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A comparative screening of the catalytic activity of nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics in the one-pot synthesis of 1,6-diamino-4-aryl-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile derivatives

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Abstract A four-component reaction of hydrazine hydrate, ethyl cyanoacetate, malononitrile, and aromatic aldehydes was achieved in the presence of nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics (M^{II}: Mn, Fe, Co, Ni, Cu, Zn, Cd) as heterogeneous catalysts to produce N-amino-2-pyridones. The reactions were performed in the presence of different catalysts, and it is observed that $CdZr_4(PO_4)_6$ nanocrystallines are the best catalysts among those examined. Atom economy, excellent yields in short times, high catalytic activity, recycling of catalyst, and environmental benignity are some of the important features of this protocol.

Keywords $M^{II}Zr_4(PO_4)_6$ ceramics · N-amino-2-pyridones · Catalytic activity · One pot

Introduction

Syntheses of heterocyclic compounds have become an important area of research in organic chemistry. The improvement of new efficient methods for the synthesis *N*-heterocycles with structural diversity is one major class of modern synthetic organic

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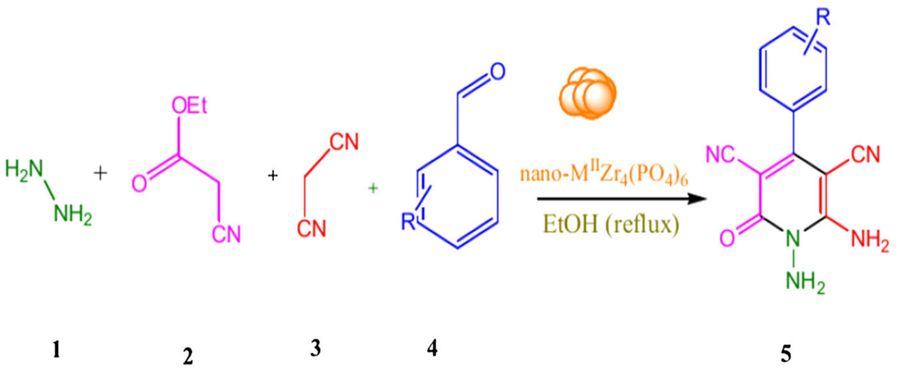
chemists [1–3]. Among a large variety of heterocyclic compounds, 2-pyridone derivatives are valuable synthetic scaffolds for both medicinal and synthetic organic chemists [4, 5]. Pyridones exhibit important biological properties such as antibacterial [6], antifungal [7], antitumor [8], and potential HIC-1 specific transcriptase inhibitors [9]. The synthesis of 2-pyridones has been reported using K_2CO_3/H_2O under microwave irradiation [10], bipyridinium chlorochromate (BPCC) [11], magnesium oxide (MgO) and bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) [12], piperidine [13–16], and Et_3N [17, 18]. However, some of the reported methods have disadvantages including long reaction times, harsh reaction conditions, and use of toxic and non-reusable catalysts. Therefore, to avoid these limitations, the exploration of an efficient and reusable catalyst with high catalytic activity for the preparation of 2-pyridines is still favored.

Recently, fused heterobicyclic systems containing the 1,2,4-triazinopyridinone moiety have been prepared by heterocyclization of N-amino-2-pyridones with different reagents [19]. Meanwhile, reactions of some active carbonyl compounds with 4-aryl-1,6-diamino-2-oxo-1,2- dihydro-pyridine-3,5-dicarbonitrile derivatives have been documented in recent years [20]. Therefore, the development of efficient, clean, and environmentally friendly approaches using new catalysts for the synthesis of 1,6-diamino-2-oxo-4-phenyl-1,2-dihydropyridine-3,5-dicarbonitrile derivatives is an important task for organic chemists. Synthesis of bioactive compounds should be simple, flexible, and comprehensive in organic synthesis. Multi-component reactions (MCRs) are very flexible, atom economic in nature, convergent, facile, and are usually considered for the development of environmentally benign synthetic methods [21–24]. The possibility of performing multicomponent reactions under moderate conditions with a heterogeneous catalyst could improve their effectiveness from operating cost and ecological points of view [25, 26]. Nanocrystalline structures are used as convenient and efficient catalysts in many organic reactions due to their high surface-to-volume ratio and large number of low-coordination sites per unit area [27, 28].

$MZr_4(PO_4)_6$ structure ceramics are interesting because of their unique properties and potential applications in diverse fields [29, 30]. We combined the advantages of ultrasonic approach and solvothermal method to design an efficient method for the synthesis of nanocrystalline $MZr_4(PO_4)_6$ ceramics [31]. In this study, we reported the use of nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics as an efficient catalyst for the preparation of 1,6-diamino-4-phenyl-2-oxo-1,2-dihydropyridine-3,5-dicarbonitriles by the four-component condensation reactions of hydrazine hydrate, ethyl cyanoacetate, malononitrile, and aromatic aldehydes (Scheme 1). Extraordinarily, the best results obtained in using $CdZr_4(PO_4)_6$ nanocrystallines as an efficient catalyst.

Experimental

Reagent grade chemicals were purchased from Sigma-Aldrich or Merck and were used without further purification. A multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany), equipped with a converter/transducer and titanium



Scheme 1 Synthesis of N-amino-2-pyridones in the presence of nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics(M^{II}: Mn, Fe, Co, Ni, Cu, Zn, Cd)

oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 200 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. All melting points are uncorrected and were determined in a capillary tube on Boetius melting point microscope. FT-IR spectra were recorded with KBr pellets using a Magna-IR, spectrometer 550 Nicolet. NMR spectra were obtained on a Bruker 400 MHz spectrometer (^{1}H NMR at 400 Hz, ^{13}C NMR at 100 Hz) in DMSO-d_6 using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) are given in Hz. The mass spectra were recorded on a Joel D-30 instrument at an ionization potential of 70 eV. CHN compositions were measured by Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips X'pert diffractometer with monochromatized Zr Kα radiation ($\lambda = 1.5406$ Å). In order to investigate the particle size and morphology of the synthesised structures of nano-$CdZr_4(PO_4)_6$, FE-SEM images of the products visualized by a HITACHI S4160 Field Emission Scanning Electron Microscope.

Preparation of nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics

Nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics were prepared according to the method reported in the literature, with some modification [31]. All the chemical reagents used in our experiments were analytical grade (Sigma-Aldrich or Merck Company) and were used as received without further purification. In this work, nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics were prepared via solvothermal method that assisted sonochemical method. $ZrOCl_2$ was used as zirconium source. Firstly 1 mmol of $ZrOCl_2.8H_2O$ and 1 mmol of metalsources (see Table 1) were added in 15 mL of $HO(CH_2)_2OH$ and sonicatedat 30 W power to completely dissolution. Afterward, 0.8 mL H_3PO_4 (85 %), 4 mmol of NH_4Cl, and 1.4 mL of CH_3NH_2 water solution (25.0–30.0 %) were added consecutively and sonicated for 30 min. Then, the reaction mixture was transferred into a Teflon-lined autoclave under autogenous pressure at 200 °C for 5 days. When the reaction was completed, dispersed

Table 1 Comparison of metal sources to prepare $M^{II}Zr_4(PO_4)_6$

Sources	$MnZr_4(PO_4)_6$	$FeZr_4(PO_4)_6$	$CoZr_4(PO_4)_6$	$NiZr_4(PO_4)_6$	$CuZr_4(PO_4)_6$	$ZnZr_4(PO_4)_6$	$CdZr_4(PO_4)_6$
$M^{II}SO_4 \cdot xH_2O$	–	–	–	–	–	–	–
$M^{II}(NO_3)_2 \cdot xH_2O$	✓	–	✓	✓	✓	✓	–
$M^{II}(OAc)_2 \cdot xH_2O$	–	–	–	–	–	–	✓
$(NH_4)_2M^{II}(SO_4)_2 \cdot xH_2O$	–	✓	–	–	–	–	–

precipitate was obtained. The solid was filtered and washed with distilled water and ethanol several times. Subsequently, the product was dried at 50 °C for 5 h and calcined at 700 °C for 2 h. Afterward the solid was added to 20 mL of DMF and sonicated at 95 W for 2 h. Finally, the resulting product was filtered, washed with distilled water and absolute ethanol, and dried at 150 °C for 2 h in vacuum to afford pure nano-$M^{II}Zr_4(PO_4)_6$ ceramics.

General procedure for the preparation of N-amino-2-pyridones

A mixture of hyrazine hydrate (2 mmol), ethyl cyanoacetate (2 mmol), malononitrile (2 mmol), aromatic aldehydes (2 mmol), and 0.06 mol% of $CdZr_4(PO_4)_6$ nanocrystalline in ethanol (5 mL) was refluxed with stirring for the specific time (Table 3). The reaction was monitored by TLC. After cooling, the reaction mixture was dissolved in acetone and the mixture stirred for 2 min. The suspended solution was filtered and the heterogeneous catalyst was recovered. The acetone was evaporated and the solid separated out was filtered and recrystallized with ethanol to get pure product. The structures of the products were fully established on the basis of their ^1H NMR, ^{13}C NMR, and FT-IR spectra (See Supplementary information).

Results and discussion

In the beginning, we prepared nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics by solvothermal method that assisted sonochemical method. In our initial experiments, the reactions were established based on the reactions between $ZrOCl_2$ and different metal sources. These reactions were carried out using various metal salts such as nitrates, sulfates, and acetates. As shown in Table 1, in most cases the best results were obtained by reaction with nitrate salts, also for $FeZr_4(PO_4)_6$and $CdZr_4(PO_4)_6$, Mohr's Salt and cadmium (II) acetate were the best choices, respectively.

In order to investigate the particle size and morphology of the synthesis structures $M^{II}Zr_4(PO_4)_6$, FE-SEM images of the products visualized by a HITACHI S4160 Field Emission Scanning Electron Microscope. The size and morphology synthesized nanomaterials are shown in Fig. S1–S7 (see Supplementary information); the size of nanostructures is in the range of 20–150 nm. Also, XRD patterns of synthesized nanocrystallines are shown in Fig. S1–S7 (see Supplementary information). All reflection peaks can be readily indexed to pure crystalline phase of nanocrystalline $M^{II}Zr_4(PO_4)_6$. The crystallite size diameter (D) of these nanoparticles was calculated by the Debye–Scherrer equation ($D = K\lambda/\beta\cos\theta$), where FWHM (full-width at half-maximum or half-width) is in radians and θ is the position of the maximum of diffraction peak, K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the X-ray wavelength. The results show that nanostructures were obtained with an average diameter of 20–150 nm. This range of nanostructures can be used as catalyst in organic reactions.

Initially, we carried out the MCR between hydrazine hydrate, ethyl cyanoacetate, malononitrile, and 4-chlorobenzaldehyde as a model reaction in the presence of different catalysts. Several reactions were scrutinized using different solvents such as ethanol (EtOH), acetonitrile (CH_3CN), water (H_2O), dimethylformamide (DMF), and solvent-free conditions. The best results were obtained under reflux conditions in ethanol (yield: 93 %). The model reaction was carried out in the presence of various nanocatalysts such as nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics (M^{II}: Mn, Fe, Co, Ni, Cu, Zn, Cd). When the reaction was carried out using $CuZr_4(PO_4)_6$, $ZnZr_4(PO_4)_6$, and $CdZr_4(PO_4)_6$ nanocatalysts, the product could be obtained in moderate to good yields of 62, 75, and 93 %, respectively. From the results, it is observed that $CdZr_4(PO_4)_6$ nanocrystalline is the best catalyst among those examined which were reported in Table 2. When 0.04, 0.06, and 0.08 mol% of $CdZr_4(PO_4)_6$ nanocrystalline were used, the yields were 87, 93, and 93 % respectively. Consequently, 0.06 mol% of $CdZr_4(PO_4)_6$ nanocrystalline was expedient and excessive amount of $CdZr_4(PO_4)_6$ nanocrystalline did not change the yields considerably. Nanocatalysts are highly active since most of the particle surfaces are available for catalysis because chemical reactions take place mainly on the surface of the particles. However, the catalyst activity is influenced by factors such as acid–base properties, geometric structure (particularly pore structure), size and morphology of the particles, the distribution of sites, and the polarity of the surface sites [25, 26, 32]. It is important to note that nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics (M^{II}: Mn, Fe, Co, Ni, Cu, Zn, Cd) have diverse activity in the synthesis of N-amino-2-pyridones. The size and morphology of the particles of $FeZr_4(PO_4)_6$ and

Table 2 Optimization of reaction conditions using different catalysts and solvents

Entry	Solvent (reflux)	Catalyst (mol%)	Time (min)	Yield[a] %
1	EtOH	–	200	12
2	EtOH	$ZrOCl_2$ (0.8)	100	40
3	EtOH	$MnZr_4(PO_4)_6$ NPs(0.08)	60	53
4	EtOH	$FeZr_4(PO_4)_6$ NPs (0.07)	70	43
5	EtOH	$CoZr_4(PO_4)_6$ NPs(0.07)	65	45
6	EtOH	$NiZr_4(PO_4)_6$ NPs (0.06)	60	47
7	CH_3CN	$CuZr_4(PO_4)_6$ NPs (0.06)	50	55
8	EtOH	$CuZr_4(PO_4)_6$ NPs (0.06)	50	62
9	CH_3CN	$ZnZr_4(PO_4)_6$ NPs (0.06)	50	66
10	EtOH	$ZnZr_4(PO_4)_6$ NPs (0.06)	50	75
11	CH_3CN	$CdZr_4(PO_4)_6$ NPs (0.06)	45	78
12	EtOH	$CdZr_4(PO_4)_6$ NPs(0.04)	40	85
13	**EtOH**	**$CdZr_4(PO_4)_6$NPs (0.06)**	**30**	**93**
14	EtOH	$CdZr_4(PO_4)_6$ NPs (0.08)	30	93
15	H_2O	$CdZr_4(PO_4)_6$ NPs (0.08)	60	35
16	–	$CdZr_4(PO_4)_6$ NPs (0.06)	70	45
17	DMF	$CdZr_4(PO_4)_6$ NPs (0.06)	130	50

Hyrazine hydrate (2 mmol), ethyl cyanoacetate (2 mmol), malononitrile (2 mmol), 4-chloro benzaldehyde (2 mmol)

[a] Isolated yield

$\mathrm{NiZr_4(PO_4)_6}$ are similar. Thus, yields of $\mathrm{FeZr_4(PO_4)_6}$ and $\mathrm{NiZr_4(PO_4)_6}$ are moderate and similar (43-47 %). Among nanocrystalline $\mathrm{M^{II}Zr_4(PO_4)_6}$ ceramics, M: Mn, Fe, Co, Ni, Cu, Zn are in period 4 in the Periodic Table, and typical electronic structure of these transition metal atoms can be written as [ ]$ns^{1-2}(n-1)d^m$ (n = period, $m = 1$–10). Electronic configuration states of $\mathrm{M^{II}}$: Mn, Fe, Co, Ni, Cu, Zn are d^5, d^6, d^7, d^8, d^9, d^{10}. When the electronic configuration is d^{10}, the activity is maximum compared to other configurations. Therefore, $\mathrm{ZnZr_4(PO_4)_6}$ and $\mathrm{CdZr_4(PO_4)_6}$ have the maximum of activity. The element of group 12 in the first transition series is zinc (Zn) with configuration [Ar] 4 s^2 $3d^{10}$. Cd (cadmium) is in period 5 and group 12 in the Periodic Table with configuration [Kr] 5 s^2 $4d^{10}$. The $(n\text{-}1)d$ orbitals that are involved in the transition metals are very significant because they influence properties such as magnetic character, variable oxidation states, formation of colored compounds, and catalytic activity [29, 30, 33–38]. Perhaps, higher activity of $\mathrm{CdZr_4(PO_4)_6}$ than $\mathrm{ZnZr_4(PO_4)_6}$ is due to electronic configuration of Zn (II) and Cd (II). The nano-$\mathrm{CdZr_4(PO_4)_6}$ activate the C=O groups effectively for better reaction with nucleophiles in the synthesis of N-amino-2-pyridones compared to other nanocrystalline $\mathrm{M^{II}Zr_4(PO_4)_6}$ ceramics.

We also investigated recycling of nanocrystalline $\mathrm{M^{II}Zr_4(PO_4)_6}$ ceramics ($\mathrm{M^{II}}$: Mn, Fe, Co, Ni, Cu, Zn, Cd) as catalyst under reflux conditions in ethanol. The results showed that $\mathrm{CdZr_4(PO_4)_6}$ nanocrystalline can be reused several times without noticeable loss of catalytic activity (Yields 93–92 %) (Fig. 1).

With these encouraging results in hand, we turned to explore the scope of the reaction using different aromatic aldehydes as substrates under the optimized reaction conditions (Table 3).

In this reaction, a plausible mechanism, which involves Knoevenagel condensation, Michael addition, and cyclization to form N-amino-2-pyridones catalyzed by nano-$\mathrm{CdZr_4(PO_4)_6}$ (Scheme 2). Firstly, we assumed that the reaction occurs via a Knoevenagel condensation between malononitrile and aldehyde in the presence of nano-$\mathrm{CdZr_4(PO_4)_6}$ to form the intermediate **I** with the loss of a water molecule. Meanwhile, hydrazine hydrate reacts with ethyl cyanoacetate to form intermediate **II**. The Michael addition of the enolizable intermediate **II** with intermediate

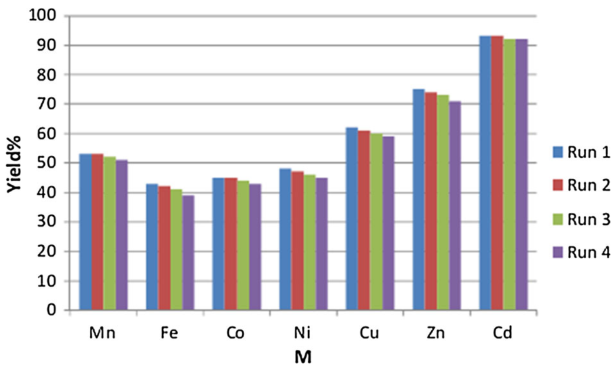


Fig. 1 Recycling of nanocrystalline $\mathrm{M^{II}Zr_4(PO_4)_6}$ ceramics in the synthesis of **5b**

Table 3 Synthesis of N-amino-2-pyridones using $CdZr_4(PO_4)_6$ nanocrystalline

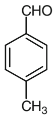
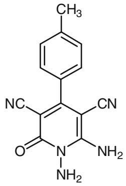
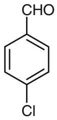
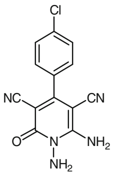
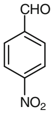
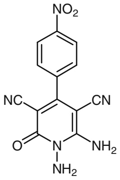
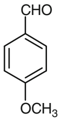
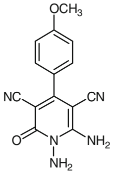
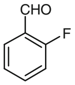
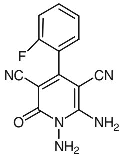
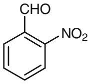
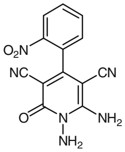
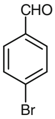
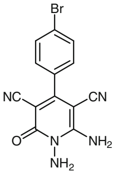
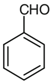
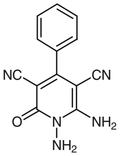
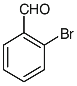
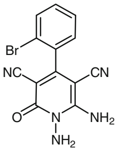
Entry	Aldehyde	Product	Time (min)	Yield %[a]	M.P °C (ref)
1		 **5a**	41	85	238–240 [12]
2		 **5b**	30	93	242–243 [12]
3		 **5c**	30	93	226–228 [12]
4		 **5d**	45	82	222–224 [12]
5		 **5e**	33	90	249–251

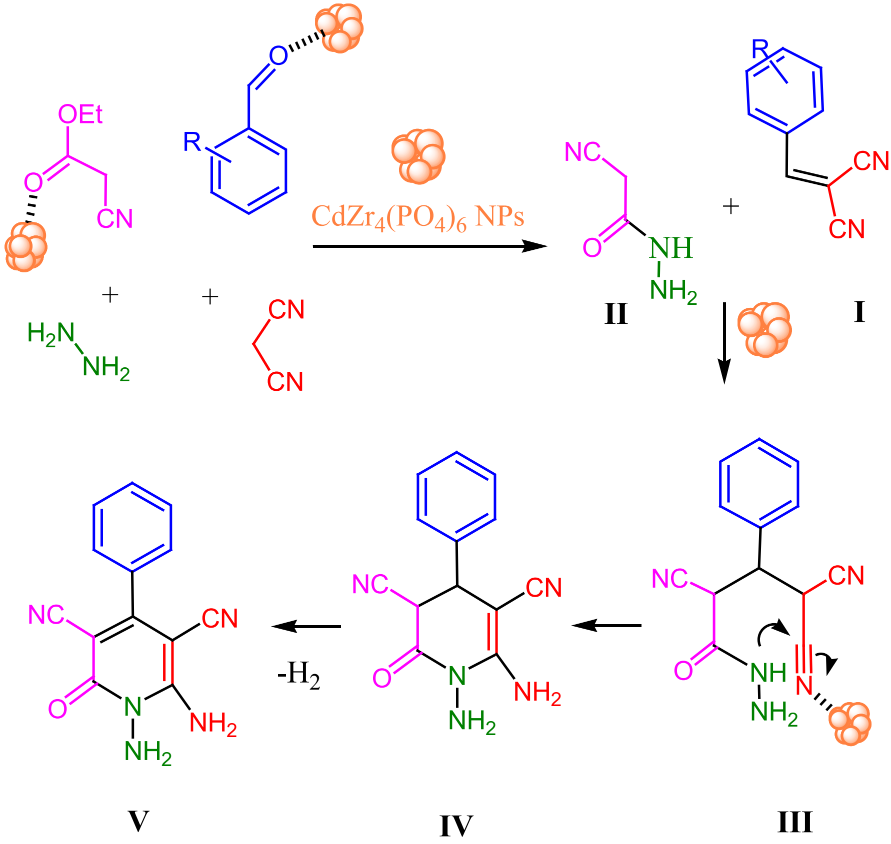
Table 3 continued

Entry	Aldehyde	Product	Time (min)	Yield %[a]	M.P °C (ref)
6		 **5f**	35	88	234–236
7		 **5g**	31	89	234–236
8		 **5h**	31	88	237–239 [12]
9		 **5i**	33	90	231–233

Hyrazine hydrate (2 mmol), ethyl cyanoacetate (2 mmol), malononitrile (2 mmol), benzaldehydes (2 mmol) under reflux conditions in ethanol in the present of $CdZr_4(PO_4)_6$ nanocrystalline

[a] Isolated yield

I followed by intramolecular cyclization of the resulting species **III** produced N-amino-2-pyridones. In this mechanism the nano-$CdZr_4(PO_4)_6$ activates the C=O and C≡N groups for better reaction with nucleophiles. These surface atoms behave as the centers where chemical reactions are catalytically stimulated.



Scheme 2 Proposed reaction pathway for the synthesis of N-amino-2-pyridones

Conclusion

In conclusion, we compared the catalytic activity of nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics in the one-pot synthesis of N-amino-2-pyridones. Among nanocrystalline $M^{II}Zr_4(PO_4)_6$ ceramics, nanocrystallines with electronic configuration d^{10} for M^{II} have the maximum of activity.

In this study, an efficient, environmentally benign, and simple methodology for the preparation of N-amino-2-pyridones in the presence of $CdZr_4(PO_4)_6$ nanocrystalline is reported. The procedure offers several advantages including cleaner reaction profiles, excellent yields, shorter reaction times, and simple experimental and reusability of the catalyst and little catalyst loading. These green nanocatalysts could be used for other noteworthy organic reactions and transformations. Further exploration of similar protocols are underway in our laboratory. Meanwhile, this recoverable catalyst will provide a usual platform for heterogeneous catalysis, green chemistry, and environmentally benign protocols in the near future.

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