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### Gd<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> perovskite as a novel and efficient catalyst for synthesis of dioxodecahydroacridine derivatives

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#### ABSTRACT

In this work, perovskite-type material Gd<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> was fabricated by sol-gel method. To prepare this nanopowder, metal salts, citric acid as the complexing agent and water as solvent were used. A series of common analytical techniques were used to characterize the crystallinity, morphology, specific surface area and grain size of the nanopowders. The composition and morphology of the nanopowders by energy dispersive X-Ray spectrometer (EDX) and scanning electron microscopy (SEM) is studied. BET analysis for surface accurate area of sample and Fourier transform infrared (FTIR) spectra were used to study the structure of nanopowders. Also X-Ray diffraction (XRD) patterns show that single perovskite phase is completely formed after calcination treatment. Moreover, in this study, 1,8-dioxo-decahydroacridine derivatives were generated via one-pot four-component condensation, under solvent-free conditions at the presence of a perovskite as a new, efficient, heterogeneous, green and recyclable catalyst with excellent yields.

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#### Keywords

Perovskite, Nanopowder, Heterogeneous catalyst, Hantzsch-type condensation, Four-component reactions

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#### **1. Introduction**

Multicomponent reactions (MCRs) have emerged as efficient and powerful tools in modern synthetic organic chemistry because the syntheses of complex organic molecules from simple and readily available substrates can be achieved in a very fast and efficient manner without the isolation of any intermediate <sup>[1-5]</sup>. MCRs have emerged as efficient, atom economic, time saving and powerful tools in modern synthetic organic chemistry for the synthesis of pharmacologically and biologically important targets as they increase the efficiency of the reaction and avoid the multiple steps along with saving solvents and chemicals <sup>[6]</sup>. 1,8-Dioxodecahydroacridines and their derivatives are polyfunctionalized 1,4-dihydropyridine derivatives that contain a large family of medicinally important compounds that have attracted much attention because of their diverse pharmacological and therapeutic properties, such as antimalarial <sup>[7]</sup>, antitumor <sup>[8]</sup>, anticancer<sup>[9]</sup>, bronchodilator, anti-atherosclerotic and antidiabeticagents [10-13] 1.4-Dihydropyridines and their derivatives were synthesized with the Hantzsch procedure, which involves the three component condensation of an aromatic aldehyde, dimedone and ammonium acetate or amines in the presence of several catalysts such as p-dodecylbenezenesulfonic acid (DBSA) <sup>[14]</sup>, tris(pentafluorophenyl)borane <sup>[15]</sup>, acidic ionic liquids <sup>[16]</sup>, proline <sup>[17]</sup>, ceric ammonium nitrate (CAN)<sup>[18]</sup> and triethylbenzylammonium chloride (TEBAC)<sup>[19]</sup>. However, most of these reported procedures have disadvantages such as use of hazardous organic solvents, long reaction times, and low yields and harsh reaction conditions. Thus, the development of efficient, easy, and environmentally friendly methods using new heterogeneous and reusable catalysts for the synthesis of 1,8-dioxodecahydroacridines is still necessary.

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Traditional ABO<sub>3</sub> perovskite-type mixed oxides have been known as catalysts or catalyst precursors for several organic reactions at very low catalyst loadings <sup>[20-23]</sup>. The great stability of the perovskite structure allows partial substitution at the A sites and/or the B sites modifying the catalytic, structural and redox properties. Generally speaking, A-site replacement mainly affects the amount of sorbed oxygen, whereas B-site replacement influences the nature of sorbed oxygen <sup>[24,25]</sup>. The large variety of properties displayed by perovskite oxides is due to the ability of the framework to accommodate cations of various sizes and valences and to tolerance towards anionic and cationic vacancies. Perovskites have many possible applications, e.g., in membranes for gas separation <sup>[26]</sup> as catalysts <sup>[27,28]</sup>, as promising adsorbents <sup>[29,30]</sup>, in electrical devices <sup>[31]</sup>, as ferromagnetic material <sup>[32]</sup>, and in sensors <sup>[33]</sup>. The redox properties of the B ions, the nature and concentration of oxygen adspecies, and the existence of lattice defects are generally believed to be responsible for the good catalytic activity of these perovskite-type oxides <sup>[34,35]</sup>. In general, perovskite with a partial substitution of the A or B cations (A<sub>x</sub>A'<sub>1-x</sub>BO<sub>3</sub>) / (AB<sub>1-x</sub>B'<sub>x</sub>O<sub>3</sub>) have received much attention in catalysis.

In the present study,  $Gd_{0.7}Sr_{0.3}MnO_3$  nanopowders (GSMO NPs) fabricated by sol-gel method show the best catalytic performance for synthesis of 1,8-dioxo-decahydroacridine derivatives. Moreover, the effect of different solvents was investigated and the catalytic efficiency was compared with traditional catalyst under similar conditions.

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#### 2. Experimental

#### 2.1. General remarks

All chemicals were available commercially and used without additional purification. A series of common analytical techniques were used to characterize the crystallinity and morphology of the nanopowders. The FT-IR spectra were recorded on a Perkin-Elmer BX-II IR spectrometer. For structural investigation of calcined powder at 700°C XRD measurements were carried out in the angle region of  $(2\theta = 20 \text{ to } 70^\circ)$  using CuK $\alpha$  radiation on a Rigaku D/MAXRB XRD diffractometer equipped with a curved graphite monochromator. The composition and morphology of the nanopowders by energy dispersive X-Ray spectrometer (EDX) and scanning electron microscopy (SEM) was studied. The SEM of the type LEO 1450VP (V = 30 kV) was equipped with an EDX spectrometer of the type Inca 400 (Oxford Instruments). The surface accurate area of sample was calculated using BET method from the nitrogen adsorption isotherms obtained at 77 K on samples out gassed at 250°C with the use of a Micromeritics Accusorb 2100E apparatus. The melting points of products were determined with an Electrothermal 9200 melting point apparatus.

#### 2.2. Synthesis of catalyst

The perovskite precursors in this work were prepared by sol-gel method. Appropriate amounts of Gadolinium nitrate  $Gd(NO_3)_3.6H_2O$ , strontium nitrate  $Sr(NO_3)_2$ , Manganese acetate  $Mn(CH_3COO)_2$ , citric acid and distilled water were used as starting materials. The molar ratio of citric acid to metal ions was 4:1. Metal nitrates were dissolved in distilled water and then citric acid was added slowly to the metal solution at room temperature under constant magnetic

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stirring. The solution was refluxed with stirring for 2h to convert it to a stable complex. To make a gel, it was heated at 50°C for 2h on a heater. A dry gel was obtained by placing the sol in an oven and heating slowly to 110°C for 12 h and then calcined at 700°C for 6h to obtain the nanopowders using perovskite-type oxides.

#### 2.3. Typical procedure for the synthesis of 1,8-Dioxodecahydroacridines

A mixture of dimedone (2 mmol), aromatic aldehyde (1 mmol), ammonium acetate or aromatic amines (1 mmol), and nanoparticle catalysts (0.001g) was heated in the oil bath at 120°C for the appropriate time. During the procedure, the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature and hot ethanol was added. The catalyst was insoluble in hot ethanol and it could therefore be recycled by a simple filtration. The product was then collected from the filtrate .After that it cooled to room temperature and recrystallized from distilled water to give compounds 4a-k in high yields.

#### 3. Results and Discussion

#### 3.1. FT-IR spectroscopy

Fourier transform infrared spectra were obtained as a powerful method to determine the structure and measurement of chemical species. Fig. 1 show the FTIR spectra of the GSMO NPs in the range of 400--4000 cm<sup>--1</sup>, calcined at 700°C for 6h in air. The FTIR spectrum is similar to the most other ABO<sub>3</sub>-type perovskite compounds which have common BO<sub>6</sub> oxygen-octahedral structure <sup>[36-38]</sup>. Relatively strong peak show the typical M--O--C pair vibrations around 1400-1600 cm<sup>-1 [39]</sup>. An intermediate absorption band about 1081 and 1201 cm<sup>-1</sup> corresponded to C--O

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bond <sup>[40]</sup> and the anti-symmetric  $NO_3^{-}$  stretching vibration <sup>[41]</sup>, respectively. The characteristic band is observed at 1726 cm<sup>-1</sup> and corresponds to the C = O bond. The FTIR spectra of calcined samples show the vanishing of bands related to complexing agent. The strong band at 523 cm<sup>-1</sup> in the far IR spectra corresponds to the M--O stretching vibration mode and this peak is characteristics of perovskite oxides.

#### 3.2. X-ray diffraction

Fig. 2 shows the XRD patterns of the GSMO NPs prepared by sol--gel method and calcined at 700°C for 6 h. The diffractograms reveal that the crystalline perovskite structure is the main phase for synthesized catalyst. The diffraction peaks at 20 angels appeared at 22.8, 33.1,41,48, 59.3 and 69.6 can be assigned to scattering from the (100), (110), (111), (200), (211) and (220).XRD data shows GSMO NPs crystallizes in an orthorhombic phase with a = 5.42, b = 5.56 and c = 7.62<sup>[42]</sup>. The crystallite grain size of the monophase samples was determined the full width at half-maximum width (FWHM) of the XRD ( $2\theta = 33.1^{\circ}$ ) peak using the Scherrer formula:

$$D_{hkl} = \frac{0.96\lambda}{\beta_{hkl} \cos\theta_{hkl}}$$

Where  $D_{hkl}(nm)$  is the particle size perpendicular to the normalline of (hkl) plane,  $\beta_{hkl}$  is the full width at half maximum,  $\theta_{hkl}(Rad)$  is the Bragg angle of (hkl) peak, and  $\lambda$  (nm) is the wavelength of X-ray. The crystallite size of GSMO NPs calcinated at 700°C was about 17nm.

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#### 3.3. Morphology, pore structure and surface area

Scanning electron microscopy (SEM) of perovskite oxide (GSMO) prepared by the sol--gel method and calcined at 700°C is shown in Fig. 3. Based on the SEM images, porosity of the surface is evident and it seems that the particles have grown with uniform size. The particles size of GSMO NPs that were propagated on the surface seems to be in the range of 25--63 nm. The surface looks rough with relatively large holes that probably caused by a sudden removal of a large amount of gas when the sample was directly inserted in to the hot furnace of  $700^{\circ}$ C. Energy-dispersive X-ray (EDX), as shown in Fig. 4, indicates the existence of Gd, Sr, Mn and O elements as well as the phase purity in these nanoparticles. The specific surface area of the nanocatalyst was measured by the Brunauer-Emmett-Teller (BET) method (Fig. 5). Results showed that the average of specific surface area and mean pore diameter of GSMO NPs were 98.66 m<sup>2</sup>/g and 28.782 nm, respectively. So, it seems that the large specific surface area of GSMO nanoparticles is an advantage for the catalytic synthesis of 1.8- dioxodecahydroacridines and their derivatives. Several methods to calculate the mesopore size distribution from adsorption isotherm data have been developed <sup>[43,44]</sup>. Most computational methods are based on the BJH model by Barrett, Joyner and Halenda<sup>[45]</sup>. The pore size distribution of GSMO catalyst is shown in Fig.6. A result showed that radius of the pore as to peak was 12.24 nm. Therefore the relatively large pore sizes can facilitate the transport of reactants and products through the porous structure of GSMO NPs, which is a characteristic of the porous materials.

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#### 3.4. Catalytic application in synthesis of 1,8-dioxodecahydroacridines

The one-pot synthesis of 1,8-dioxodecahydroacridines was achieved by the three-component condensation of aromatic aldehydes, dimedone and ammonium acetate in the presence a heterogeneous catalyst(Scheme 1). At first, to optimize the reaction conditions, the reaction was carried out by heating a mixture of benzaldehyde (1 mmol), dimedone (2 mmol), and ammonium acetate (1 mmol) at different catalysts and different loading of the catalyst. Effective catalysis was demonstrated down to 0.4mol% (0.001 g) of GSMO NPs (table 1). A further increase in the amount of catalyst did not have any significant effects on the product yield, as well as in the absence of catalyst a very low amount of the desired product was formed (entry 1). However other catalysts such as  $Kf_{\gamma}Al_2O_3$ ,  $NH_4OAc.Al_2O_3$ ,  $FeCl_3.SiO_2$  and  $ZnCl_2.SiO_2Al_2O_3$  were examined, but GSMO NPs can act as high efficiency catalyst with fast time and excellent yields of the obtained products (entry7). Moreover, the reaction was carried out in various solvents and under solvent-free conditions. As shown in Table 2, solvent-free condition gave the best result in terms of reaction time and yield. Also we conducted this reaction in different temperatures; it was observed that taking reaction in the room temperature gave low yields of the desired products (table 3, entry 1). The yield increased sharply when the temperature was raised from room temperature to 120°C. It should be noted that increasing the reaction temperature did not improve the yield. Thus, a range of 1,8-dioxodecahydroacridinesunder was prepared under the optimized reaction conditions using various aromatic aldehydes (1), dimedone (2) and ammonium acetate (3). All desired products were formed as shown in table 4. The results showed that the reactions of electron-withdrawing aldehydes have higher yields compared to the reactions of electron donating aldehydes.

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#### 3.4.1. A plausible mechanism for synthesis of 1,8-dioxo-decahydroacridine

A proposed mechanism for the condensation of an aromatic aldehyde, dimedone and ammonium acetate in the presence of GSMO NPs as a Brönsted acidic catalyst for the synthesis of 1,8-dioxodecahydroacridines is shown in Scheme 2. Initially; aromatic aldehyde (1) and dimedone (2) coordinates to the Lewis acidic site present at the catalyst surface (I,II). Then, the elimination of the water leads to intermediate (7) via Knoevenagel condensation (III). On the other hand, the condensation reaction between dimedone and ammonium acetate leads to intermediate (8, IV). Formation of intermediate (9) takes place through a Hantzsch-like mechanism via conjugate addition of the intermediate (8) to the intermediate (7, V). Finally, intra-molecular nucleophilic attack of nitrogen to carbon containing hydroxyl group leads to final product (4).

#### **3.4.2. Reusability of catalyst**

To evaluate the stability of catalytic activity, reusability of the catalyst was also investigated. For this purpose, we again studied the same model reaction under optimized conditions. When the reaction was completed, the reaction mixture was cooled to room temperature, and hot ethanol was added. The catalyst was separated by filtration, dried at 70°C under vacuum, and reused for a similar reaction. As shown in Fig.7, GSMO NPs could be reused at least five times without significant loss of activity.

#### 4. Conclusions

In summary, nanoparticles of perovskite type  $Gd_{0.7}Sr_{0.3}MnO_3$  were synthesized using sol--gel method in the presence of citric acid as complexing agents. A study of the morphological,

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structural and catalytic properties of the  $Gd_{0.7}Sr_{0.3}MnO_3$  NPs was carried out by means of various analytical techniques. XRD and microscopic analyses indicated that the GSMO NPs prepared by calcinating the gel precursor at 700°C for 6 h, have suitable crystallinity with the orthorhombic perovskite structure. In addition, GSMO NPs were successfully used as a new, green, nonvolatile. efficient recyclable heterogeneous catalyst for the synthesis of 1.8dioxodecahydroacridines under solvent-free conditions. Catalytic activity results revealed that the, GSMO NPs exhibited excellent catalytic performance in the condensation of various aromatic aldehydes, dimedone and ammonium acetate. Because of its small particle size and high specific surface area, the GSMO NPs provides a favorable surface for the reactants and the reaction completes successfully in terms of excellent yield. We have found that the reactions of electron-withdrawing aldehydes have higher yields and short reaction times compared to the reactions of electron donating aldehydes. High yields, short reaction times, high performance of catalyst even after five runs and very low loading of catalyst (0.001 g) are some of the advantages of this protocol.

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Table 1.Condensation reaction of benzaldehyde, dimedone and ammonium acetate in the

presence of different catalysts and different loading of the catalyst<sup>a</sup>.

Entry	Catalyst	Catalyst loading (g)	Time (h)	Yield (%) <sup>b</sup>
1	-	-	40	30
2	$Kf.\gamma Al_2O_3$	0.001	20	65
3	NH <sub>4</sub> OAc.Al <sub>2</sub> O <sub>3</sub>	0.001	20	60
4	FeCl <sub>3</sub> .SiO <sub>2</sub>	0.001	20	85
5	$ZnCl_2.SiO_2$	0.001	20	85
6	$Gd_{0.7}Sr_{0.3}MnO_3$	0.0005	20	80
7	$Gd_{0.7}Sr_{0.3}MnO_3$	0.001	20	92
8	$Gd_{0.7}Sr_{0.3}MnO_3$	0.002	20	92

<sup>a</sup>Reaction conditions: benzaldehyde (1mmol), dimedone (2mmol) and ammonium acetate

(1mmol) at 120°C.

<sup>b</sup>Isolated yields.

Table 2.Initial solvent effect studies for synthesis of 1,8-dioxo-decahydroacridines in the

presence of Gd<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>.<sup>a</sup>

Entry	Solvent	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>
1	$H_2O$	Reflux	120	80
2	CH <sub>3</sub> CN	Reflux	300	30
3	EtOH	Reflux	300	70
4	MeOH	Reflux	300	65
5	Ethyl acetate	Reflux	300	-
6	n-Hexane	Reflux	300	80
7	Solvent-free	120	20	92

<sup>a</sup>Reaction conditions: benzaldehyde (1mmol), dimedone (2mmol) and ammonium acetate

(1mmol) 0.4 mol% nano-Gd<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> in 2 mL solvent, stirring.

<sup>b</sup>Isolated yields.

Table 3.Optimization of temperature for synthesis of 1,8-dioxo-decahydroacridines under

solvent-free conditions<sup>a</sup>.

Entry	Temp (°C)	Time (h)	Yield $(\%)^{b}$
1	-	120	50
2	50	20	40
3	70	20	50
4	90	20	65
5	100	20	72
6	110	20	85
7	120	20	92
8	130	20	92

<sup>a</sup>Reaction conditions: benzaldehyde (1mmol), dimedone (2mmol) and ammonium acetate

 $(1mmol)\ 0.4\ mol\%\ nano-Gd_{0.7}Sr_{0.3}MnO_3.$ 

<sup>b</sup>Isolated yields.

Table 4.Synthesis of various 1,8-dioxo-decahydroacridines in the presence of nano-

 $Gd_{0.7}Sr_{0.3}MnO_3^{a}$ .



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4	3-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	$ \begin{array}{c}                                     $	15	94	294-296 (288-291) [47]
5	4-MeC <sub>6</sub> H <sub>4</sub>	Me O O O H H 4e	20	90	274-276 (269-271) [47]
6	4-OHC <sub>6</sub> H <sub>4</sub>	OH O O H H 4f	20	88	308-3011 (307-309) [46]
7	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	NO <sub>2</sub> O O H H 4g	15	93	284-288 (286-289) [47]

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8	1 MaOC H	OMe	20	88	272 274
8	4-MeOC <sub>6</sub> H <sub>4</sub>		20	88	(288-291) [47]
9	2-ClC <sub>6</sub> H <sub>4</sub>		15	93	222-225 (221-223) [47]
10	4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	NMe <sub>2</sub> O O O H H 4i	20	86	263-265 (264-266) [48]
11	3,4- (MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	OMe OMe O O O O O O O O O O O O O O H A H A k	15	82	259-263 (260-263) [48]

<sup>21</sup> ACCEPTED MANUSCRIPT

<sup>a</sup>Reaction conditions: benzaldehyde (1mmol), dimedone (2mmol) and ammonium acetate

(1mmol) 0.4 mol% nano-Gd<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> (0.001g), stirring at 120°C.

<sup>b</sup>Isolated yields.

# <sup>22</sup> ACCEPTED MANUSCRIPT



**Fig.1**. FT-IR spectra of GSMO NPs before (a) and after (b) calcination at  $700^{\circ}$ C.

# <sup>23</sup> ACCEPTED MANUSCRIPT



Fig.2. XRD pattern of GSMO NPs calcined at 700°C.

# <sup>24</sup> ACCEPTED MANUSCRIPT



Fig.3. SEM images of GSMO NPs.

# <sup>25</sup> ACCEPTED MANUSCRIPT



Fig.4. Energy dispersive X-ray (EDX) spectrum of the GSMO NPs.

<sup>26</sup> ACCEPTED MANUSCRIPT



Fig.5. N2 adsorption--desorption isotherm of GSMO NPs is calcinated at 700°C.



**Fig.6**. BJH plot of GSMO is calcinated at  $700^{\circ}$ C.

# <sup>28</sup> ACCEPTED MANUSCRIPT



**Fig.7**. Yield refers to isolated products from the benzaldehyde (1mmol), dimedone (2mmol) and ammonium acetate (1mmol) 0.4 mol% nano- $Gd_{0.7}Sr_{0.3}MnO_3$  (0.001g), under solvent-free conditions.

# <sup>29</sup> ACCEPTED MANUSCRIPT



Scheme 1. Synthesis of compounds 4a--4k.

# <sup>30</sup> ACCEPTED MANUSCRIPT



Scheme 2.A plausible mechanism using nano-Gd<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>

## <sup>31</sup> ACCEPTED MANUSCRIPT