A NOVEL, GREEN AND HETEROGENEOUS CERIA-BASED SOLID LEWIS ACID CATALYST ASSISTED ONE-POT MULTI-COMPONENT SYNTHESIS OF DIHYDRO-PYRANO[2,3-C]PYRAZOLES

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ABSTRACT

A green and easy protocol for Dihydro-pyrano[2,3-c]pyrazoles, were synthesized in the presence of Ceria-Molybdenum mix metal oxides (Ce-Mo MMO) as a recyclable solid heterogeneous Lewis acid catalyst and one-pot four-component synthesis from the reaction between 3-nitro benzaldehydes, malononitrile ethyl acetoacetate and hydrazine hydrate. Here, the Ce-Mo MMO catalyst was designed, prepared and utilized as a catalyst in a various organic reaction. The present protocol offers several superiorities like short reaction time, high percent yield, clean reaction, simple separation technique and recoverable catalyst and it also shows the same catalytic activity when it was reused in consecutive reaction.

Keywords: Catalyst, Synthesis, Dihydropyrano[2,3-c]pyrazoles, Lewis Acid, Heterogeneous Mix Metal Oxide, Cerium Molybdenum (Ce-Mo).

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INTRODUCTION

According to the green chemistry approach, catalyst and organic compound synthesis procedures must be eco-friendly and alternative. Green chemistry focus on using environmental friendly synthetic mixtures and simple reaction conditions. In the progress of our research work that synthesis of a heterogeneous catalyst, we have designed and synthesized Ce-Mo MMO catalyst. It was synthesized by the co-precipitation method.¹⁻⁴

Recently, from 2-4 decades, mixed metal oxides increase demand in catalysis, because of their versatile properties, it is stable in different organic-inorganic acids, as well as stable in high reaction temperature for a long time with reusable ability. In the Lanthanide series, especially ceria with other metal-containing oxides such mixed metal oxides have been rewarded much interest. Materials of ceria can promptly form redox sites $Ce^{4+/3+}$ and assisting enhance catalytic application.⁵⁻⁷ In the last few years, ceria with other metal-containing oxides are synthesized by various methods and used in a different fields such as cosmetics, gas sensors, fuel cells; solid-state electrolytes and acts as a promoter of catalysts.⁸ Catalytic or oxidation/ reduction, stability of $Ce^{4+/3+}$ can be significantly improved by the insertion of a transition metal such as $Zr^{2+/4+}$, $Ti^{3+/4+}$, $Pt^{2+/4+}$, $Pd^{2+/4+}$, $Rh^{2+/4+}$, Cu^{2+}/Al^{3+} , Si^{4+} , Hf^{4+} , Au^{2+} etc.⁹⁻¹² Ceria based metal oxides used as a catalyst in organic transformations.¹³⁻¹⁵ Subsequently, there is an impressive interest in the synthesis and development of novel catalyst with higher reaction quotient, low cost, great reusability, eco-friendly catalyst. Literature survey reveals that many organic reactions are accelerated in presence of a catalyst. Ceria metal-containing mixed metal oxides have been sustainable alternatives due to the presence of Lewis acidity¹²⁻¹⁶ and used as a catalyst in organic synthesis such as 1,3-Diols, Polyhydroquinolines,¹³⁻¹⁵ this component containing pharmaceutical product and are in great demand in drug synthesis because of the biological significance.¹⁷

Early 2-3 decades, researchers have shown more interest in the preparation of dihydro-pyrano[2,3-c]pyrazole derivatives due to their different therapeutic and pharmacological properties, it has bioactive and

pharmacologically important such synthons are essential in synthetic chloromphenicol and ciprofloxacin drug intermediates as shown A-F, it shows antibacterial and antifungal activity but compound E shows better activity than compound F,¹⁷⁻¹⁹ also applicable in cosmetics, pigments and potential biodegradable/or green agrochemicals.²⁰

Fig.1 Bioactive and Pharmacologically Important Synthons.

Similarly, it shows biological activity such as anticancer,²¹⁻²² antimicrobial,²³⁻²⁴ anti-inflammatory, antiviral,²⁵ inhibitors of yeast α -glycosidase,²⁶ Furthermore, in human chk1 kinase inhibitors,¹⁷⁻²⁷ biodegradable agrochemicals,²⁸ and molluscicidal activities²⁹ etc.

In 1974 H. H. Otto et al have prepared 4H-pyrano[2,3-c]pyrazole in the presence of a base catalyst.³⁰ literature survey reveals that there are several methods have been reported, for the synthesis of pyrano[2,3-c]pyrazole derivatives by using different catalysts such as Nano-titania sulfuric acid,³¹ mix metal oxide $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ (polyphosphoric acid),³²⁻³³ ZrO_2 nanoparticles,³⁴⁻³⁵ L-Proline, Amberlyst A-21,³⁶⁻³⁸ Mg-Al Hydrotalcite, γ -Alumina,³⁹⁻⁴⁰ $\text{Fe}_3\text{O}_4@\text{SiO}_2$, @piperidinium benzene-1,3-disulfonate Ionic liquid,⁴¹⁻⁴² electrochemically induced condition,⁴³ some methods use a homogeneous catalyst, those are difficult for separations and some methods have needed a specific condition such as Microwave, or combined microwave and ultrasound irradiation,⁴⁴⁻⁴⁶ Ultra-sonication,⁴⁷ above-mentioned methods have several drawbacks, therefore there need to develop a new alternative route. Herein, We report a novel, green and heterogeneous ceria-based solid Lewis acid catalyst-assisted one-pot multicomponent synthesis of dihydropyrano[2,3-c]pyrazoles.

EXPERIMENTAL

Chemicals and Instruments

Experimental material, analytical grade chemical and solvent were purchased from Sigma, Alpha-Assar, Merck, and Spectrochem used as such. The melting point was taken in an open capillary and it is uncorrected. FT-IR spectrum was recorded on Bruker analyzer. ^1H , ^{13}C , and HR-MS were recorded on 400 MHz Bruker Advance in CDCl_3 / DMSO. The XRD were recorded on Bruker 8-D advance and BET surface area was calculated by N_2 adsorption performed on Quanta-chrome CHEMBET 3000 instruments.

General Procedure for the Synthesis of Catalyst

6.57 gm. of Ceric ammonium nitrate were dissolved in the required quantity of deionized water to form a cleared solution ($\text{pH} \approx 6$) 1:1 ammonia was added in that solution till its complete precipitation, simultaneously, a solution of 9.88 g of Ammonium heptamolybdate was dissolved in required deionized water and It was added in a previously prepared Ceric ammonium nitrate solution, the 5% polyethylene glycol was used as structure-directing agent, then the reaction mixture was stirred 2-3 hr and precipitate kept for overnight, filter, dried and calcined at 500°C for 4 hr. The formation of Ce-Mo MMO catalyst was confirmed by different characterization techniques such as FTIR, XRD, FE-SEM and EDX. Prepared Ce-Mo MMO was used as a catalyst in the synthesis of Dihydropyrano-[2,3-c]-pyrazoles.

A Typical Procedure for (2a) Derivatives

A mixture was prepared by adding 3-nitro benzaldehyde (0.227 g), malononitrile (0.066 g) ethyl acetoacetate (0.130g), hydrazine hydrate (0.108 g) and 0.050 g of Ce-Mo, MMO as a catalyst. The reaction mixture was refluxed up to the completion of the reaction in presence of ethanol. The reaction was monitored by using TLC (pet ether: ethyl acetate 3:2). Then few ml of cold water was added with continuous stirring to obtain the crude product. During the crystallization process, the catalyst and product were separated. The same procedure was used for the preparation of other derivatives.

RESULTS AND DISCUSSION

Synthesis of highly reactive and reusable solid heterogeneous catalyst by using green approach; considering eco-friendly catalyst and balance reaction side product and considering with including percent atom economy is an emerging and challenging area of researchers. The government applies rules and regulations for minimization of the environmental pollutant; pollution having a serious suggestion for the pharmaceutical industry toward the implementation of innovative "Clean technology" and encourages the utilization of different heterogeneous catalyzed chemical processes.⁴⁸⁻⁴⁹ Here, we have minimized hard steps in synthesis as well as reaction byproduct in a chemical reaction and apply one-pot low-temperature organic transformations.

Present research work deals with the synthesis of heterogeneous catalysts and study of the catalytic activity for the synthesis of dihydropyranopyrazoles from benzaldehydes, malononitrile and ethyl-acetoacetate, hydrazinehydrate using Ce-Mo MMO as Lewis acid catalyst.

Characterization of the Catalyst

The XRD pattern of the CMMO catalyst calcined at 500°C for 4 hrs is shown in Fig.2 The result is in accordance with crystal arrangement with unit cell parameter $a = 18.42$, $b = 19.10$, $c = 06.10$ and $\alpha = 90$, $\beta = 90$, $\gamma = 90$, observed with corresponding to 2θ and the planes (hkl) $2\theta = 23.52$ (340), 25.87 (520), 27.52 (051), 29.11 (600), 39.14 (800). In XRD pattern shows the highest peak at $2\theta = 25.87$ and hkl plane at (520) correspond to the orthorhombic phase.⁵⁰

In FT-IR spectra the bands at 476 cm^{-1} presence of bending vibration of Ce-O-Mo/ Ce-O-Ce / Mo-O-Mo, 815 cm^{-1} presence of Ce-O/Ce-Mo stretching frequency, $1126\text{--}985\text{ cm}^{-1}$ stretching vibration of Ce-O-Mo/ Ce-O-Ce / Mo-O-Mo. The absorption band at $3693\text{--}3456\text{ cm}^{-1}$ corresponds to the presence of bridge hydroxyl group (Ce-OH-Mo). SEM image of catalyst are shown in Fig.-3. The surface area of catalyst is shown in Table-1. In next step to investigate the scope of catalyst to apply in MCR(2a) and construct a new procedure.

Fig.-2: XRD Pattern of Ce-Mo MMO Catalyst calcined at 500°C

In general, the experimental procedure is so simple, in this method a short reaction time is required and it takes place within 2 -10 min. gives excellent yields up to 85–93%. The experimental procedure contains a

variety of substituted aldehydes containing different substituent's donating and withdrawing group, e.g. $-\text{Cl}$, $-\text{CH}_3$, $-\text{OH}$, $-\text{S}$, $-\text{OMe}$, $-\text{NO}_2$ was more effective in this MCRs to give better yields (85–93%) within 05–10 min; next step we tried to construct a library of dihydro-pyranopyrazole derivatives using (2a) a model reaction conditions shown in Table-2.

Table-1: BET Surface Area of Ce-Mo MMO Catalyst

Total Pore Volume (cm^3/g)	Average Pore Size (Å)	Surface Area (m^2/g)
0.03052	39.11	31.23

Fig.-3: SEM Image of Ce-Mo MMO Catalyst calcined at 500°C

Table-2: Synthesis of Dihydropyrano [2,3-c]-pyrazole derivatives using Ce-Mo MMO Catalyst

Entry	R	Yield (%) ^a	Melting Point (°C)	
			Observed	Reported
2a	3- NO_2	92	190-192	189-191 ³⁵
2b	H	93	230-233	232-234 ¹
2c	4-Cl	92	230-232	232-234 ³⁴
2d	4- CH_3	85	1175-177	174-176 ³⁵
2e	4- NO_2	90	248-250	250-252 ³⁴
2f	4-OH	87	222-323	221-223 ³⁵
2g	Thiophene	85	207-209	240-243 ¹
2h	5-Br 2-OH	92	222-224	225-227 ³⁴
2i	3- NO_2 4-OH	90	176-178	189-191 ³⁴
2j	3-OH	86	246-248	247-249 ¹

Scheme-1: Synthesis of (2a) catalyzed by Ce-Mo mix Metal Oxide (CMMO)

Probable Reaction Mechanism

Initially first stage catalyst reacts with an aldehyde to increase the electrophilicity of carbonyl carbon ($>\text{C}=\text{O}$), enolate of malononitrile immediately attack and form IA intermediate.

Scheme-2: Mechanism of Modal Reaction (2a)

On the other hand catalyst reacts with ethyl acetoacetate and increases the electrophilicity of acetate carbonyl carbon ($>\text{C}=\text{O}$) at same time hydrazine hydrate nucleophile attack to give IB intermediate, it was enolise and attack on initially prepared IA intermediate those catalytically activated. In these steps, there action accelerated as well as started cyclic form onward and catalyst reacts periodically (intermediate IIIA, IIIB, IIIC). Finally, after completion of reaction to form a target molecule such as Dihydropyrano[2,3-c]pyrazoles IV.

Table-3: Optimization Reaction Condition in Modal Reaction 2a

S. No.	Solvent	Amount of Catalyst (mg)	Reaction Time	Yield (%) ^a
1	Water	----	2-4 hr	-----
2	Water	100	2-4 hr	20
3	Water: Ethanol (1:1)	100	01 hr	50
4	Ethanol	100	10-20 min	92
5	Acetonitrile	100	1 hr	50
6	Acetonitrile: Water (1:1)	100	1 hr	65
7	Ethanol	50	05-10 min	93 ^b (92.8, 92.5, 92.2) ^c
8	Ethanol	25	40 min	80

Table-4: Comparisons of the Catalyst with reported Method^a

S. No.	Catalyst/Conditions	Catalyst (mg)	Time	%Yield ^b	Ref.
1	Trifluoroethanol, reflux	--	5h	90	51
2	60°C EtOH	Yb(PFO) ₃	5 h	90	52
3	Sonication EtOH	Nano-La _{0.7} Sr _{0.3} MnO ₃	12 min	92	32
4	30 mol%; H ₂ O; reflux	γ-Alumina	50 min	80	40

5	DCM, TEA, R.T.	----	25-30min.	56-72	26
6	Water, R.T.	Sodium benzoate	60 min.	78-91	53
7	Micro Wave irradiation	Pipridine, ethanol	08 min.	61-66	54
8	Ethanol, Reflux	Ce-Mo MMO	5-10 min.	85-93	Our results

Reusability of Catalyst

On completion of the catalytic reactions, the heterogeneous solid catalyst Ce-Mo MMO was recollected through filtration for further reuse of the next batch reaction. Then, they are carefully washed consecutively with acetone. Then the recollected catalyst was dried in a furnace at 110°C for 10-15 min. and reused in the synthesis of (2a) as a model reaction, the reusability of Ce-Mo MMO catalyst was tested up to three-time and found without loss of its catalytic activity.

Spectroscopic Data a Representative Sample (2a)

Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ = 1.8(s, 3H, CH_3) 4.88(s, 1H, CH) 7.07(s, 2H, NH_2), 7.6(m, 2H, Ar), 8.0-8.14(m, 2H, Ar), 12.2(s, 1H, NH); ^{13}C NMR (400 MHz, CDCl_3): 9.73, 35.58, 56.03, 96.62, 120.52, 121.82, 121.98, 130.24, 134.38, 135.87, 146.80, 147.83, 154.65, 161.11; FT-IR (cm^{-1}): 3471(NH_2), 3216, 3112, 2193($\text{C}=\text{N}$), 2158, 1651, 1599, 1524, 1400, 1044, 807, 741; Mass (GC-MS): (m/z) $\text{M}^+ = 297.10$

CONCLUSION

In summary, we have prepared Ce-Mo mixed metal oxides by coprecipitation method and used as heterogeneous Lewis acid catalyst for one-pot synthesis of dihydro-pyrano[2,3-c]pyrazoles to gives excellent yields. This catalyst offers several advantages such as reusability without loss of its catalytic activity up to three cycles, easy to separate, easy to handle. In the synthesis of organic transformation milder reaction condition, better yield, simple experimental procedure and easier work-up procedure. The overall process becomes eco-friendly and becomes a green synthetic protocol.

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