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Multicomponent synthesis of C-tethered bispyrazol-5-ols using CeO_2 nanoparticles as an efficient and green catalyst

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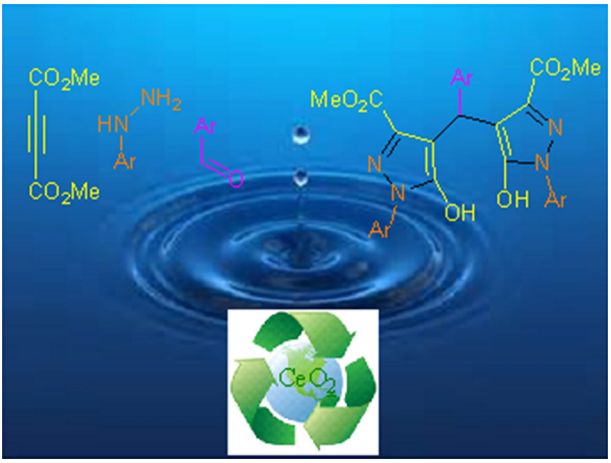
Abstract CeO_2 nanoparticles have been used as an efficient catalyst for the preparation of C-tethered bispyrazol-5-ols by pseudo five-component reaction of phenylhydrazine, acetylenedicarboxylates, and aromatic aldehydes at 70 °C in water. The use of no hazardous organic solvent, as well as atom economy, short reaction times, little catalyst loading and high yields of products are some of the important features of this protocol.

Graphical Abstract



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Introduction

The pyrazol ring system represents a common scaffold in numerous bioactive compounds and has a number of pharmacological properties. The pyrazole derivatives exhibit important biological properties, such as anti-malarial activity [1], fungicidal activity against *wheat rust*, *phoma asparagi* and antiviral activity against *TMV* [2], antibacterial activity [3], inhibition of mycobacterium tuberculosis [4], anti-inflammatory and antioxidant activities [5], having the highest selectivity for CB_1 receptors [6], antiallergic activity [7] and antimicrobial activities [8]. Consequently, looking for efficient and simple methods for the synthesis of pyrazoles is an interesting challenge that is at the forefront of organic chemistry. In recent years, multicomponent reactions (MCRs) have been extensively utilized to produce heterocyclic compounds with biological activity. These reactions provide instantaneous access to complex compound libraries with diverse functionality [9–13]. In addition, MCRs are environmentally friendly, and play a prominent role in green chemistry [14, 15]. Therefore, the design of new MCRs with green procedures has attracted great attention. Organic reactions carried out in water, without the use of any hazardous and flammable organic solvents, are one of the current challenges, especially in the areas of drug discovery, organic synthesis, and environmentally benign synthesis [16]. The possibility of performing multicomponent reactions with a green catalyst in water as a green solvent plays a prominent role in green chemistry. In recent years, nano-catalysts have emerged as an alternative approach for the improvement of many significant organic reactions [17–22]. Recently, many of these catalysts have worked for millions of turnovers, at high reaction rates, and with high selectivity. Therefore, there is a vital need to design new types of sustainable heterogeneous catalysts for chemical synthesis. Among various nanoparticles, cerium nanoparticles have received considerable attention because of their unique properties and potential applications in diverse fields. CeO_2 has received much attention due to its many attractive characteristics, such as unique UV absorption ability [23], ferromagnetism properties [24], depollution of noxious compounds from gaseous streams originating from industrial productions and from automobiles, as well as its being a major part of catalyst formulation for the dehydrogenation of ethylbenzene to styrene [25] and a crucial addition to current a series of three-way catalysts (TWCs) [26]. Recently, cerium and CeO_2 nanoparticles were used as an appropriate catalyst in many reactions, including synthesis of cyclic ureas [27], polyhydroquinolines [28], 1,4-disubstituted-1,2,3-triazoles [29], direct synthesis of imines from alcohol and amine [30], 1,3-diols [31], hydration of nitriles to amides [32], and conversion of carbon dioxide into dimethyl carbonate with 2-cyanopyridine [33]. The synthesis of C-tethered bispyrazol-5-ols has been reported using MCR in the presence of acetic acid as catalyst and solvent [34]. This method has certain drawbacks, including use of non-reusable catalyst and utilization of specific conditions. Ideally, use of green solvent and utilizing environmental and

green catalysts that can be simply recycled at the end of reactions are some of the important features of each protocol. Herein, we wish to report a highly efficient procedure for the preparation of C-tethered bispyrazol-5-ols using CeO_2 nanoparticles as an efficient catalyst at 70 °C in water (Scheme 1).

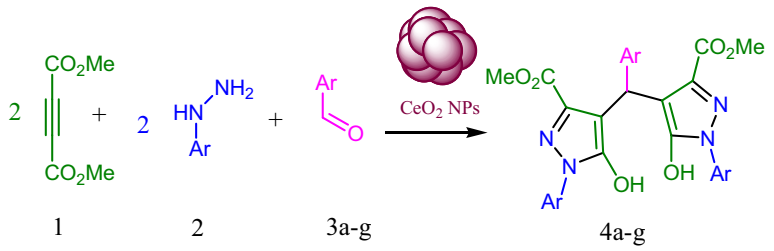
Experimental

Chemicals were purchased from the Sigma-Aldrich and Merck in high purity. All of the materials were of commercial reagent grade and were used without further purification. All melting points are uncorrected and were determined in capillary tubes on a Boetius melting point microscope. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker 400 MHz spectrometer with DMSO-d_6 as solvent, using tetramethylsilane (TMS) as an internal standard; the chemical shift values are in δ. Fourier transform infrared spectroscopy (FTIR) spectrum was recorded on Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm^{-1}. The elemental analysis (C, H, N) was obtained from a Carlo ERBA Model EA 1108 analyzer. The N_2 adsorption/desorption analysis (BET) was performed at −196 °C using an automated gas adsorption analyzer (Tristar 3000, Micromeritics).

Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with mono chromatized Cu Kα radiation ($\lambda = 1.5406$ Å). Microscopic morphology of products was visualized by scanning electron microscopy (SEM) (MIRA 3 TESCAN).

Preparation of CeO_2 nanoparticles

Nano CeO_2 was prepared according to the method reported in the literature, with some modification [35]. CeO_2 nanoparticles were prepared by a co-precipitation procedure with post-annealing in air. Briefly, 3 g of highly pure $Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in a mixture of 50 ml deionized water and 20 ml alcohol. Afterward, the appropriate amount of aqueous ammonia solution (28 wt%) was added to the above solution until the pH value reached 8. Then the mixture was stirred for 4 h at room temperature and then dried at 80 °C for 6 h. After, the solid was treated at 700 °C for 2 h to gain the CeO_2 nanoparticles.



Scheme 1 Synthesis of C-tethered bispyrazol-5-ols using CeO_2 nanoparticles

General procedure for the synthesis of C-tethered bispyrazol-5-ols

A mixture of acetylenedicarboxylate (2 mmol) phenylhydrazine (2 mmol) and CeO_2 nanoparticles (4 mol%, 14 mg) as catalyst were mixed in H_2O and then stirred at room temperature for 5 min. Then the aromatic aldehyde (1 mmol) was added into the mixture. The new mixture was stirred at 70 °C for an appropriate time. Then it was allowed to cool to room temperature. The formed precipitate was isolated by filtration. The product was dissolved in hot CH_3OH and the catalyst was filtered. After cooling, the crude products were precipitated. The precipitate was washed with EtOH to afford the pure product and then dried well under vacuum pump.

Spectral data of products

Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-nitro phenyl)methyl)-5-hydroxy-1-phenyl-1H-pyrazole-3-carboxylate (**4a**) Golden powder, mp 216–217 °C; IR (KBr) (ν_{max}/cm^{-1}): 3433.44, 3072.26, 2954.06, 1731.84, 1600.26, 1515.65, 1444.51, 1346.64, 1214.58, 1114.29, 841.23; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.85 (*s*, 6H, 2OCH$_3$), 4.81 (2OH exchanged with water of DMSO-d_6), 6.91 (*s*, 1H, CH), 7.29–7.43 (*t*, $J = 7.6$ Hz, 6H, H-Ar), 7.51 (*d*, $J = 8$ Hz, 2H, H-Ar), 7.79–7.85 (*m*, 4H, H-Ar), 8.14 (*d*, $J = 7.6$ Hz, 2H, H-Ar); anal. calcd for $C_{29}H_{23}N_5O_8$: C, 61.16; H, 4.07; N, 12.30; Found: C, 61.12; H, 4.12; N, 12.42.

Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-chlorophenyl)methyl)-5-hydroxy-1-phenyl-1H-pyrazole-3-carboxylate (**4b**) White powder, mp 226–228 °C; IR (KBr) (ν_{max}/cm^{-1}): 3429.09, 3068.70, 2952.85, 1718.90, 1599,42, 1492.71; ^{1}HNMR (400 MHz, CDCl$_3$): δ (ppm) 3.91 (*s*, 6H, 2OCH$_3$), 6.18 (*s*, 1H, CH), 7.23 (*m*, 2H, H-Ar), 7.26 (*m*, 2H, H-Ar), 7.38 (*m*, 2H, H-Ar), 7.47 (*m*, 4H, H-Ar),7.80 (*m*, 4H, H-Ar), 10.57 (2OH); anal. calcd for $C_{29}H_{23}ClN_4O_6$: C, 62.31; H, 4.15; N, 10.02; Found: C, 62.24; H, 4.19; N, 9.90.

Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(2,4-dichlorophenyl)methyl)-5-hydroxy-1-phenyl-1H-pyrazole-3-carboxylate (**4c**) White powder, mp 207–209 °C; IR (KBr) (ν_{max}/cm^{-1}): 3442.10, 2922.78, 1726.22, 1597.00, 1499.92,1209.66,1110.18; ^{1}HNMR (400 MHz, DMSO-d_6): δ (ppm) 3.77 (*s*, 6H, 2OCH$_3$), 4.69 (2OH exchanged with water of DMSO-d_6), 6.72 (*s*, 1H, CH),7.12–7.78 (*m*, 13H, H-Ar); ^{13}CNMR (100 MHz, DMSO-d_6): δ (ppm) 31.13, 52.07, 105.23, 122.43, 122.63, 126.88, 127.02, 129.11, 129.27, 129.54, 131.56, 131.99, 133.88, 138.35, 157.26, 162.84; anal. calcd for $C_{29}H_{22}Cl_2N_4O_6$: C, 58.70; H, 3.74; N, 9.44; Found: C, 58.65; H, 3.79; N, 9.51.

Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(3-methylphenyl)methyl)-5-hydroxy-1-phenyl-1H-pyrazole-3-carboxylate (**4d**) green powder, mp 199–200 °C; IR (KBr) (ν_{max}/cm^{-1}): 3429.92, 3027.60, 2951.71, 1722.51,1600.24,1494.43, 1209.78, 1122.14, 863.29,761.80, 691.56; ^{1}HNMR

(400 MHz, DMSO-d_6): δ (ppm) 2.19 (*s*, 3H, CH_3), 3.83 (*s*, 6H, $2OCH_3$), 4.83 (2OH exchanged with water of DMSO-d_6), 6.76 (*s*, 1H, CH), 6.93–7.76 (*m*, 14H, Ar-H); ^{13}CNMR (100 MHz, DMSO-d_6): δ (ppm) 31.09, 31.97, 52.37, 107.99, 122.81, 123.36, 124.88, 126.96, 127.46, 128.31, 128.41, 129.37, 137.42, 137.53, 138.51, 142.65, 162.41. anal. calcd for $C_{30}H_{26}N_4O_6$: C, 66.91; H, 4.87; N, 10.40; Found: C, 66.99; H, 4.94; N, 10.32.

Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(phenyl)-methyl)-5-hydroxy-1-phenyl-1H-pyrazole-3-carboxylate (**4e**) brown powder, mp 287–289 °C; IR (KBr) (ν_{max}/cm^{-1}): 3427.79, 2954.15, 1707.83, 1599.70, 1575.00, 759.86, 697.42; ^{1}HNMR (400 MHz, DMSO-d_6): δ (ppm) 3.356 (*s*, 6H, $2OCH_3$), 3.772 (2OH, exchanged with water of DMSO-d_6), 6.695 (*s*, CH, 1H), 7.04–7.90 (*m*, 15H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 32.23, 51.49, 105.37, 121.29, 125.30, 125.67, 128.01, 128.99, 130.54, 137.30, 139.77, 140.22, 158.50, 164.30. anal. calcd for $C_{29}H_{24}N_4O_6$: C, 66.41; H, 4.61; N, 10.68; Found: C, 66.48; H, 4.72; N, 10.58.

Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(2-chloro-phenyl)methyl)-5-hydroxy-1-phenyl-1H-pyrazole-3-carboxylate (**4f**) white powder, mp 267–269 °C; IR (KBr) (ν_{max}/cm^{-1}): 3420.09, 2957.63, 1723.60, 1595.93, 1552.37, 1207.75, 1131.41, 765.34; ^{1}HNMR (400 MHz, DMSO-d_6): δ (ppm) 3.772 (*s*, 6H, $2OCH_3$), 4.691 (2OH exchanged with water of DMSO-d_6), 7.347 (*s*, 1H, CH), 7.503 (*m*, 6H, Ar-H), 7.776 (*m*, 8H, Ar-H); ^{13}CNMR (100 MHz, DMSO-d_6): δ (ppm): 31.15, 51.67, 102.04, 122.58, 122.81, 127.36, 127.85, 129.39, 129.55, 131.45, 131.92, 133.20, 138.77, 141.06, 151.96, 162.98. anal. calcd for $C_{29}H_{23}ClN_4O_6$: C, 62.31; H, 4.15; N, 10.02; Found: C, 62.24; H, 4.19, N, 10.09.

Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)(4-methylphe-nyl)methyl)-5-hydroxy-1-phenyl-1H-pyrazole-3-carboxylate (**4g**) Green powder,

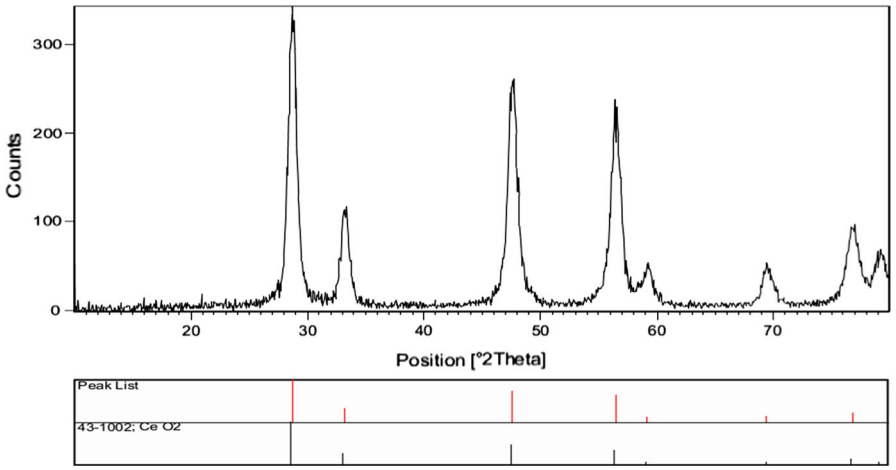


Fig. 1 XRD images of CeO_2 NPs NPs

mp; 195–197 °C, IR (KBr) (ν_{max}/cm^{-1}): 3432.33, 3063.23, 2952.85, 1729.77, 1602.65, 1506.83, 1447.80, 1207.52, 1122.80; ^{1}HNMR (400 MHz, DMSO-d_6): δ (ppm) 2.196 (*s*, 3H, CH_3), 3.760 (*s*, 6H, 2OCH_3), 4.319 (2OH exchanged with water of DMSO-d_6), 6.68 (*s*, 1H, CH), 6.76–7.77 (*m*, 14H, Ar-H), ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm): 29.3, 31.3, 51.68, 113.83, 122.81, 123.36, 124.88, 126.96, 127.46, 128.41, 129.37, 138.51, 142.65, 162.41. anal. calcd for $C_{30}H_{26}N_4O_6$: C, 66.91; H, 4.87; N, 10.40; Found: C, 66.98; H, 4.96; N, 10.35

Results and discussion

The catalyst was prepared by the co-precipitation technique, with aqueous ammonia solution as the precipitating agent. The XRD patterns for the CeO_2 nanoparticle is shown in Fig. 1. The pattern agrees well with the reported pattern for CeO_2 nanoparticles (JCPDS No. 43-1002). The crystalline size was calculated from FWHM using Scherrer's formula and was observed to be 9–11 nm. The morphology and particle size of CeO_2 NPs was investigated by scanning electron microscopy (SEM), as shown in Fig. 2. The SEM images prove particles with diameters that are in the range of nanometers.

The choice of a suitable reaction medium is of vital importance for successful synthesis. Initially, we had explored and optimized different reaction parameters for the synthesis of C-tethered bispyrazol-5-ols by the pseudo five-component reaction of phenylhydrazine (2 mmol), acetylenedicarboxylates (2 mmol) and 4-nitrrobenzaldehyde (1 mmol) as a model reaction. As shown in Table 1, the solvent has a great effect on the acceleration of the reactions. Several reactions were scrutinized using various solvents, such as EtOH, CH_3CN, $CHCl_3$ and water. The best results were obtained at 70 °C in H_2O and the reaction gave satisfying results in the presence of CeO_2 nanoparticles (Table 1). The polarity, dipole moment,

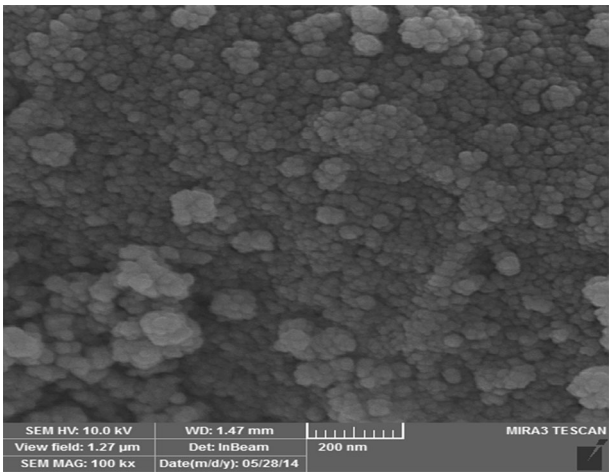


Fig. 2 SEM images of CeO_2 NPs NPs

Table 1 Optimization of reaction conditions using different catalysts

Entry	Solvent	Catalyst (mol%)	Time (min)	Surface area (m^2/g)	Yield (%)[a]
1	H_2O	–	360	–	Nil
2	CH_3CN	CuO (4)	60	2.2	24
3	EtOH	NiO (3)	65	2.1	32
4	$CHCl_3$	CuO (3)	80	0.9	15
5	EtOH	Al_2O_3 (5)	60	11.6	37
6	H_2O	CaO (4)	55	1.2	30
7	H_2O	ZrO_2 (5)	40	4.9	54
8	EtOH	CuI (4)	55	1.9	50
9	EtOH	Nd_2O_3 (4)	45	3.2	53
10	EtOH	CAN[b] (2)	40	–	58
11	EtOH	ZrO_2 (5)	45	4.9	51
12	H_2O	CeO_2 (bulk)	38	5.2	63
13	EtOH	CeO_2 NPs (3)	32	33.2	75
14	H_2O	CeO_2 NPs (2)	22	33.2	85
15	**H_2O**	**CeO_2NPs (4)**	**18**	**33.2**	**90**
16	H_2O	CeO_2 NPs (6)	18	33.2	91

Phenylhydrazine (2 mmol), acetylenedicarboxylates (2 mmol), and 4-nitrobenz-aldehyde (1 mmol)

Entry 15 is bold due to the best yield in 18 min for the reaction

[a] Isolated yield

[b] Cerium(IV) ammonium nitrate

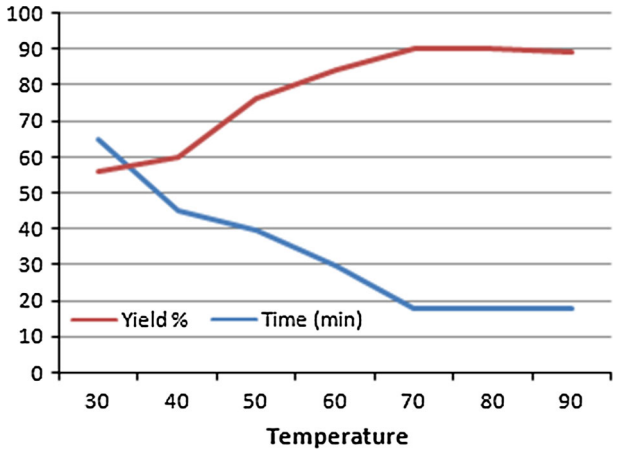


Fig. 3 Effects of temperature variation on the yield and time of the model reaction

polarizability and hydrogen bonding of a solvent determine what type of compounds it is able to dissolve. In this reaction, the use of polar solvents favors the reaction mechanism. The catalyst showed best activity in water compared to other organic solvents such as EtOH, CH_3CN, and $CHCl_3$. Water with a dielectric constant of

about 80 carried out reactions in good to excellent yields. Therefore, the use of polar solvents with high dielectric constant favors the condensation reactions. Also, the activity and stability of the CeO_2 nanoparticles in water is maximal compared to other solvents for the synthesis of C-tethered bispyrazol-5-ols. The significant results presented in Table 1 are related to the hydrogen bonding between water or ethanol and substrates that promote nucleophilic attack of the reactants.

When 2, 4, and 6 mol% of CeO_2 nanoparticles were used, the yields were 85, 90, and 90 % respectively. Therefore, performing the reaction with a higher catalyst loading (6 mol%) had no significant effect on yield. The model reactions were carried out in the presence of diverse catalysts, including NiO, CuO, Al_2O_3, CaO, ZrO_2, CuI and CAN. When the reaction was carried out using CAN, CuI, ZrO_2 NPs and CeO_2 NPs as the catalyst, the product could be obtained in a moderate to good yield. To optimize the experiment temperature, the mixture was heated at different temperatures (30, 40, 50, 60, 70, 80, 90 °C) (Fig. 3). The time of reaction was decreased when the reaction temperature was raised from 50 to 70 °C. Therefore, 70 °C was chosen as the reaction temperature for all subsequent reactions.

With these hopeful results in hand, we turned to investigate the scope of the reaction using various aromatic aldehydes as substrates under the optimized reaction conditions (Table 2).

In the recycling procedure of CeO_2 NPs, the product was dissolved in hot CH_3OH and the catalyst was filtered. The solution was filtered and the heterogeneous catalyst was recovered. The recovered CeO_2 NPs was washed three to four times with water and ethyl acetate, and dried at 100 °C for 5 h. We also investigated recycling of the CeO_2NPs as catalyst for the synthesis of 4a. The results showed that CeO_2 NPs can be reused several times with a slightly decreased activity (run 1, 90 %; run 2, 89 %, run 3, 89 %; run 4, 88 %, run 5, 87 %). The catalyst could be reused for five times with a minimal loss of activity. The activity of CeO_2 NPs might be decreased by number of the regenerations. The morphology and particle size of CeO_2 nanoparticle was investigated by scanning electron microscopy (SEM) before use and after five times of reuse, with images shown in Fig. 4. The SEM of CeO_2 nanoparticles before and after the reaction showed identical images. Interestingly, the morphology of the nanoparticles remained unchanged

Table 2 Synthesis of C-tethered bispyrazol-5-ols using CeO_2 NPs at 70 °C in water

Entry	Aldehyde (Ar)	Product	Time (min)	Yield (%)[a]	mp (°C)	Lit. mp. (ref)
1	4-NO_2–C_6H_4	**4a**	18	90	216–217	– [34]
2	4-Cl–C_6H_4	**4b**	18	88	226–228	– [34]
3	2-4-Cl–C_6H_3	**4c**	22	86	207–209	–
4	3-Me–C_6H_4	**4d**	25	83	199–200	–
5	C_6H_5	**4e**	20	85	287–289	–
6	2-Cl–C_6H_4	**4f**	22	85	267–269	–
7	4-Me–C_6H_4	**4g**	24	83	195–197	–

[a] Isolated yield

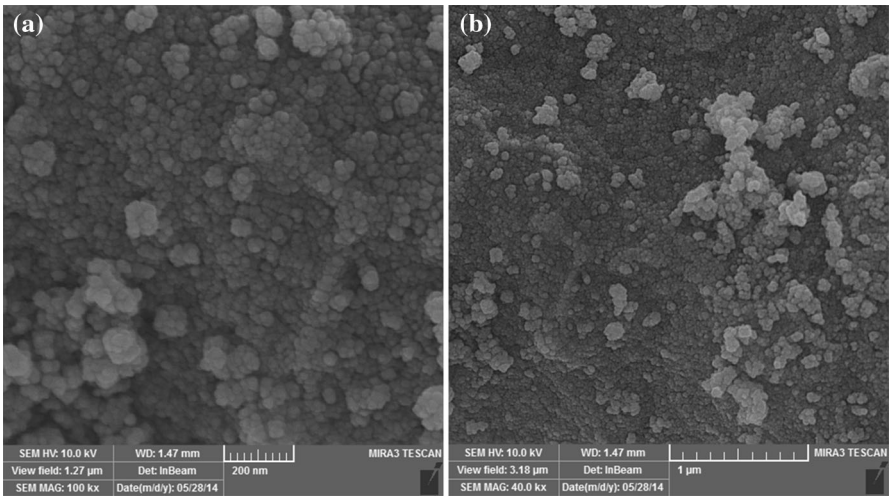


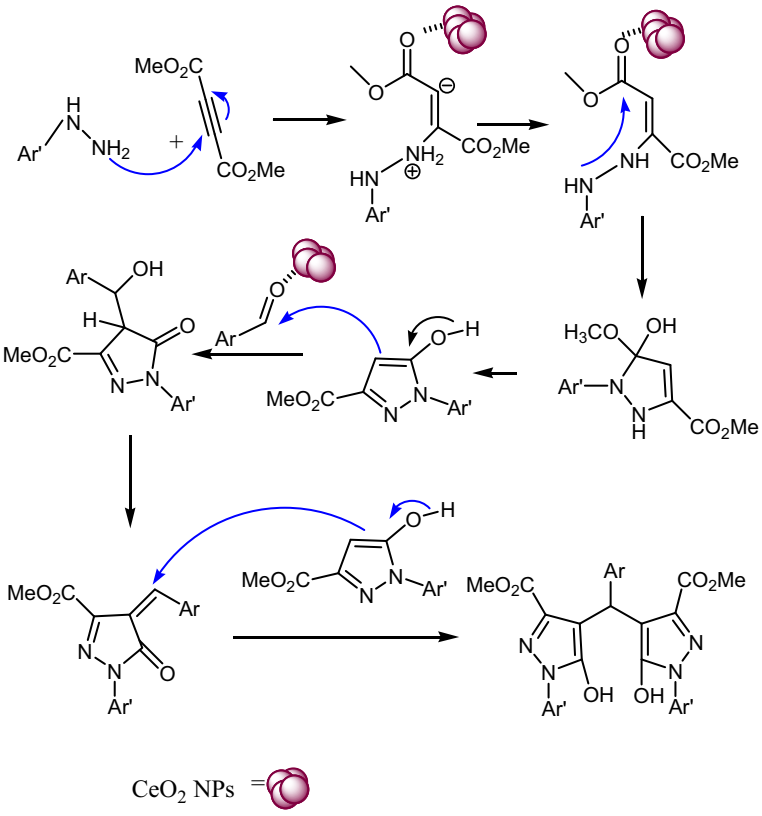
Fig. 4 SEM of CeO_2 nanoparticles **a** before use, **b** after five times of reuse

before and after reaction. We believe that this is also a possible reason for the extreme stability of the CeO_2 nanoparticles presented herein.

The mechanism of these domino reactions is proposed in Scheme 2. The chemistry of rare earth elements differs from main group and transition metals due to the nature of the *4f* orbitals, which are 'buried' inside the atom and are shielded from the atom's environment by the *4d* and *5p* electrons. The chemical nature and the existing form of the catalyst play a vital importance for the reaction. These characterization results clearly prove that ceria contains surface oxygen vacancy sites as Lewis acidic sites. The surface population of vacancy sites depends on the preparation method. During the reaction, water is adsorbed on these sites with only medium strength and does not poison these sites, which explains why the ceria catalyst is stable in water. We believe that the present findings will open a new vista of ceria catalysts in aqueous reactions and greatly contribute to the understanding of other oxides as heterogeneous catalysts [31]. The chemical nature and the existing form of the catalyst play a vital importance for the reaction. From the results, it is obvious that the CeO_2 nanoparticle is the best catalyst among those examined and reported in Table 1.

Theoretically, nanoscale heterogeneous catalysts should present higher surface areas, which are chiefly responsible for their catalytic activity. We tested CeO_2 bulk with surface area 5.2 m^2/g and CeO_2 NPs with surface area 33.2 m^2/g; yields were 63 and 90 %, respectively. So, the increased surface area owing to small particle size improved reactivity.

An initial condensation of acetylenedicarboxylate and phenylhydrazine generated 1,3-dipole intermediate, which sequentially underwent proton transfer and aminolysis of the ester group, generating the pyrazolone derivative in situ. The pyrazolone derivative was subjected with aromatic aldehydes, leading to arylidene pyrazolones. In this mechanism, the surface atoms of CeO_2 NPs activate the C=O



Scheme 2 Probable mechanism for the formation of C-tethered bispyrazol-5-ols using CeO_2 nanoparticles

group for better reaction with nucleophiles. These surface atoms behave as the centers where chemical reactions could be catalytically stimulated. So the arylidene pyrazolones were further reacted with pyrazolones generated in situ to give the final C-tethered bispyrazol-5-ols derivatives.

Conclusion

In conclusion, we have developed a simple, green and highly efficient protocol for the synthesis of C-tethered bispyrazol-5-ols using CeO_2 nanoparticles as an efficient catalyst at 70 °C in water. The procedure offers several advantages, including cleaner reaction profiles and use of simply available reagents; it is cheap, has high yields, a shorter reaction time and has easy experimental reusability of the catalyst and little catalyst loading. This green nanocatalyst could be used for other noteworthy organic reactions and transformations. Further investigations of similar protocols are happening in our laboratory.

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