

Novel One-pot Synthesis of Pyrazolopyranopyrimidinones Using Newly Produced γ -Alumina Nanoparticles as Powerful Catalyst

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ABSTRACT: γ -Alumina nanoparticles (γ -Al₂O₃ NPs) were prepared via a new and simple synthetic route and characterized by field emission scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The catalytic activity of prepared γ -Al₂O₃ NPs was investigated for the new one-pot, four-component synthesis of some fused tri-heterocyclic compounds containing pyrazole, pyran, and pyrimidine. In another investigation, the recyclability of the prepared nanocatalyst was also studied. It was proved that the nanoparticles can act effectively for at least four cycles without appreciable loss in activity. This novel procedure has some advantages such as high efficiency, simplicity, high rate, and environmental safety.

KEYWORDS: γ -Al₂O₃ nanoparticles; One-Pot; Pyrazole; Pyran; Pyrimidine.

INTRODUCTION

Efficient catalysis is an important factor of “green chemistry”. In fact, design and use of environmentally benign catalysts are the main challenges facing chemists [1, 2]. In recent years, numerous attempts were made on promoting organic reactions by helping nanocatalysts because nano-sized catalysts usually show better activity due to a larger surface area rather than their bulk cases [3-5]. Among solid catalysts, metal oxides are the largest family of catalysts in heterogeneous catalysis which are utilized

both for their acid-base and redox properties [6-8].

Organic synthesis strategies that can provide rapid production of complex organic molecules from simple substrates are of the main research interests. Using MultiComponent Reactions (MCRs) with a wide range of applicability in the field of synthetic organic chemistry provides a facile and quick route to a large number of libraries of organic compounds [9].

Recently, catalyzed-multicomponent assembling reactions

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1021-9986/2018/3/63-71

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using metal oxide nanoparticles provide an efficient route to the construction of complex organic molecules [9-11]. However, the application of Al₂O₃ nanoparticles and as a catalyst in synthetic organic chemistry remains essentially unexplored.

Biologically, compounds incorporating pyran, pyrazole, and pyrimidine rings have been attracting widespread attention because of their pharmacological properties [12-15]. Herein, after the synthesis and characterization of γ -Al₂O₃ NPs via a new method, we report a simple, green, and efficient strategy for the synthesis of pyrazolopyranopyrimidinones through the four-component one-pot reaction using γ -Al₂O₃ NPs as a safe and recyclable catalyst.

EXPERIMENTAL SECTION

Chemicals and materials

All chemicals were purchased from Merck and Aldrich. The pore size and surface area measurements were performed with a Micrometrics ASAP-2010 instrument by adsorption of nitrogen at 77K. IR spectra were recorded on a FT-IR JASCO-680. ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance 2 model. Field emission scanning electron microscopy (FE-SEM) studies of the nanostructures were carried out with a JEOL JEM 3010 instrument operating at an accelerating voltage of 300 kV. X-Ray Diffraction (XRD, D8, Advance, Bruker, AXS) patterns were obtained for characterization of the heterogeneous catalyst.

General procedure for preparation of γ -Al₂O₃ NPs

High-purity Gibbsite (99.99%) (10 g), ammonium bicarbonate (20 g), and deionized water (3 mL) were mixed and placed in a 300 mL Teflon-lined autoclave at 85 °C for 10 h. The mixture was cooled under stirring at room temperature about 30 min. Finally, the as-prepared mixture was calcinated at 450 °C for 60 min to produce γ -Al₂O₃ nanoparticles under thermal decomposition conditions [16].

Synthesis of 5 using γ -Al₂O₃ NPs

Ethyl acetoacetate (0.13 mL, 1 mmol) and γ -Al₂O₃ NPs (7 mol%) were added to a solution of hydrazine hydrate (96%, 0.05 mL, 1 mmol) in H₂O/EtOH (5 mL, 50/50) over 20 min. Then, aromatic aldehyde (1 mmol)

and barbituric acid (1 mmol) were added to the mixture and heated under reflux for an appropriate time. The progress of the reaction was monitored by TLC technique. After completion of the reaction, the mixture was cooled and the precipitates were filtered, dried, and dissolved in hot EtOH to separate the catalyst. The pure product was obtained after recrystallization from EtOH.

Spectral data

Compound 5b: IR (KBr) ν = 3138, 3041, 2907, 1678, 1579, 1518, 1349; ¹H NMR (DMSO-d₆, 400 MHz): δ 13.37 (br, 1H), 10.27 (s, 2H), 8.11 (d, 2H, J=8.0 Hz), 7.33 (d, 2H, J=8.0 Hz), 2.26 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 159.99, 151.20, 150.63, 145.54, 143.64, 131.78, 127.98, 123.12, 114.47, 104.86, 91.02, 31.04, 9.96.

Compound 5d: IR (KBr) ν = 3215, 3054, 1686, 1623, 1588, 1488, 1369, 836, 870; ¹H NMR (DMSO-d₆, 400 MHz): δ 13.01 (br, 1H), 10.19 (s, 2H), 7.27 (d, 2H, J=8.0 Hz), 7.06 (d, 2H, J=8.0 Hz), 5.41 (s, 1H), 2.23 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 160.35, 150.57, 141.58, 134.64, 129.92, 128.59, 128.06, 127.71, 127.27, 89.45, 30.16, 9.96.

Compound 5e: IR (KBr) ν = 3077, 3003, 2951, 2228, 1671, 1624, 1602, 1378; ¹H NMR (DMSO-d₆, 400 MHz): δ 13.30 (br, 1H), 10.24 (s, 2H), 7.69 (d, 2H, J=8.0 Hz), 7.25 (d, 2H, J=8.0 Hz), 5.49 (s, 1H), 2.24 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 160.07, 150.61, 148.85, 143.70, 132.17, 131.83, 131.47, 127.80, 119.05, 108.22, 104.84, 89.73, 31.08, 9.95.

Compound 5f: IR (KBr) ν = 3212, 1689, 1606, 1511, 1426, 1249, 1177; ¹H NMR (DMSO-d₆, 400 MHz): δ 12.96 (br, 1H), 10.15 (s, 2H), 6.96 (d, 2H, J=8.0 Hz), 6.77 (d, 2H, J=8.0 Hz), 5.37 (s, 1H), 3.69 (s, 3H), 2.22 (s, 1H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 160.57, 157.06, 154.89, 150.59, 137.46, 134.35, 128.10, 127.63, 125.12, 113.92, 113.18, 54.89, 9.99.

Compound 5g: IR (KBr) ν = 3221, 2962, 1690, 1622, 1462, 1388; ¹H NMR (DMSO-d₆, 400 MHz): δ 13.12 (br, 1H), 10.18 (s, 2H), 7.08 (d, 2H, J=8.0 Hz), 6.97 (d, 2H, J=8.0 Hz), 5.40 (s, 1H), 2.81 (sep, 1H, J=8 Hz), 2.22 (s, 3H), 1.17 (s, 3H), 1.116 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz): δ 160.60, 150.60, 145.18, 143.50, 139.92, 129.43, 126.58, 126.49, 125.72, 105.91, 91.39, 32.89, 23.95, 23.90, 23.52, 9.98.

Compound 5h: IR (KBr) $\nu = 3182, 3039, 1680, 1652, 1495, 1400, 1363, 1193$; ^1H NMR (DMSO- d_6 , 400 MHz): δ 12.88 (br, 1H), 10.13 (s, 2H), 6.88 (d, 2H, $J=8.0$ Hz), 6.62 (d, 2H, $J=8.0$ Hz), 5.35 (s, 1H), 2.83 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (DMSO- d_6 , 100 MHz): δ 162.70, 154.12, 150.28, 146.09, 136.49, 127.20, 119.93, 112.61, 111.16, 109.47, 91.43, 40.58, 29.50, 10.01.

Compound 5i: IR (KBr) $\nu = 3200, 2937, 1686, 1625, 1592, 1506, 1462, 1129$; ^1H NMR (DMSO- d_6 , 400 MHz): δ 13.16 (br, 1H), 10.17 (s, 2H), 6.37 (s, 2H), 5.39 (s, 1H), 3.65 (s, 6H), 3.62 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (DMSO- d_6 , 100 MHz): δ 167.46, 152.28, 150.54, 143.64, 138.41, 135.82, 112.42, 111.41, 106.68, 104.38, 91.03, 59.88, 56.02, 55.67, 30.35, 10.03.

Compound 5j: IR (KBr) $\nu = 3430, 3202, 3026, 1685, 1646, 1624, 1453, 1394, 1263$; ^1H NMR (DMSO- d_6 , 400 MHz): δ 12.96 (br, 1H), 10.19 (s, 2H), 6.50 (d, 2H, $J=8.0$ Hz), 6.46 (d, 2H, $J=8.0$ Hz), 5.35 (s, 1H), 2.22 (s, 3H); ^{13}C NMR (DMSO- d_6 , 100 MHz): δ 160.64, 156.98, 150.59, 144.07, 143.59, 128.63, 124.76, 117.39, 113.71, 112.29, 89.35, 30.32, 9.97.

Compound 5k: IR (KBr) $\nu = 3212, 3050, 1688, 1650, 1495, 1363, 1199$; ^1H NMR (DMSO- d_6 , 400 MHz): δ 13.16 (br, 1H), 10.22 (s, 2H), 7.84-7.82 (m, 1H), 7.79-7.75 (m, 2H), 7.50 (s, 1H), 7.44-7.42 (m, 2H), 7.24 (d, 1H, $J=8.0$ Hz), 5.60 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (DMSO- d_6 , 100 MHz): δ 160.55, 150.55, 143.62, 140.12, 132.81, 131.45, 129.39, 127.50, 127.31, 127.19, 126.08, 125.77, 125.10, 124.29, 105.74, 81.06, 30.64, 10.05.

Compound 5l: IR (KBr) $\nu = 3021, 2954, 1694, 1610, 1479, 1391, 1303$; ^1H NMR (DMSO- d_6 , 400 MHz): δ 12.29 (br, 1H), 11.14 (s, 2H), 7.34-7.27 (m, 4H), 5.37 (s, 1H), 2.19 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (DMSO- d_6 , 100 MHz): δ 167.76, 153.64, 151.65, 150.63, 143.12, 135.47, 131.86, 130.18, 128.04, 125.44, 89.19, 19.37, 16.91, 10.28.

RESULTS AND DISCUSSION

γ -Alumina nanoparticles (γ - Al_2O_3 NPs) were prepared and characterized by Field Emission Scanning Electron Microscopy (FE-SEM), X-Ray Diffraction (XRD), and Fourier Transform InfraRed (FT-IR) spectroscopy.

Fig. 1 shows the XRD pattern for γ - Al_2O_3 NPs. The XRD pattern of γ - Al_2O_3 NPs is matched with the (JCPDS 00-004-0880) diffraction standard card that shows intensities of

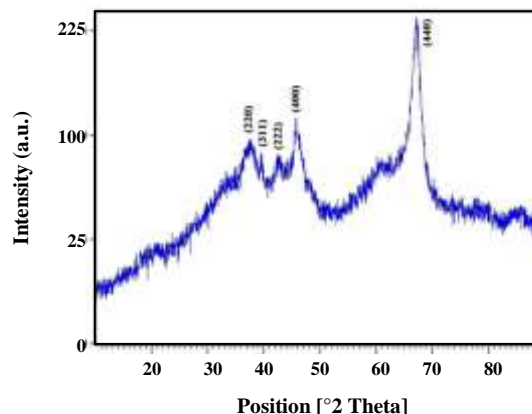


Fig. 1: X-ray diffraction pattern for γ - Al_2O_3 NPs.

the peaks due to γ - Al_2O_3 . Three broad diffraction peaks at 2θ angles around 38.0° , 46.0° , and 66.0° corresponding to the (311), (400), and (440) planes, respectively. The intensity of the characteristic peaks is significantly in agreement with the standard data for the nano-sized γ -alumina structure [17, 18].

The FT-IR spectra of the natural gibbsite as a precursor and synthesized γ - Al_2O_3 NPs in the range 400 – 4000 cm^{-1} can be observed in Fig. 2. The characteristic absorbance at 400 – 1000 cm^{-1} as broadband can be ascribed to Al-O vibration, which is consistent with the reported IR spectra for γ -alumina in the literature. Furthermore, a broad peak around 3100 – 3600 cm^{-1} and weak peaks in the region 1100 – 1400 cm^{-1} can be assigned as stretching bending vibrations of hydroxyl groups in the γ -alumina NPs, respectively [19, 20].

Fig. 3 shows the FE-SEM image for the morphology of the as-prepared γ - Al_2O_3 . As can be seen, the synthesized γ -alumina nanoparticles are relatively uniform and spherical in shape with an average diameter of 20 nm.

The porous character of the as-prepared γ - Al_2O_3 NPs was carried out by N_2 adsorption analysis. The Barrett–Joyner–Halenda (BJH) pore size distribution curve derived from adsorption data of the isotherms clearly shows the main peak with the pore size centered at 5 nm, for one type of pores (Fig. 4A). Both N_2 sorption isotherms exhibit the typical type-IV curve with a H_2 hysteresis loop indicating pore interconnectivity in agreement with IUPAC classification (Fig. 4B) [21]. The specific surface area and pore volume of the catalyst were calculated as 352.48 m^2/g and 0.49 cm^3/g , respectively.

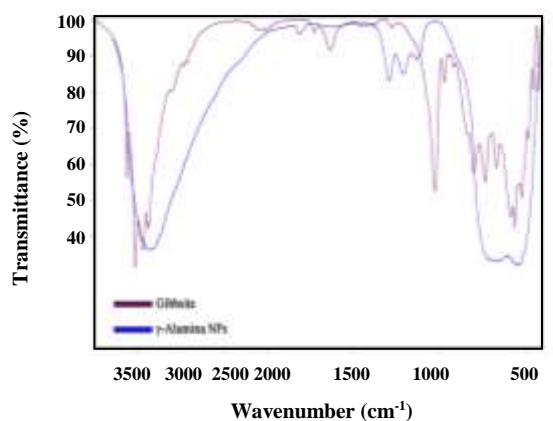


Fig. 2: FT-IR spectra for the comparison of gibbsite and γ - Al_2O_3 NPs.

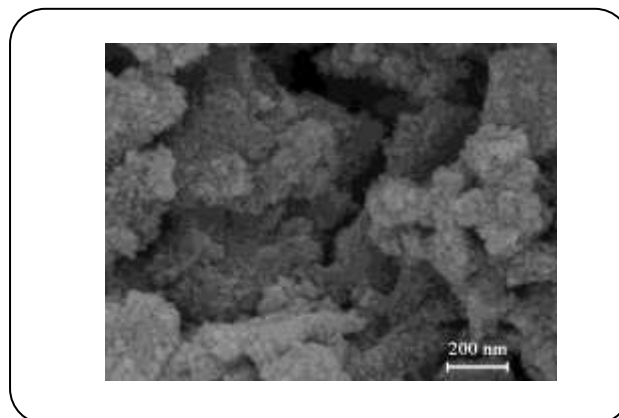


Fig. 3: FE-SEM image of γ - Al_2O_3 NPs.

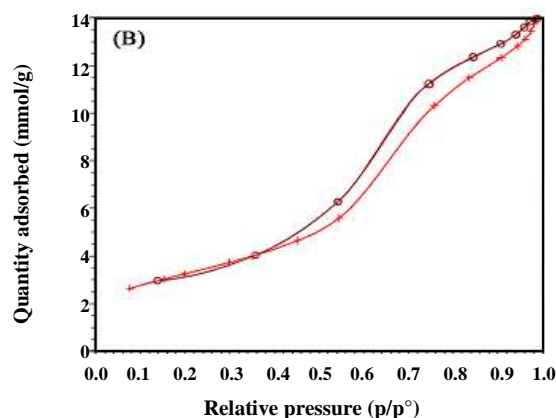
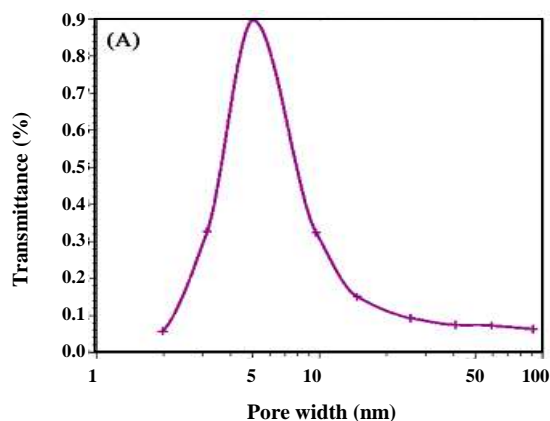


Fig. 4: Barrett-Joyner-Halenda (BJH) (nm) and N_2 adsorption-desorption analysis (B) of the catalyst.

A new strategy to synthesize the fused tri-heterocyclic compounds containing pyrazole, pyran, and pyrimidine moieties which possess high biological activity might be very interesting. Thus, in connection with our interest in the development of efficient catalyzed routes to heterocycles [22-24], as shown in Scheme 1, as-synthesized γ - Al_2O_3 NPs was employed as a catalyst for the synthesis of tri-heterocyclic compounds **5** via a one-pot, four-component reaction of ethyl acetoacetate (**1**), hydrazine hydrate (**2**), barbituric acid (**3**), and aromatic aldehydes (**4**).

As a first step towards our goal, we needed to establish reliable conditions for the synthesis of compounds **5**. In order to find suitable conditions, the synthesis of **5a** was chosen as a model.

Table 1 shows the effect of a catalyst on the reaction rate and product yield. The use of γ - Al_2O_3 NPs (3 mol%)

gave the desired product in low yield together with observable intermediates. Among the various amounts of γ - Al_2O_3 NPs examined, 7 mol% was the most effective, and its use resulted in the formation of **5a** in 92% yield. Also, when substrates reacted in the absence of any catalyst, no desired product was obtained in a reasonable yield as determined by Thin-Layer Chromatography (TLC) technique. Besides, when nanoparticles were used in comparison with bulk case (7 mol%), the one-pot reaction proceeded more quickly to produce pyranopyrazolopyrimidinones in a higher yield.

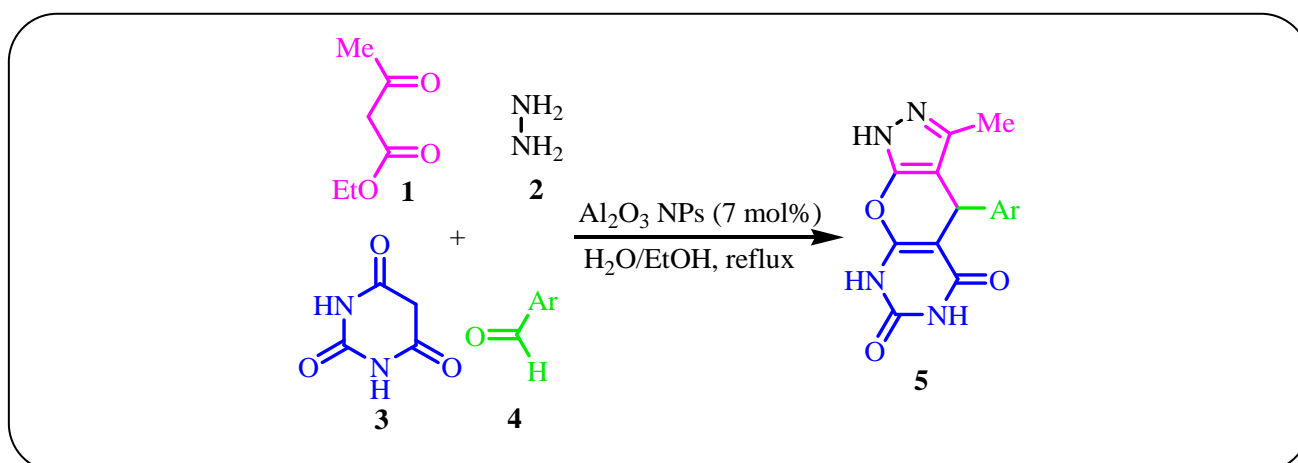
The solvent also played an important role in this reaction. As shown in Table 2, much higher yield was obtained when the reaction was carried out under reflux in a mixture of EtOH/ H_2O (1:1). It should be also noted that decreasing the reaction temperature to 25 °C decreased the desired product yield (about 30% after 60 min).

Table 1: Effect of catalyst amount on the synthesis of 5a. Reaction time: 90 min.

Entry	Catalyst amount (mol%)	Yield (%)
1	-	10
2	3	45
3	7	92
4	10	92
5	7 (Bulk)	63

Table 2: Effect of various solvents on the synthesis of 5a. Reaction time: 90 min.

Entry	Solvent (10 mL)	Yield (%)
1	-	0
2	EtOH	73
3	H ₂ O	62
4	H ₂ O/EtOH	92
5	CH ₂ Cl ₂	23

**Scheme 1: Synthesis of pyrazolopyranopyrimidinones using $\gamma\text{-Al}_2\text{O}_3$ NPs.**

After screening, the generality of the reaction was subsequently explored (Table 3). Arylaldehydes carrying both electron-withdrawing/donating groups reacted efficiently to afford the corresponding products in good yields.

Although there is no exact chemical structure for alumina in the literature, a plausible mechanistic proposal which might be catalyzed by metal oxide species is presented in Scheme 2. Initial addition of the hydrazine (**2**) to the ethyl acetoacetate (**1**) promoted by Al_2O_3 may generate an intermediate **6**. Simultaneously, the intermediate **7** is produced through the Knoevenagel condensation of barbituric acid (**3**) with aldehyde (**4**).

In the next step, the intermediate **7** undergoes a Michael addition with the intermediate **6** and generates a new intermediate **8**. Finally, **8** undergoes an intramolecular cyclization reaction followed by H₂O elimination to afford the tri-heterocyclic product **5** and complete the catalytic cycle.

The catalytic efficiency and recyclability of nanocatalysts in organic transformations often depend on the size, composition, shape, and their interaction with the reactant [26]. In this research, $\gamma\text{-Al}_2\text{O}_3$ NPs showed good recyclability. For example, the activity of the $\gamma\text{-Al}_2\text{O}_3$ NPs was investigated in the synthesis of **5a** over

Table 3: Synthesis of triheterocyclic compounds 5 using Al_2O_3 NPs (7 mol%) in EtOH/H₂O (1:1).

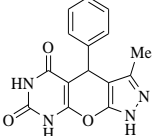
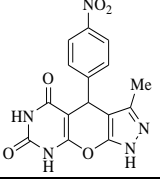
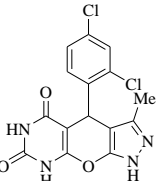
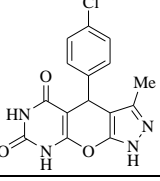
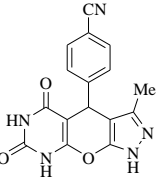
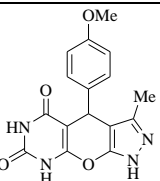
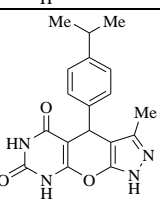
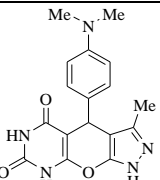
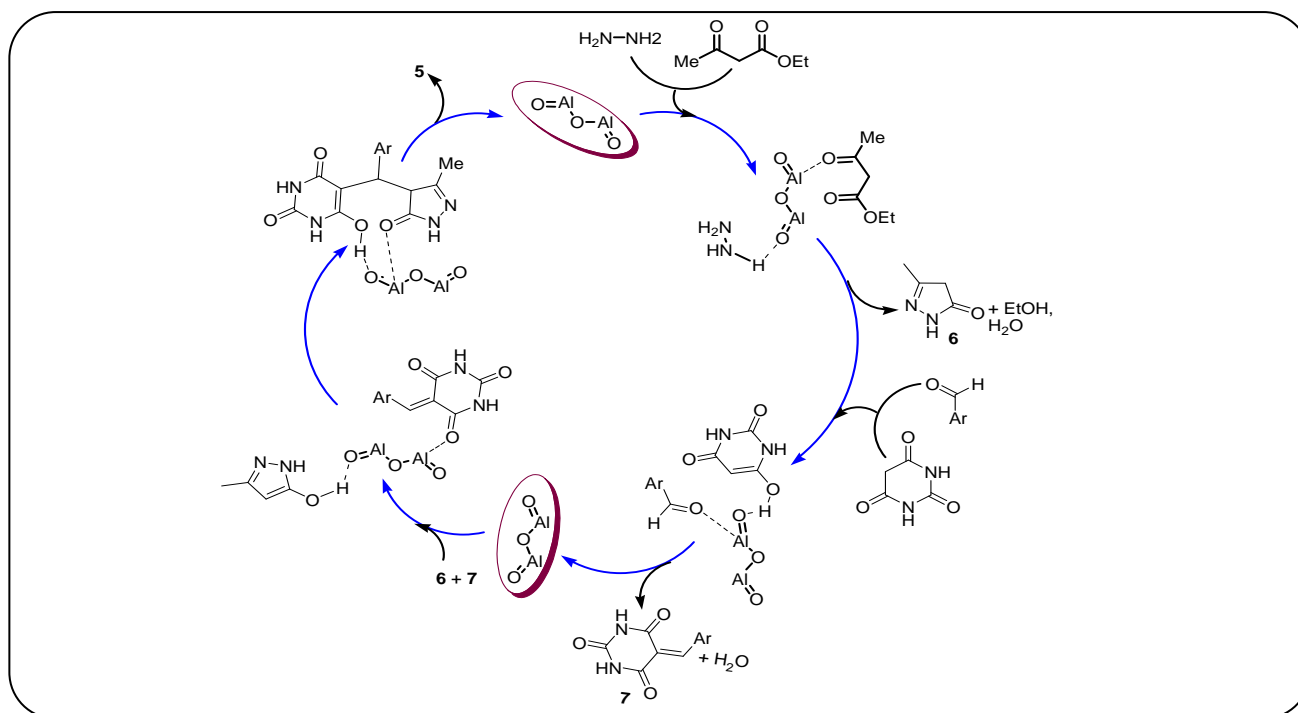
Entry	Product	Time (min)	Yield (%) ^a	M.p. (°C)
5a		90	92 ^b	217-219
5b		80	89 ^b	232-234
5c		110	90 ^b	230-232
5d		85	92 ^b	221-223
5e		80	85	242-244
5f		120	87	228-230
5g		110	83	218-220
5h		120	85	260-262

Table 3: Synthesis of triheterocyclic compounds 5 using Al_2O_3 NPs (7 mol%) in EtOH/ H_2O (1:1).

Entry	Product	Time (min)	Yield (%) ^a	M.p. (°C)
5i		115	90	252-254
5j		125	87	263-265
5k		110	85	246-248
5l		95	88	262-263

Scheme 2: Suggested mechanism for the synthesis of 5 using Al_2O_3 NPs.

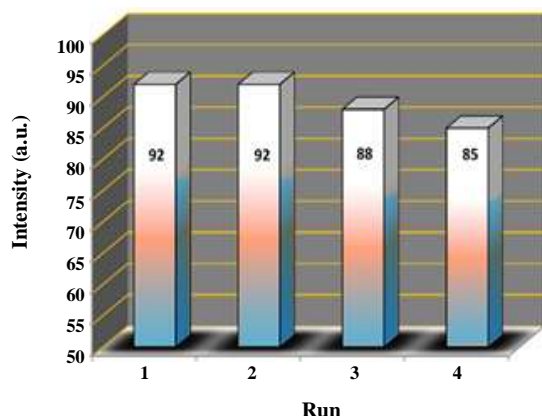


Fig. 5: Recyclability of the γ -Al₂O₃ NPs catalyst in the synthesis of 5a over four runs. Reaction time: 90 min.

four runs, during which a small appreciable loss was observed in the catalytic activity (Fig. 5).

CONCLUSIONS

In summary, a new facile synthesis of γ -Al₂O₃ NPs has been presented. As discussed, the γ -Al₂O₃ NPs represented a good catalytic activity for the one-pot, four component synthesis of fused heterocyclic systems like pyrazolopyranopyrimidinones as biologically important compounds. The γ -Al₂O₃ NPs may be used as an efficient heterogeneous catalyst for the organic reactions in the coming years. This method has some advantages such as the use of a safe and recyclable catalyst, avoidance of toxic solvents, high product yields, short reaction times, and an easy work-up procedure.

Acknowledgment

The authors gratefully acknowledge Islamic Azad University (Gachsaran Branch).

Received : Dec. 5, 2015 ; Accepted : Oct. 16, 2017

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