



# Mesoporous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>: An Efficient Catalyst for Synthesis of 4,5-dihydro-1,3,5-triphenyl-1H-pyrazole

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## ABSTRACT

Mesoporous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nano sized mixed metal oxide (MMO's) used as a catalyst readily synthesized by hydrothermal method in high pressure autoclave. It shows highly efficient, recyclable and mild catalyst for the condensation reaction of substituted chalcone and phenyl hydrazine hydrate to obtain 4,5-dihydro-1,3,5-triphenyl-1H-pyrazole derivatives in excellent yields of product at short reaction times under simple experimental condition. The synthesized material particle size was controlled by CTAB as structure directing agent and calculated by BET Surface area. The structural characteristic of catalyst is identified by XRD, SEM, EDS, TEM analysis. The acidic strength of catalyst was measured by Ammonia-Temperature Programmed Desorption (NH<sub>3</sub>-TPD).

## 1. Introduction

Mesoporous mixed metal oxides attracted more attention within the area of catalysis as a result of their various properties and applications [1, 2]. The superior properties are to boost the rate of reaction, reusability and environmentally green approach. The O, N, S and P hetero atom containing organic moieties are called as heterocyclic compounds.

The nitrogen containing heterocyclic compounds has a unique role within the progress of heterocyclic chemistry. Pyrazoline are nitrogen containing heterocyclic basic unit of drug molecules extensively used as synthons in various organic synthesis like pyrazoline, isoxazoles and isothiazols [3-10].

There were only a few reports on the synthesis of pyrazoline compounds, which were synthesized by using various sorts of catalysts like ZnO nanoparticles [11], Copper (II) chloride [12],  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-PW<sub>12</sub> nanoparticles [13], Nano-SiO<sub>2</sub>, H<sub>14</sub>[NaP<sub>3</sub>W<sub>30</sub>O<sub>110</sub>]/SiO<sub>2</sub> [14] etc.

The modified structures of pyrazoline having considerable interest owing to it possesses a various biological activity, such as antibacterial, antitumor,

anticancer, antitubercular etc. [15].

Pyrazolines also acting as hole transporting material in OLED (organic electroluminescent device) thanks to presence of  $\pi$  conjugated system which is generated by one in all the nitrogen atom [16, 17].

In the literature survey, there are various methods for the synthesis of pyrazoline derivatives such as in 19<sup>th</sup> century Fischer and Knoevenagel, developed most well-like method for the preparation of 2-pyrazolines [18]. In 1998, Powers et al. [19]

reported that presence of sodium hydroxide as catalyst but there is a drawback due to longer the reaction time (8 h) (A).

Synthesis of 3, 5-diaryl-2-pyrazolines (B) in the presence of acetic acid reported at 2005 by Levai. The economic and environmental related issue suffers in these reactions. Revanasiddappa et al., (2010) reported the synthesis and biological evaluation of some novel pyrazoline derivatives.

Synthesized compounds, antibacterial and antifungal activities were evaluated and most of the compounds were moderately active against the bacteria and fungi [20] (C). Jyothi et al., (2012) also synthesized some novel pyrazolines with antimicrobial activity. This is a two-step process [21] (D).

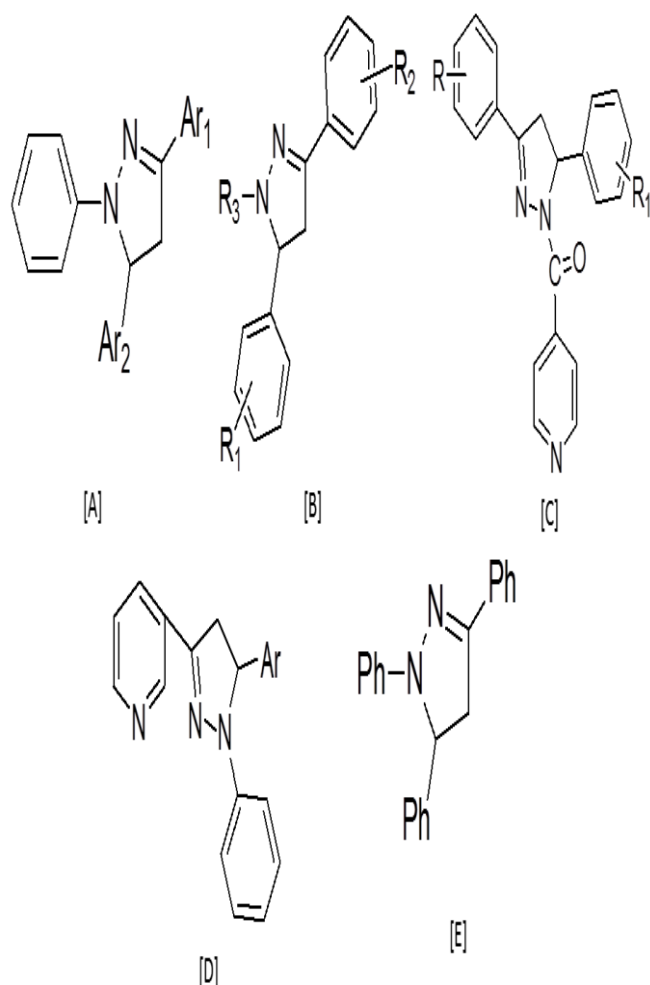
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Fazael et al in 2010 [22], Chalcone (1 mmol), Phenyl hydrazine (1 mmol) and  $H_3PW_{12}O_{40}$  (4 mol%) in EtOH (5 mL) at 45°C(E). The antimicrobial activities of those compounds are given in scheme.

Different types of hetero or homogeneous catalyst were utilized for the synthesis of pyrazole derivative but the best results about percentage of yield, purity of compound and ecofriendly nature were observed in metal oxides due to their recyclability and active catalytic nature [23].

Our research group currently performing on the development of supported and un-supported metal nanoparticles, and its applications as heterogeneous catalysis for the synthesis of bioactive heterocyclic organic compounds, mainly containing  $SiO_2$ ,  $SnO_2$ ,  $CeO_2$  etc. [24-28].

In continuation of our interest towards the development and characterization of new heterogeneous catalyst for the synthesis of bioactive heterocyclic compounds [29, 30].



All these Pyrazoline derivatives shows Antimicrobial, Antibacterial, Antidepressant, Anticancer, Antitumor, Antiandrogenic, Antioxidant etc activities.

Here we report, the synthesis, characterization and

catalytic application of mesoporous  $SiO_2:Al_2O_3$  efficient solid heterogeneous catalyst for the synthesis of 4,5-dihydro-1,3,5-triphenyl-1H-pyrazole.

The noticeable advantage of the current strategy is to introduce simple and eco-friendly procedure for the preparation of pyrazols.

## 2. Results and Discussion

The model reaction is used to study catalytic activity of catalyst and their effect on the reaction. The expected product is not obtained, when the catalyst is absent in the reaction mixture (Table 1, entry 1).

To investigate the effect of catalyst amount, the standard model reaction was carried out using different amounts of catalyst, ranging from 0.05 to 0.2 g (Table 1, entry, 2-5), and observed that 0.1g of catalyst was sufficient to complete the reaction efficiently (Table 1, entry 3).

Effect of different solvent was investigated and shown in Table 2.

The choice of solvent is somewhat critical.

These results indicate that ethanol is the best solvent to give good yields of product within shorter reaction time at a particular temperature.

**Table 1.** Effect of catalyst amount for the reaction of substituted chalcone and phenyl hydrazine hydrate.

Entry	Catalyst amount (g)	Time (min)	Yield (%) <sup>b</sup>
1	Without catalyst	120	No reaction
2	0.05	90	75
3	0.10	60	95
4	0.15	60	85
5	0.20	60	82

Reaction condition: chalcone (1 mmol), phenyl hydrazine hydrate (1 mmol),  $SiO_2-Al_2O_3$ . Isolated Yield<sup>b</sup>

Catalyst is materials that influence the response changes with look at of quantity of solvent, at variable temperature, quantity of catalyst and reaction time.

In this connection, Table 3 summarized a literature observed of diverse catalyst utilized in this unique response and differentiates the consequences with our catalyst and discovered that to received true yield in shorter response time.

**Table 2.** Optimization of model reaction using several solvents(a).

Entry	Solvent	Time (min)	Temperature (°C)	Yield (%) <sup>a</sup>
1	Solvent Free	60	90	--
2	EtOH	60	85	95 <sup>b</sup>
3	Water	60	120	--
4	Water + Ethanol	70	120	45
5	MeOH	75	90	50

<sup>a</sup>Reaction condition: Chalcone (1 mmol), Phenylhydrazine hydrate (1 mmol), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. Isolated Yield<sup>b</sup>.

**Table 3.** Effect of different type of catalyst for the reaction of chalcone and phenyl hydrazine hydrate.

Entry	Catalyst	Solvent (mL)	Temp (°C)	Amount of Catalyst	Reaction time (h)	Yield (%) <sup>(b)</sup> /Ref
1	CH <sub>3</sub> COOH	6	RT	6	120	95.5 [31]
2	CH <sub>3</sub> COONa	0.01	32	0.01	120	92 [32]
3	HCOOH	10	85	2.5	25	82 [33]
4	Graphene Oxide NPs	20	80	2.5	180	95 [34]
5	H <sub>2</sub> SO <sub>4</sub>	30	90	0.5	480	80 [35]
6	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	15	85	0.1	60	95

**Reaction condition:** chalcone (1 mmol), phenyl hydrazine hydrate (1 mmol), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. Isolated Yield<sup>b</sup>

After optimizing the reaction condition, the generality of this method was examined by the reaction of substituted chalcone (1) and phenylhydrazine hydrate (2) in the presence of 0.1g SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> as a catalyst, the results are shown in Table 4.

In all cases, aromatic aldehydes with substituent carrying either electron-donating or electron withdrawing groups reacted successfully and gave the products in excellent yields because of excellent catalytic material. Representative synthesized compounds were characterized by spectral data and compared (<sup>1</sup>H NMR, <sup>13</sup>C NMR, FTIR and Mass spectra) with authentic samples.

This comparison revealed that the compounds synthesized by this newly developed method were exactly similar in all aspects to the reference compounds.

As per the industrial and economical point of view, we focus our attention towards the recovery and reusability of the catalyst.

The catalyst was separated, washed with n-hexane dried at 80°C for 2 h before the next catalytic run.

The reusability of the catalyst was investigated three times and it was found to retain almost consistent activity (Table 4, entry 3a).

**Table 4.** One step synthesis of 4,5-dihydro-1,3,5-triphenyl-1H-pyrazole derivatives.

Entry	R	Time (min)	Yield (%) <sup>a</sup>	Melting point (°C) Found Literature
3a	C <sub>6</sub> H <sub>5</sub>	60	95 (95, 94, 92) <sup>b</sup>	132-133 134
3b	4-MeC <sub>6</sub> H <sub>4</sub>	65	92	127-128 128
3c	4-OMeC <sub>6</sub> H <sub>4</sub>	60	95	109-110 111
3d	4-ClC <sub>6</sub> H <sub>4</sub>	70	93	133-134 136
3e	3-BrC <sub>6</sub> H <sub>4</sub>	60	96	142-143 143
3f	2-ClC <sub>6</sub> H <sub>4</sub>	70	94	132-133 134
3g	3-ClC <sub>6</sub> H <sub>4</sub>	65	95	135-136 136

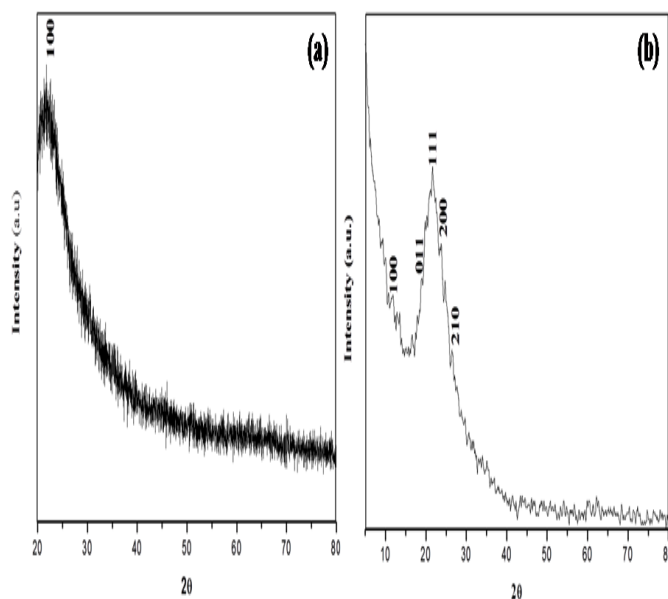
**Reaction condition:** Substituted chalcone (1mmol) and Phenylhydrazine hydrate (1mmol), SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst (0.1g) refluxing in oil bath, Isolated yield<sup>(a)</sup>. Yield after consecutive cycles<sup>b</sup>

Substituted chalcone (I) react with Phenyl hydrazine hydrate (II) to obtained the intermediate (1E)-2-phenyl-1,3-diphenylallylidene)hydrazine (III) is on intramolecular cyclization reaction to form a five member pyrazole ring to obtained the final product 4,5-dihydro-1,3,5-triphenyl-1H-pyrazole derivatives (IV) (scheme 2).

### 2.1 XRD Analysis

The XRD pattern is focus on the geometry and crystallinity of synthesised material. The powder X-ray diffraction pattern of  $\text{SiO}_2$  shows the broad peak at  $21.74^\circ$  with a 100 plane indicate the amorphous nature of silicon dioxide (JCPDS card no 01-086-1561) shown in Fig.1(a). The XRD pattern of synthesised  $\text{SiO}_2\text{-Al}_2\text{O}_3$  is shown in Fig.1

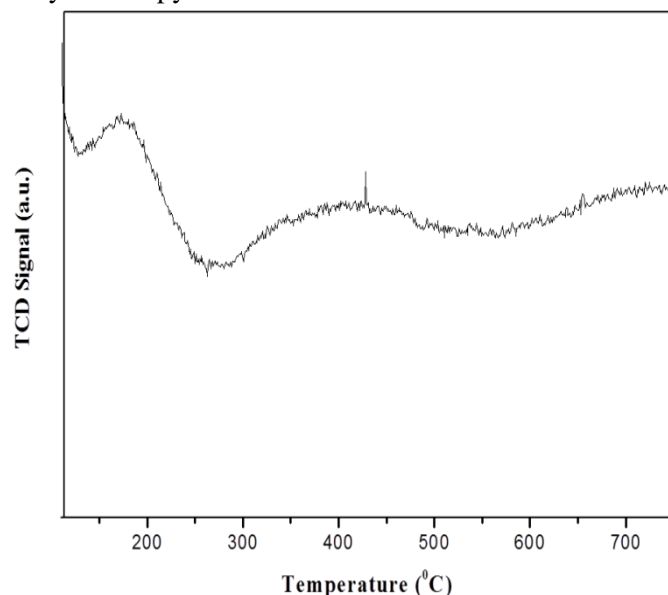
(b) the XRD pattern shows the orthorhombic crystal structure which is matched with JCPDS card no 84-1566 having parameters  $a=7.503$ ,  $b=7.738$ ,  $c=5.804$ . Here broad peak at  $21.74^\circ$  indicate 111 plane with sharp point that the crystalline nature of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  enhanced.



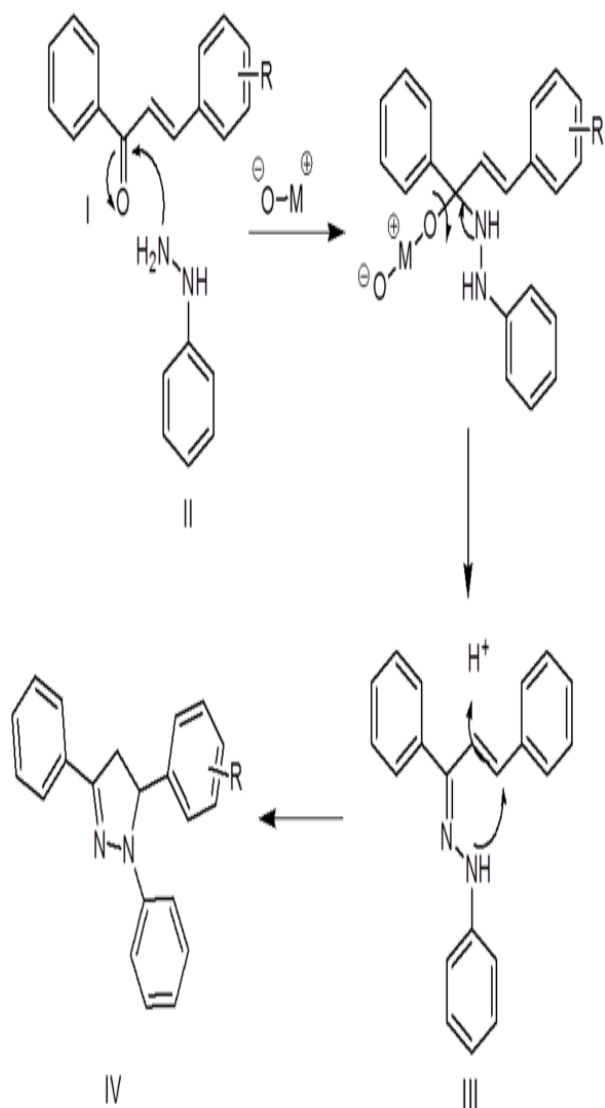
**Fig 1.** XRD pattern of a)  $\text{SiO}_2$ , b)  $\text{SiO}_2\text{-Al}_2\text{O}_3$  mixed metal oxides.

### 2.2 TD Analysis

$\text{NH}_3$ -TPD introduce about the total concentration and strength of acidic sites Bronsted and Lewis [38]. From  $\text{NH}_3$ -TPD investigation, it was found that the ammonia desorbed in three different regions. In first region 0.00155 mmol/g of  $\text{NH}_3$  desorbed at  $185.3^\circ\text{C}$  to presence of Lewis acidic sites, while in the second and third region 0.00394 mmol/g, 0.00552 mmol/g of  $\text{NH}_3$  desorbed at  $428.1^\circ\text{C}$  and  $691.0^\circ\text{C}$  Bronsted acidic sites respectively. Therefore the total strength of acidic sites present in  $\text{SiO}_2\text{-Al}_2\text{O}_3$  was found to be 0.01101 mmol/g (Fig. 2). The presence of both weak Lewis and strong Bronsted acidic sites in  $\text{SiO}_2\text{-Al}_2\text{O}_3$  can be attributed by the Ammonia-TPD. The number of Bronsted acidic sites play a significant role in the synthesis of 1,3,5-triphenyl-4,5-dihydro-1H-pyrazole derivatives.



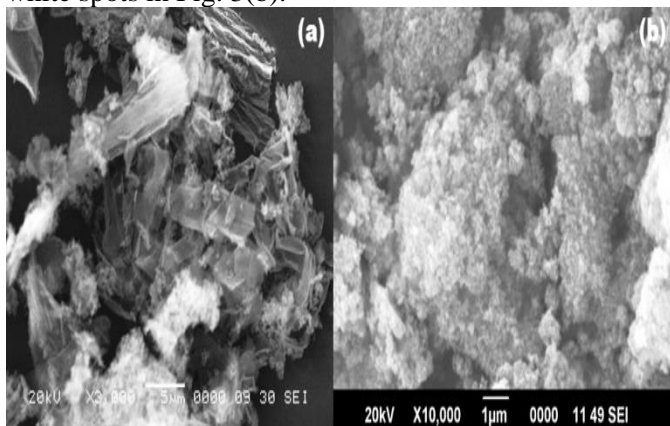
**Fig 2.**  $\text{NH}_3$ -TPD profile of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  mixed metal oxide.



**Scheme 2** Schematic representation of plausible mechanism of 4,5-dihydro-1,3,5-triphenyl-1H-pyrazole

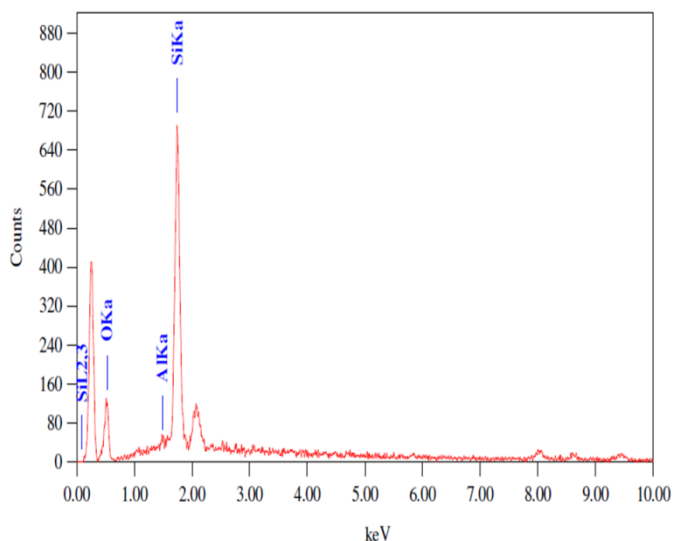
### 2.3 SEM-EDS Analysis

Surface morphology of the prepared  $\text{SiO}_2\text{-Al}_2\text{O}_3$  was studied by SEM image. In Fig.3(a) shows the flakes like structure of  $\text{SiO}_2$  oxide. When  $\text{Al}_2\text{O}_3$  doped on the surface of  $\text{SiO}_2$  which is seen on the surface indicated by white spots in Fig. 3(b).



**Fig 3.** SEM image of a)  $\text{SiO}_2$  b)  $\text{SiO}_2\text{-Al}_2\text{O}_3$  of mixed metal oxide.

Elemental composition of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts is represented in Fig.4 intense peaks in the figure show the presence of Si, Al and O with 57.91, 1.94 and 40.15 mass % respectively. The minimum stoichiometric ratio was maintained.



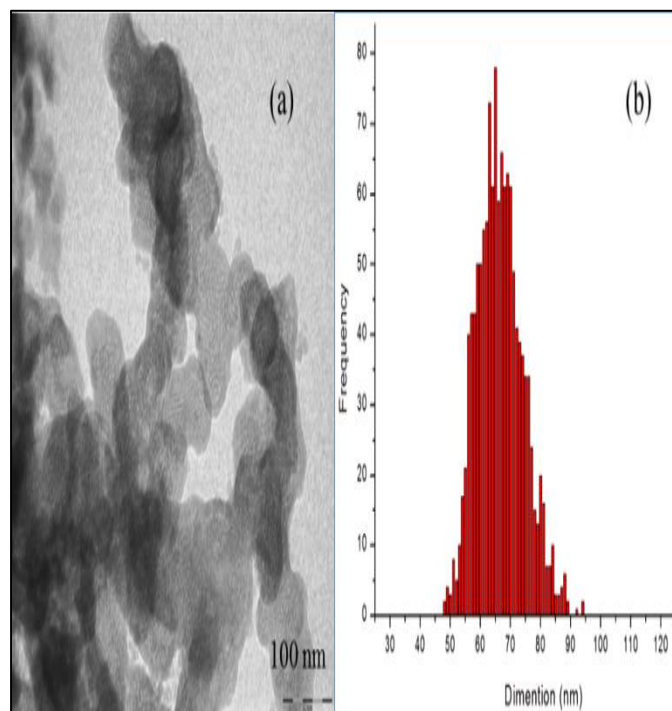
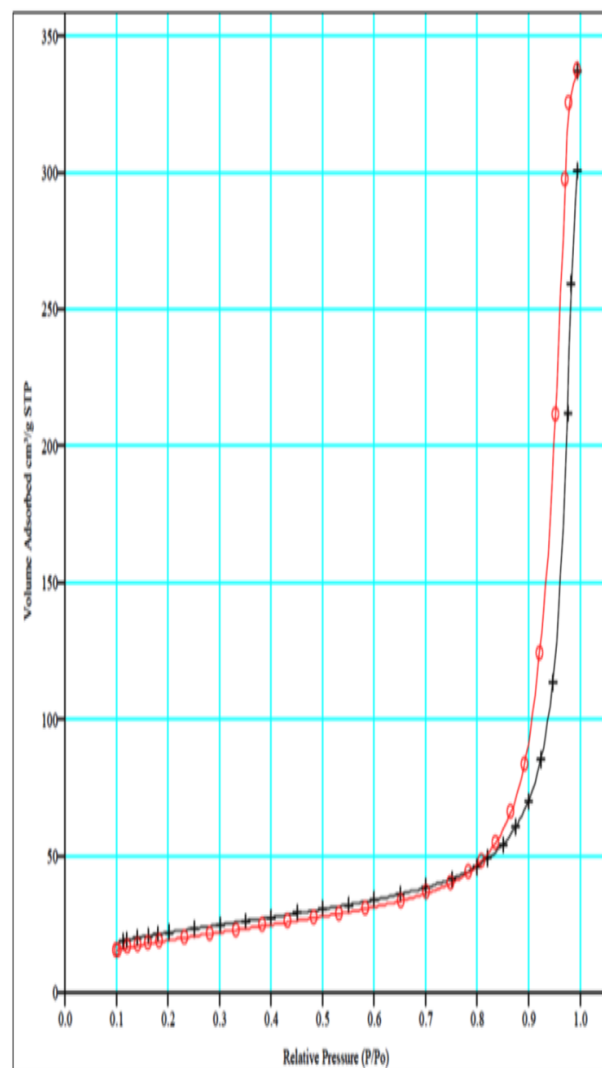
**Fig 4.** EDS spectrum of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  mixed metal oxide.

### 2.4 TEM Analysis

In Fig.5(a) shows TEM image of  $\text{SiO}_2\text{-Al}_2\text{O}_3$ , which were used to calculate size distributions and average particle size of catalyst.

The maximum and minimum size of particles was found 66 nm and 7.68 nm respectively. Size distribution were shown in Fig.5 (b).

Asymmetric histograms of these images due to the lack of detection of particles are less than 1nm. The powder XRD patterns also confirm the presence of a crystalline phase.



**Fig 5.** TEM image of a) calcined  $\text{SiO}_2\text{-Al}_2\text{O}_3$  b) Associate particle histogram of  $\text{SiO}_2\text{-Al}_2\text{O}_3$ .



### 2.5 BET Surface Area and Porosity Analysis

The unique and intrinsic properties of nanocomposite material  $\text{SiO}_2\text{-Al}_2\text{O}_3$  was characterized by the  $\text{N}_2$ -BET method.

The  $\text{N}_2$  adsorption-desorption isotherms provide information on the textural properties of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  and the specific surface area shown in Fig 6.

The BET Surface area, average pore diameter and pore volume of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  depicted in Table 5.

The amount of  $\text{N}_2$  gas adsorbed-desorbed at a given pressure allows determining the surface area of material. The isotherm curve indicates large volume was adsorbed on the surface of the material.

Single point BET surface area at  $P/P_0$  is 80.3224  $\text{m}^2/\text{g}$ , it means prepared material has a higher surface area. Due to this, the material gives higher catalytic activity.

Similarly, adsorption average pore diameter for same material is 27.39 nm, and BJH pore volume is 0.32  $\text{cm}^3/\text{g}$ . Smaller the pore volume of material, the greater the catalytic activity.

**Fig 6.**  $\text{N}_2$  adsorption/ desorption isotherm of  $\text{SiO}_2\text{-Al}_2\text{O}_3$ .

**Table 5.** BET surface area, average pore diameter and microspore volume of  $\text{SiO}_2\text{-Al}_2\text{O}_3$ .

Sample	Surface Area ( $\text{m}^2/\text{g}$ )	Average pore diameter (nm)	Micro pore volume ( $\text{cm}^3/\text{g}$ )
$\text{SiO}_2\text{-Al}_2\text{O}_3$	80.33	27.39	0.32

## 3. Experimental

### 3.1 Instruments and Characterization

The prepared  $\text{SiO}_2\text{-Al}_2\text{O}_3$  mixed metal oxide characterized by analytical instrumental techniques such as XRD, SEM, EDS, TEM, FTIR and BET surface area. X-ray diffraction (XRD) analysis of the calcined  $\text{SiO}_2\text{-Al}_2\text{O}_3$  was carried out with a Phillips X-ray diffractometer in a diffraction angle range  $2\theta(^{\circ})=20$  to 80 using  $\text{Cu-K}\alpha$  radiation with a wavelength of 1.540598 Å.

Surface morphology and elemental analysis of the  $\text{SiO}_2\text{-Al}_2\text{O}_3$  were carried out using a JEOL-JEM 2300 (LA) scanning electron microscope with an electron dispersion spectroscope (SEM-EDS) attachment.

Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (JASCO FTIR/4100, Japan) from 4000 to 400  $\text{cm}^{-1}$ .

### 3.2. Synthesis of Mesoporous $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixed metal oxide

The Mesoporous  $\text{SiO}_2\text{-Al}_2\text{O}_3$  mixed metal oxide prepared by hydrothermal method. In a typical synthesis, tetraethyl orthosilicate (TEOS), was added to a mixture of 1g cetyltrimethyl ammonium bromide (CTAB), 5 mL sodium hydroxide (NaOH) to reach solution upto 9.5  $\text{pH}$  and an aqueous solution of aluminum nitrate  $[\text{Al}(\text{NO}_3)_3]$  to stirred at room temperature for 24 h.

The resulting mixture hydrothermally treated at 150°C for 5 h in high pressure autoclave at 400 rpm having autogeneous pressure 54 psi at the volume 250 mL of mixture.

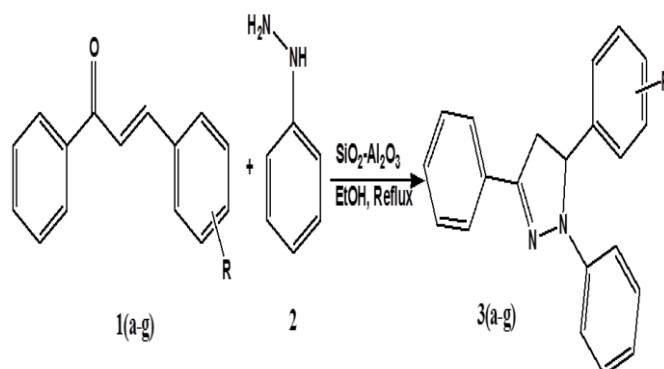
Then the mixture was cooled at room temperature, the solid material obtained which was filtered and washed with deionised water, dried at 80°C for 6 h and finally calcined at 500°C for 3 h.

### 3.3. General procedure for the synthesis of 1,3,5-triphenyl-4,5-dihydro-1H-pyrazole Derivatives

A mixture of substituted chalcone 1 (1 mmol), phenylhydrazine hydrate 2 (1 mmol) in presence of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  0.1g was heated at 85°C reflux for 60 min in 15 mL EtOH.

The completion of the reaction indicated by TLC, hot ethanol was added in reaction mixture and the catalyst was filtered off.

To purify the product by recrystallization with aqueous ethanol was determined by comparison by checking its physical constants (melting points),  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR and Mass spectra with the literature.



**Scheme 1**

**3.4 Spectral Data of Representative Compound 4,5-dihydro-1,3,5-triphenyl-1H-pyrazole (Table 4 Entry 3a);** Yellow crystal, m.p. 134°C (Lit [3a], m.p. 132-133°C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ), 300 MHz:  $\delta$  = 6.70-7.70 (m, 15H), 3.80 (t, H), 1.25 (d, 2H); IR (KBr,  $\nu_{\text{max}}$ ): 1589  $\text{cm}^{-1}$  (C=N), 1489  $\text{cm}^{-1}$  (C=C);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta(\text{ppm})$ : 43.6, 64.5, 173.4, 119.1, 125.9, 128.6, 129.1, 132.7, 142.6, 144.9, 146.7, 151.4. **ES-MS:**  $m/z$  299.12 ( $\text{M}^{+2}$ ) 300.16 ( $\text{M}^{+3}$ ).

**5-(4-chlorophenyl)-4,5-dihydro-1,3-diphenyl-1H-pyrazole (3b);** (Table 4 Entry 3a);  $^1\text{H}$  NMR ( $\text{CDCl}_3$

**300MHz:**  $\delta$  = 6.50-7.75 (m, 14H), 4.01 (t, H), 1.25 (d, 2H); **IR (KBr,  $\nu_{\text{max}}$ ):** 1589  $\text{cm}^{-1}$  (C=N), 1489  $\text{cm}^{-1}$  (C=C).

#### 4. Conclusion

In summary, we have successfully prepared  $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalyst by hydrothermal treatment and it had been characterized by modifying instrumental techniques, to confirm its morphology, crystalline nature, particle size, acidity, surface area and catalytic activity. The catalyst gives interesting results of 4,5-dihydro-1,3,5-triphenyl-1H-pyrazole derivatives than reported method. The used catalyst shows environmental friendly character, reusable, highly efficient and cheap. The final products are formed within short time with better to higher yield and straightforward procedure.

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