_3N_4 hybrid nanocomposite: an efficient and eco-friendly recyclable catalyst for the trimethylsilyl protection of hydroxyl groups and synthesis of α-aminophosphonates

Hossein Ghafuri,[a*] Ghazaleh Jafari,[a] Nahal Goodarzi,[a] Afsaneh Rashidizadeh[a]

[a] Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran16846-13114, Iran

**E-mail: ghafuri@iust.ac.ir*

Abstract

Recently considerable attention has been devoted to heterogeneous catalysts. Generally, heterogeneous catalysts offer several advantages such as mild reaction conditions, high throughput and ease of work-up procedures. Among the heterogeneous catalysts investigated, polymeric mesoporous graphitic carbon nitrides (g-C_3N_4) has attracted much attention recently due to strong van der Waals interactions between the layers, g-C_3N_4 is chemically stable against acid, base and organic solvents and also thermogravimetric analysis (TGA) reveals that g-C_3N_4 is thermally stable even in air up to 600 ^{o}C, which can be attributed to its aromatic C-N heterocycles. More importantly, g-C_3N_4 is only composed of two earth-abundant elements: carbon and nitrogen. This not only suggests that it can be easily prepared at low cost, but also its properties can be tuned by simple strategies without significant alteration of the overall composition. The last approach is considered as the most efficient way to design of high-performance heterogeneous catalysts utilizing the g-C_3N_4 as catalyst support. An interesting phenomenon is that the modification is mainly focused on metal oxides. Zirconia (ZrO_2) is a physically rigid material with chemical inertness. It has high resistance against attacks by acids, alkalis, oxidants and reductants. In this study, ZrO_2/g-C_3N_4 hybrid nanocomposite has been shown to be an excellent catalyst for the conversion of alcohols and phenols into their corresponding trimethylsilyl ethers with hexamethyldisilazane (HMDS) under solvent-free condition and for the synthesis of α-aminophosphonates. In addition, the ZrO_2/g-C_3N_4 can be easily recycled after separation from the reaction mixture without considerable loss in catalytic activity.

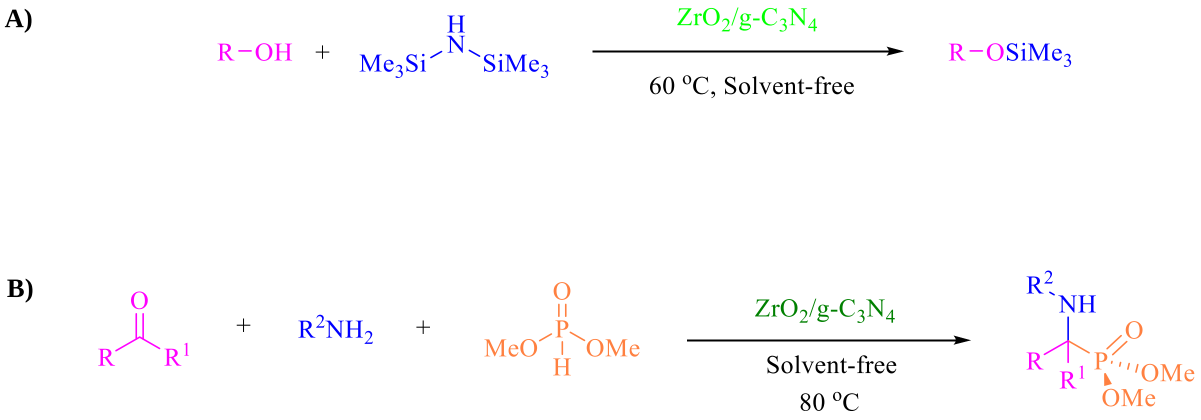
Keywords: Graphitic carbon nitride (g-C_3N_4), Zirconia, ZrO_2/g-C_3N_4, Protection of alcohols, α-aminophosphonates.

---

1. Introduction

Recently, Heterogeneous catalysts have received considerable attention due to numerous applications in many areas of the chemical industry. They offer several advantages such as easy separation from the reaction medium, reusability without noticeable loss of activity, and afforded desired products in high yields and purity [1]. A large number of metal oxides including TiO_2, ZrO_2, ZnO, Fe_3O_4, Al_2O_3, and CeO_2 have been investigated as the heterogeneous catalysts in organic synthesis [2]. Among these, zirconia (ZrO_2) is a chemically inert inorganic metal oxide materials which has high resistance against attacks by acids, alkalis, oxidant and reductants. In addition, zirconia is a biologically inert material and it has been used as implant and dentistry materials. While various attempts have been reported to improve catalytic activity of the zirconia

[3]. Polymeric mesoporous graphitic carbon nitride (g-C_3N_4) has drawn more and more attention due to large surface areas, high thermal and chemical stability, easily recycled, and particular physical features. Besides, the simple preparation for g-C_3N_4 was also attractive to its practical applications. Generally, carbon nitride materials can be facilely synthesized by direct heating nitrogen-rich precursors such as urea, thiourea, melamine, dicyandiamide, and cyanamide. Further, the rich nitrogen on the g-C_3N_4 can also provide abundant anchor sites for active species when g-C_3N_4 is used as heterogeneous catalyst support [4]. Therefore, ZrO_2 have been successfully supported on g-C_3N_4 [5]. In this study, we reported the synthesis of ZrO_2/g-C_3N_4, by a mixing calcination method, as a promising heterogeneous catalyst for the protection of hydroxyl groups and preparation of α-aminophosphonate derivatives (Scheme A, B).



Scheme 1. Protection of alcohols with HMDS catalyzed by ZrO_2/g-C_3N_4 (A), and synthesis of α-aminophosphonates by ZrO_2/ g-C_3N_4 (B).

2. Experimental

2.1. General

All solvents, chemicals and reagents were purchased from Merk, Fluka and Aldrich chemical companies. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were obtained over the region 400-4000 cm^{-1} with a Shimadzu IR-470 spectrometer using KBr pellets. The powder X-ray diffraction patterns were recorded using a PANalytical X-PERT-PRO MPD diffractometer with Cu Kα (λ=1.5406 Å) irradiation in the 2θ=10° to 80° with a 2θ step size of 0.02°. ^{1}H-NMR spectra were recorded on a Bruker DRX-500 Advance spectrometer at 500 MHz. All the organic products were known and the structures of the isolated products were confirmed by comparison with previously reported data.

2.2. *Preparation of ZrO_2*

Typically, 2.204 g cetyltrimethylammonium bromide (CTAB) was first dissolved in 40 mL water with stirring at 40 ^oC to obtain a clear micellar solution. Then 3.6 g zirconyl chloride was added to the solution. This combined solution was stirred for 15 min and then NaOH (1 mol L^{-1}) was added until the pH reached 11.5. After that, the mixture was transferred into a 100 mL autoclave with an inner Teflon lining and maintained at 100 ^oC for 24 h. The resulting white precipitate was collected by centrifugation, washed several times with ethanol and deionized water, and dried in an oven at 80 ^oC for 12 h.

2.3. Preparation of ZrO_2/g-C_3N_4 nanocomposite

ZrO_2 and melamine with different ratio were mixed in a motor and then grounded for 30 min. The resultant mixed powder was put into a crucible with a cover and then heated at 520 ^oC in a muffle furnace for 4 h with a heating rate of 10 ^{o}C min^{-1}. After the temperature decreased to room temperature, the ZrO_2/g-C_3N_4 hybrids with various ZrO_2 contents were obtained [5].

2.4. General procedure for the protection of hydroxyl groups using HMDS

To a mixture of benzyl alcohols (1.0 mmol) and HMDS (1.5 mmol) was added ZrO_2/g-C_3N_4 (20.0 mg) and the mixture was stirred at 60 ^{o}C for an appropriate time (Table 2). After completion of the reaction, as indicated by thin-layer chromatography (TLC), the catalyst was separated by filtration and the products were obtained by evaporation of the volatile portion under reduced pressure. All compounds are known and were characterized on the basis of their spectroscopic data (FT-IR, ^{1}H-NMR) and by comparison with those reported in the literature.

2.5. General procedure for the synthesis of α-aminophosphonates

A mixture of aldehydes (1 mmol), amine (1 mmol) and dimethylphosphite (1.2 mmol) in the presence of ZrO_2/g-C_3N_4 (20.0 mg) was stirred at 80 ^{o}C for the appropriate reaction time. The reaction was monitored using TLC (50: 50 EtOAC/n-hexane), dichloromethane was added after completion of the reaction, and the catalyst was recovered by filtration. A saturated aqueous $NaHCO_3$ solution (20 mL) and brine (20 mL) were added, the mixture was extracted with EtOAc (25 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified either by recrystallization or by preparative TLC (silica gel) (eluent: 50: 50 EtOAC/n-hexane) if necessary. The products thus obtained were characterized by MP, FT-IR, and ^{1}H-NMR spectroscopy.

2.6. Spectral data

Trimethyl(benzyloxy) silane (**1a**): IR (KBr, $\tilde{\nu}$ max cm^{-1}): 2957, 1496, 1454, 1377, 1250, 1207, 1096, 1027, 842, 727, 695 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 500 MHz): δ = 7.367.35 (5H, m), 4.72 (2H, s), 0.18 (9H, s) ppm.

Trimethyl(4-methoxybenzyloxy) silane (**1c**): IR (KBr, $\tilde{\nu}$ max cm^{-1}): 2999, 2959, 2901, 2836, 1613, 1587, 1512, 1464, 1376, 1300, 1248, 1171, 1085, 1037, 840, 751, 688 cm^{-1}; ^{1}H-NMR (CDCl$_3$, 500 MHz): δ = 7.29 (2H, d, J = 8.3 Hz), 6.91 (2H, d, J = 8.4 Hz), 4.66 (2H, s), 3.81 (3H, s), 0.18 (9H, s) ppm.

trimethyl((4-nitrobenzyl)oxy)silane (**1d**): IR (KBr, $\tilde{\nu}$ max cm^{-1}): m 1253, 1095, 844; ^{1}H-NMR (CDCl$_3$, 500 MHz): d 7.31–7.19 (4H, m), 4.72 (2H, s), 0.10 (9H, s) ppm.

Trimethylphenoxy silane (**1e**): IR (KBr, $\tilde{\nu}$ max cm^{-1}): 3039, 2960, 1596, 1492, 1252, 1164, 1070, 1024, 1002, 918, 843, 759, 692; ^{1}H-NMR(CDCl$_3$, 500 MHz): δ = 7.31 (t, 2H, J = 8.0 Hz), 7.02 (t, 1H, J = 7.3 Hz), 6.90 (d, 2H, J = 7.8 Hz), 0.34 (s, 9H) ppm.

Dimethyl[(phenyl) (phenylamino) methyl] phosphonate (**2a**): Mp: 90-92 °C; IR (KBr, $\tilde{\nu}$ max cm^{-1}): 3305, 1600, 1500, 1240, 1027; ^{1}H-NMR (500 MHz, CDCl$_3$): δ 3.51 (d, J = 10.5 Hz, 3H), 3.81 (d, J = 10.6 Hz, 3H), 4.82 (d, $^1J_{H,P}$ = 23.9 Hz, 1H), 4.84 (br, 1H), 6.61-6.72 (m, 3H),7.28-7.50 (m, 7H) ppm.

Dimethyl[(2-chlorophenyl) (phenylamino) methyl] phosphonate (**2b**): Mp: 128–129 ^{o}C. IR (KBr, $\tilde{\nu}$max cm^{-1}): 3311 (N-H), 1602, 1519, 1232, 1033; ^{1}H-NMR (CDCl$_3$, 500 MHz): δ= 3.4 (d, J = 10.4Hz, 3H), 3.8 (d, J = 10.7 Hz, 3H), 5.0 (br, NH, 1H), 5.36 (d, J = 24.6 Hz, 1H), 6.6 (d, J=-7.6 (m, 9H) ppm.

Dimethyl[(4-chlorophenyl) (phenylamino) methyl] phosphonate (**2c**): Mp: 139-140 ºC, IR (KBr, $\tilde{\nu}$ max cm^{-1}): 3319 (N-H), 1602, 1494, 1232, 1033; ^1H-NMR (500 MHz, $CDCl_3$): δ 3. 55 (d, *J* = 10.8 Hz, 3H), 3.79 (d, *J* = 10.5 Hz, 3H), 4.98(d, $^1J_{H,P}$= 24 Hz, 1H), 7.3-8.2 (m, 9H) ppm.

Dimethyl[(2,4-chlorophenyl)(phenylamino)methyl]phosphonate (**2d**): Mp: 110–112 ºC. IR (KBr, $\tilde{\nu}$ max cm^{-1}): 3313(N-H), 1602, 1521, 1236, 1 041; ^1H-NMR (300 MHz; $CDCl_3$): δ 3.5 (d, *J*= 10.5 Hz, 3H), 3.9 (d, *J* =10.6 Hz, 3H), 4.6 (br, 1H), 5.3 (d, $^1J_{H,P}$ = 24.4, 1H), 6.5- 7.5 (m, 9H) ppm.

Dimethyl [(2,6-chlorophenyl)(phenylamino)methyl]phosphonate (**2e**): Mp: 98-100 ºC, IR (KBr, $\tilde{\nu}$ max cm^{-1}) 3313 (N-H), 1602, 1521, 1236, 1041. ^1H-NMR (500 MHz, $CDCl_3$): δ= 3.58 (d, *J*=10.6, 3H), 3.80 (d, *J*=10.6, 3H), 4.79 (d, *J*=24.4, 1H), 6.60 (d, *J*= 8.0, 2H), 6.76 (m, 1H), 7.15 (t, *J*=7.6, 2H), 7.35 (d, *J*=8.2, 2H), 7.44 (m, 2H) ppm.

3. Results and discussion

The $ZrO_2/g\text{-}C_3N_4$ hybrid were prepared by direct heating of ZrO_2 and melamine. The crystalline structure of $ZrO_2/g\text{-}C_3N_4$ was investigated by XRD. As shown in figure 1, $ZrO_2/g\text{-}C_3N_4$ demonstrates diffraction peaks corresponding to both $g\text{-}C_3N_4$ and ZrO_2 [5]. The protection of hydroxyl groups (Table 1) and synthesis of α-aminophosphonates (Table 2) under solvent-free condition was carried out to evaluate the catalytic performance of the obtained $ZrO_2/g\text{-}C_3N_4$ nanocomposite. Compare to pure $g\text{-}C_3N_4$ or ZrO_2, the $ZrO_2/g\text{-}C_3N_4$ exhibited much higher catalytic activity for these reactions.

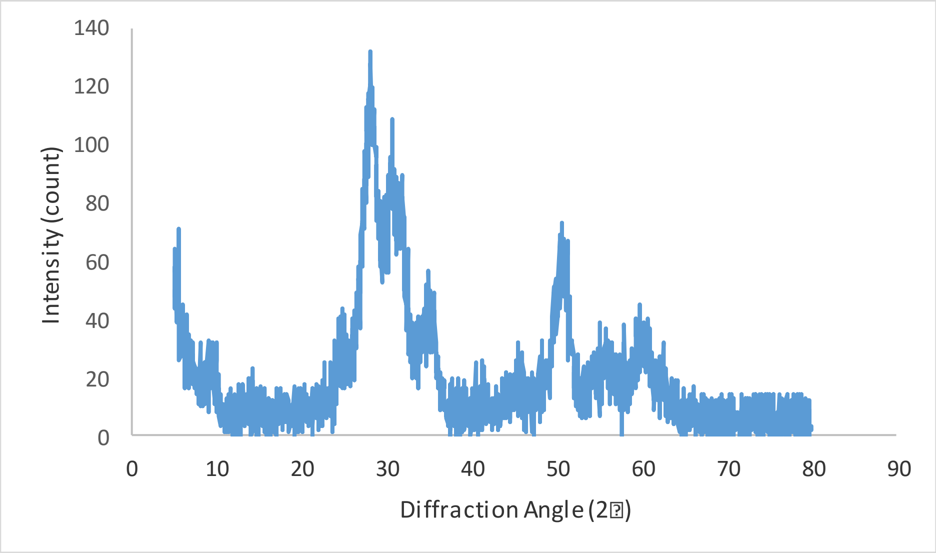


Figure. 1. The X-ray diffraction patterns of $ZrO_2/g\text{-}C_3N_4$.

Table 1. Silylation of various alcohols with HMDS in the presence of ZrO_2/g-C_3N_4 as the catalyst.

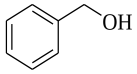
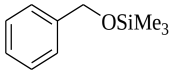
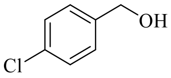
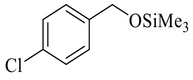
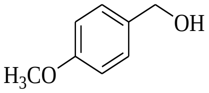
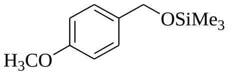
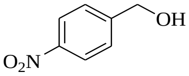
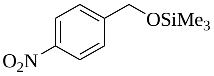
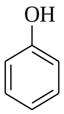
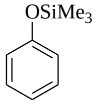
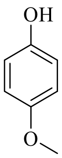
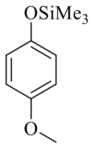
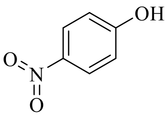
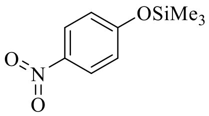
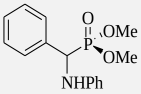
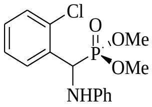
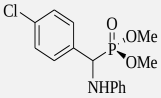
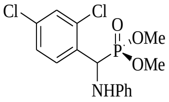
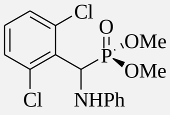
Entry	substrate	Product	Time (min)	Yield (%)
1		 1a	15	90
2		 1b	15	95
3		 1c	20	90
4		 1d	30	90
5		 1e	40	92
6		 1f	10	95
7		 1g	40	75

Table 2. Synthesis derivatives of α-aminophosphonate in the presence catalyst $ZrO_2/g\text{-}C_3N_4$.

Entry	Aldehydes	Amines	Products	Time (min)	Yield (%)	Mp(°C) (Observed)	Mp(°C)
1	PhCHO	Aniline	**2a** 	40	95	**90-92**	**[6]**
2	2-(Cl)C_6H_4CHO	Aniline	**2b** 	30	93	**128-129**	**[7]**
3	4-(Cl)C_6H_4CHO	Aniline	**2c** 	25	95	**139-140**	**[8]**
4	2,4-(Cl)$_2C_6H_3$CHO	Aniline	 **2d**	40	89	**110-112**	**[7]**
5	2,6-(Cl)$_2C_6H_3$CHO	Aniline	**2e** 	80	85	**98-100**	**[9]**

4. Conclusions

In Conclusion, we presented a simple, efficient, and rapid approach for the protection of hydroxyl groups and synthesis of α-aminophosphonates using $ZrO_2/g\text{-}C_3N_4$ as a novel and highly efficient heterogeneous catalyst under solvent-free conditions. Environmentally friendly procedure, easy separation, short reaction times, high yields and recycling of the catalyst are some of the advantages of this methodology.

Acknowledgements

The authors gratefully acknowledge the partial support from the Research Council of the Iran University of Science and Technology.

References

[1] P. Gupta, S. Paul, Solid acids: Green alternatives for acid catalysis, Catal. Today, 236 (**2014**) 153-170.

[2] V. Polshettiwar, B. Baruwati, R.S. Varma, Self-assembly of metal oxides into three-dimensional nanostructures: synthesis and application in catalysis, ACS nano, 3 (**2009**) 728-736.

[3] H. Jiang, P. Chen, S. Luo, X. Tu, Q. Cao, M. Shu, Synthesis of novel nanocomposite Fe_3O_4/ZrO_2/chitosan and its application for removal of nitrate and phosphate, Appl. Surf. Sci. 284 (**2013**) 942-949.

[4] W.-J. Ong, L.-L. Tan, Y.H. Ng, S.-T. Yong, S.-P. Chai, Graphitic carbon nitride (g-C_3N_4)-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability?, Chem. Rev. 116 (**2016**) 7159-7329.

[5] X. Wang, L. Zhang, H. Lin, Q. Nong, Y. Wu, T. Wu, Y. He, Synthesis and characterization of a ZrO_2/g-C_3N_4 composite with enhanced visible-light photoactivity for rhodamine degradation, RSC Adv. 4 (**2014**) 40029-40035.

[6] X.-J. Mu, M.-Y. Lei, J.-P. Zou, W. Zhang, Microwave-assisted solvent-free and catalyst-free Kabachnik–Fields reactions for α-amino phosphonates, Tetrahedron lett. 47 (**2006**) 1125-1127.

[7] M.T. Maghsoodlou, S.M.H. Khorassani, N. Hazeri, M. Rostamizadeh, S.S. Sajadikhah, Z. Shahkarami, N. Maleki, An efficient synthesis of α-Amino phosphonates using silica sulfuric acid as a heterogeneous catalyst, Heteroatom Chemistry: An International Journal of Main Group Elements, 20 (**2009**) 316-318.

[8] L. Lukanov, A. Venkov, One-pot synthesis of dialkyl arylaminomethyl-and (arylamino) arylmethylphosphonates and their *N*-acylated derivatives, Synthesis, 1992 (**1992**) 263-264.

[9] A. Manjula, B. Vittal Rao, P. Neelakantan, One-pot synthesis of α-aminophosphonates: an inexpensive approach, Synth. Commun. 33 (**2003**) 2963-2969.