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ZrO₂/g-C₃N₄ Hybrid Nanocomposite: An Efficient and Eco-Friendly Recyclable Catalyst for the Trimethylsilyl Protection of Hydroxyl Groups and Synthesis of α-Aminophosphonates ⁺

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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-C₃N₄) have attracted much attention recently due to strong van der Waals interactions between the layers. g-C₃N₄ is chemically stable against acidic, basic, and organic solvents, and thermogravimetric analysis (TGA) also reveals that g-C₃N₄ is thermally stable even in air up to 600 °C, which can be attributed to its aromatic C-N heterocycles. More importantly, g-C₃N₄ 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 that its properties can be tuned by simple strategies without significant alteration of the overall composition. The last approach is considered to be the most efficient way to design high-performance heterogeneous catalysts utilizing g-C₃N₄ as a catalyst support. An interesting phenomenon is that the modification is mainly focused on metal oxides. Zirconia (ZrO2) is a physically rigid material with chemical inertness. It has high resistance against attacks by acids, alkalis, oxidants, and reductants. In this study, a ZrO₂/g-C₃N₄ hybrid nanocomposite was shown to be an excellent catalyst for the conversion of alcohols and phenols into their corresponding trimethylsilyl ethers with hexamethyldisilazane (HMDS) under solvent-free conditions and for the synthesis of α -aminophosphonates. In addition, ZrO₂/g-C₃N₄ could easily be recycled after separation from the reaction mixture without considerable loss in catalytic activity.

Keywords: graphitic carbon nitride (g-C₃N₄); 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 affording desired products of high yield and purity [1]. A large number of metal oxides, including TiO₂, ZrO₂, ZnO, Fe₃O₄, Al₂O₃, and CeO₂, have been investigated as heterogeneous catalysts in organic synthesis [2]. Among these, zirconia (ZrO₂) is a chemically inert inorganic metal oxide material which has high resistance against attacks by acids, alkalis, oxidants, and reductants. In addition, zirconia is a

biologically inert material and has been used as implant and dentistry materials. While various attempts have been reported to improve the catalytic activity of zirconia [3], polymeric mesoporous graphitic carbon nitride (g-C₃N₄) has drawn more and more attention due its large surface area, high thermal and chemical stability, easy recyclability, and particular physical features. Further, the simple preparation of g-C₃N₄ also makes it attractive for practical applications. Generally, carbon nitride materials can be easily synthesized by directly heating nitrogen-rich precursors such as urea, thiourea, melamine, dicyandiamide, and cyanamide. Moreover, the rich nitrogen on g-C₃N₄ can also provide abundant anchor sites for active species when g-C₃N₄ is used for heterogeneous catalyst support [4]. Therefore, ZrO₂ has been successfully supported on g-C₃N₄ [5]. In this study, we reported the synthesis of ZrO₂/g-C₃N₄ by a mixing calcination method as a promising heterogeneous catalyst for the protection of hydroxyl groups and the preparation of α-aminophosphonate derivatives (Scheme 1A,B).



Scheme 1. Protection of alcohols with hexamethyldisilazane (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 K α (λ = 1.5406 Å) irradiation in the 2 θ = 10°–80° with a 2 θ step size of 0.02°. ¹H-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 ZrO₂

Typically, 2.204 g of cetyltrimethylammonium bromide (CTAB) was first dissolved in 40 mL of water with stirring at 40 °C to obtain a clear micellar solution. Then, 3.6 g of 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 °C 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 °C for 12 h.

2.3. Preparation of ZrO₂/g-C₃N₄ Nanocomposite

 ZrO_2 and melamine of different ratios were mixed in a mortar and then ground for 30 min. The resultant mixed powder was put into a crucible with a cover and then heated at 520 °C in a muffle furnace for 4 h with a heating rate of 10 °C min⁻¹. After the temperature decreased to room temperature, the $ZrO_2/g-C_3N_4$ hybrids of various ZrO_2 contents were obtained [5].

2.4. General Procedure for the Protection of Hydroxyl Groups Using Hexamethyldisilazane (HMDS)

ZrO₂/g-C₃N₄ (20.0 mg) was added to a mixture of benzyl alcohols (1.0 mmol) and HMDS (1.5 mmol), and the mixture was stirred at 60 °C for an appropriate amount of time (Table 1). 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 were known and were characterized on the basis of their spectroscopic data (FT-IR, ¹H-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 ZrO₂/g-C₃N₄ (20.0 mg) was stirred at 80 °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 NaHCO₃ 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 Na₂SO₄. 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 ¹H-NMR spectroscopy.

2.6. Spectral Data

Trimethyl(benzyloxy) silane (**1a**): IR (KBr, ν[~] max cm⁻¹): 2957, 1496, 1454, 1377, 1250, 1207, 1096, 1027, 842, 727, 695 cm⁻¹; ¹H-NMR (CDCl₃, 500 MHz): δ = 7.367.35 (5H, m), 4.72 (2H, s), 0.18 (9H, s) ppm.

Trimethyl(4-*methoxybenzyloxy*) *Silane* (1c). IR (KBr, v^{\sim} max cm⁻¹): 2999, 2959, 2901, 2836, 1613, 1587, 1512, 1464, 1376, 1300, 1248, 1171, 1085, 1037, 840, 751, 688 cm⁻¹; ¹H-NMR (CDCl₃, 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, v[~] max cm⁻¹): m 1253, 1095, 844; ¹H-NMR (CDCl₃, 500 MHz): d 7.31–7.19 (4H, m), 4.72 (2H, s), 0.10 (9H, s) ppm.

Trimethylphenoxy Silane (**1e**). IR (KBr, ν⁻ max cm⁻¹): 3039, 2960, 1596, 1492, 1252, 1164, 1070, 1024, 1002, 918, 843, 759, 692; ¹H-NMR(CDCl₃, 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, ν[~] max cm⁻¹): 3305, 1600, 1500, 1240, 1027; ¹H-NMR (500 MHz, CDCl₃): δ 3.51 (d, *J* = 10.5 Hz, 3H), 3.81 (d, *J* = 10.6 Hz, 3H), 4.82 (d, ¹*J*_{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 °C. IR (KBr, ν⁻max cm⁻¹): 3311 (N-H), 1602, 1519, 1232, 1033; ¹H-NMR (CDCl₃, 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 °C, IR (KBr, v^{\sim} max cm⁻¹): 3319 (N-H), 1602, 1494, 1232, 1033; ¹H-NMR (500 MHz, CDCl₃): δ 3. 55 (d, *J* = 10.8 Hz, 3H), 3.79 (d, *J* = 10.5 Hz, 3H), 4.98(d, ¹*J*_{H,P} = 24 Hz, 1H), 7.3–8.2 (m, 9H) ppm.

Dimethyl[(2,4-*chlorophenyl*)(*phenylamino*)*methyl*]*phosphonate* (**2d**). Mp: 110–112 °C. IR (KBr, v max cm⁻¹): 3313(N-H), 1602, 1521, 1236, 1 041; ¹H-NMR (300 MHz; CDCl₃): δ 3.5 (d, *J* = 10.5 Hz, 3H), 3.9 (d, *J* = 10.6 Hz, 3H), 4.6 (br, 1H), 5.3 (d, ¹*J*_{H,P} = 24.4, 1H), 6.5–7.5 (m, 9H) ppm.

Dimethyl [(2,6-chlorophenyl)(phenylamino)methyl]phosphonate (**2e**). Mp: 98–100 °C, IR (KBr, ν[~] max cm⁻¹) 3313 (N-H), 1602, 1521, 1236, 1041. ¹H-NMR (500 MHz, CDCl₃): 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 ZrO₂/g-C₃N₄ hybrids were prepared by direct heating of ZrO₂ and melamine. The crystalline structure of ZrO₂/g-C₃N₄ was investigated by XRD. As shown in Figure 1, ZrO₂/g-C₃N₄ demonstrated diffraction peaks corresponding to both g-C₃N₄ and ZrO₂ [5]. The protection of hydroxyl groups (Table 1) and synthesis of α -aminophosphonates (Table 2) under solvent-free conditions were carried out to evaluate the catalytic performance of the obtained ZrO₂/g-C₃N₄ nanocomposite. Compared with pure g-C₃N₄ or ZrO₂, the ZrO₂/g-C₃N₄ exhibited much higher catalytic activity for these reactions.



Figure 1. The X-ray diffraction patterns of ZrO₂/g-C₃N₄.

Entry	Substrate	Product	Time (min)	Yield (%)
1	ОН	OSiMe ₃ 1a	15	90
2	СІ	CI OSiMe ₃	15	95
3	Н3СО	H ₃ CO OSiMe ₃	20	90
4	O ₂ N OH	O ₂ N OSiMe ₃ 1d	30	90
5	OH	OSiMe ₃	40	92
6	OH O	OSiMe ₃	10	95
7	OSN OH	OSiMe ₃ OSiMe ₃ O Ig	40	75

Table 1. Silylation of various alcohols with HMDS in the presence of ZrO₂/g-C₃N₄ as the catalyst.

Entry	Aldehydes	Amines	Products	Time (min)	Yield (%)	Mp (°C) (Observed)	Mp (°C)
1	PhCHO	Aniline	O P OMe NHPh 22	40	95	90–92	[6]
2	2-(Cl)C6H4CHO	Aniline	Cl Cl OMe NHPh 2b	30	93	128–129	[7]
3	4-(Cl)C6H4CHO	Aniline	Cl OMe NHPh 2c	25	95	139–140	[8]
4	2,4-(Cl)2C6H3CHO	Aniline	Cl Cl Cl O P OMe NHPh 2d	40	89	110–112	[7]
5	2,6-(Cl)2C6H3CHO	Aniline	Cl NHPh Cl NHPh 2e	80	85	98–100	[9]

Table 2. Synthesis derivatives of α -aminophosphonate in the presence catalyst ZrO₂/g-C₃N₄.

4. Conclusions

In conclusion, we presented a simple, efficient, and rapid approach for the protection of hydroxyl groups and the synthesis of α -aminophosphonates using ZrO₂/g-C₃N₄ as a novel and highly efficient heterogeneous catalyst under solvent-free conditions. An environmentally friendly procedure, easy separation, short reaction times, high yields, and recycling of the catalyst are some of the advantages of this methodology.

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