Environmental Friendly Fly Ash Supported Rare Earth Metal Catalyst for Industrially Beneficial Organic Reaction

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Abstract—*A high amount (approximately 169.25 million tons) of fly ash is generated from coal based thermal power plants as a by-product, causes serious ecological as well as health problems. For safely disposal of this waste, it has been used as construction material and as adsorbent. Along with this, its applications in heterogeneous catalysis are also attracted attention of scientists in recent years. In the present study, using fly ash as the silica source, the solid acid catalyst has been synthesized with the loading of neodymium on a framework of fly ash through wet impregnation method. The prepared catalyst has been characterized using XRD, FT-IR, SEM-EDX and TGA techniques. The neodymium on silica surface of fly ash generates Lewis acidity in the catalyst, which was confirmed by using ammonia- adsorbed infrared spectroscopy and a large amount of Lewis acidic sites were measured. Furthermore, the catalytic behavior of the catalyst in the Claisen-Schmidt condensation reaction was tested. The prepared catalyst exhibited high reactivity and was found to be recyclable up to three reaction cycles, retaining its Lewis acidity and stability under liquid phase reaction condition.*

Keywords: Fly ash, Solid Lewis Acid, Claisen-Schmidt Condensation.

Introduction

Lanthanide ions have some special chemical properties and can be incorporated into the framework of silica and alumina to prepare catalysts with efficient catalytic properties [1]. Nano binary oxide systems containing RE_2O_3 and SiO_2, with controllable size and properties have been used as catalysts [2] and showed good catalytic properties in several reactions including synthesis of ammonia and oxidative coupling of methane [3]. Researchers have pointed out that the formation of rare-earth oxides/silicates inside or at the surface of amorphous SiO_2 matrix depends mainly on the precursor used, preparation method and thermal treatment. The synthesis of Ce-MCM-41 either under reflux conditions or in an autoclave is well reported in the literature [4]. Beside this, Y, Nd, and Sm incorporated in MCM-41 siliceous framework have also been well documented in the literature [5]. Nd-doped SiO_2 has also been synthesized with different molar ratios by the

impregnation method and showed that heat treatment plays an important role in developing different phases of the binary oxides [6]. However, the preparation method of these catalysts is usually not environmentally friendly and is time consuming. In addition, the cost associated with the preparation could affect the applicability of these catalysts in an industrial setting. Recently, many waste materials have been utilized as heterogeneous catalysts for many catalytic reactions [7]. For instance, fly ash (FA), the waste generated from coal-power plants, has been used as a catalyst support in many catalytic reactions [8-10]. Fly ash has been used as a support material for Fe, Cu, Ni, and V catalysts in the selective catalytic reduction of NO by ammonia. The Cu loaded fly ash displayed the highest activity [11]. TiO_2 has been used as photocatalyst to remove NO from a gas stream and it was found that after heat treatment the removal rate of NO was increased as much as 95% [12]. A highly active nano-crystalline solid acid catalyst was synthesized by loading sulphated zirconia onto CFA via a sol–gel technique. The catalyst was found efficient for liquid phase benzylation of benzene and toluene with benzyl chloride giving high conversions of benzene (87%) and toluene (93%) [11].

Fly ash has been used as a precursor to synthesize basic zeolite Na-X for biodiesel production by transesterification of sunflower oil with methanol [13]. Our study is focused on the synthesis and characterization of Nd-incorporated in fly ash (NdFA). The prepared catalyst was used for synthesis of chalcones. The goal is to use the widely available fly ash as low-cost silica and alumina sources to prepare solid acid catalysts.

Experimental

Neodymium nitrate, 4-methoxybenzaldehyde (99%) and 2-hydroxyacetophenone were purchased from S.D. Fine Chem. Ltd., India and were used as such. The coal fly ash (Class F type) used in this study was collected from Kota Super Thermal Power Station (Kota, Rajasthan, India).

The fly ash catalyst (NdFA) was synthesized by mechanical and thermal activation of fly ash at very high temperatures. Fly ash was mechanically activated and then chemically activated using an aqueous solution of $Nd(NO_3)_3.6H_2O$ (5wt%) which was added drop wise to thermally activated fly ash with constant stirring. The slurry was aged at 110°C for 6 h, then filtered and washed with water to remove leached compounds. The resulting powder was further dried at 110°C for 2h followed by calcination at 800°C for 4h in a muffle furnace.

The synthesized activated fly ash catalyst (NdFA) was characterized by XRD, SEM-EDX, TGA and FT-IR to examine the physico-chemical properties.

The crystalline nature and the crystallite size of the samples were analyzed by X-ray diffraction study by X-ray powder diffractometer (Philips X'pert) using CuK_α radiation (λ = 1.54056 Å). The samples were scanned in 2θ range of 0–80 degree at a scanning rate of 0.04 degree s^{-1}.

The FTIR study of the sample was done using an FTIR spectrophotometer (IRPrestige-21, Shimadzu) in DRS (Diffuse Reflectance System) by mixing the sample with KBr in 1:20 weight ratio. The spectrum was recorded in the range $400 – 4000\ cm^{-1}$ with a resolution of $4\ cm^{-1}$.

The detailed imaging information about the morphology and surface texture of the sample was provided by SEM (Philips XL30 ESEM TMP).

Thermogravimetric analysis (TGA) was performed using simultaneous TGA (TGA Q500V20.8 Build 34). Sample was exposed in the temperature range of 25-900ºC with a heating rate of 10ºC/min under air flow (100 cm^3/min).

The catalytic performance of the fly ash catalyst was evaluated by Claisen-Schmidt condensation between 4-methoxybenzaldehyde and 2-hydroxyacetophenone (**Scheme 1**) to give Chalcone, as test reaction in a liquid phase batch reactor.
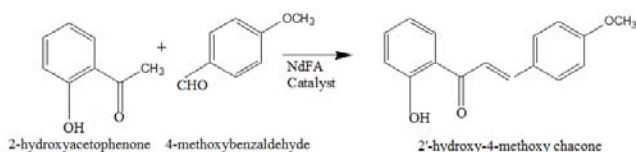
Scheme 1. Claisen-Schmidt condensation of 4-methoxybenzaldehyde with 2-hydroxyacetophenone over NdFA catalyst.

The condensation was performed in liquid phase batch reactor, which consists of 50 ml round bottom flask, magnetic stirrer and condenser. A mixture of 4-methoxybenzaldehyde (1 mmol) and 2-hydroxyacetophenone (1 mmol), was taken in round bottom flask. The catalyst, activated at 800°C for 2h (substrate to catalyst ratio = 10), was added in the reaction

mixture. The reaction mixture was kept on a hot oil bath at the 120˚C temperature for 4h.
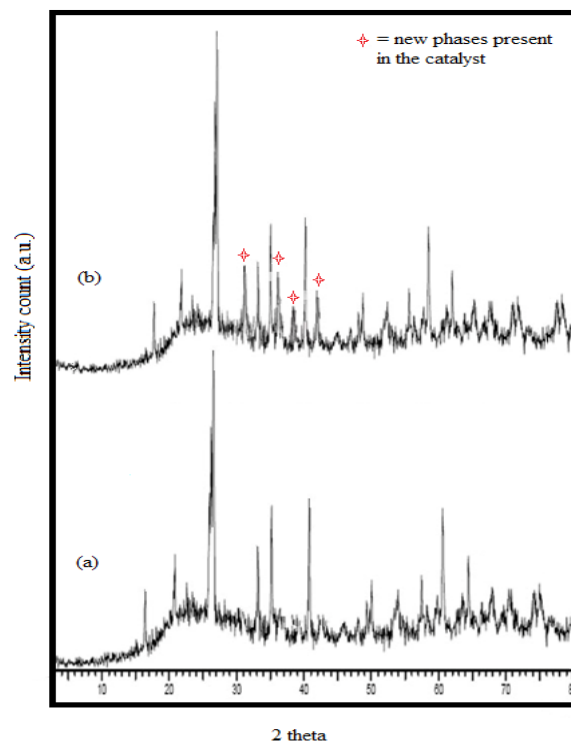
Fig. 1 XRD of (a) raw fly ash (b) NdFA catalyst

The spent catalyst (NdFA) was washed with acetone and dried in oven at 110ºC for 12h followed by activation at 650ºC for 2h before reuse in next reaction cycle under similar reaction conditions as earlier. Catalyst was reused up to three reaction cycles. Catalyst shows the same activity as in first reaction.

Results and Discussion

X-ray diffraction pattern of fly ash **(Fig. 1a)** shows the presence of crystalline phases like quartz, mullite, rutile and calcite ($CaSO_4$). The XRD patterns of the catalyst NdFA catalyst is illustrated in **Fig. 1b.**
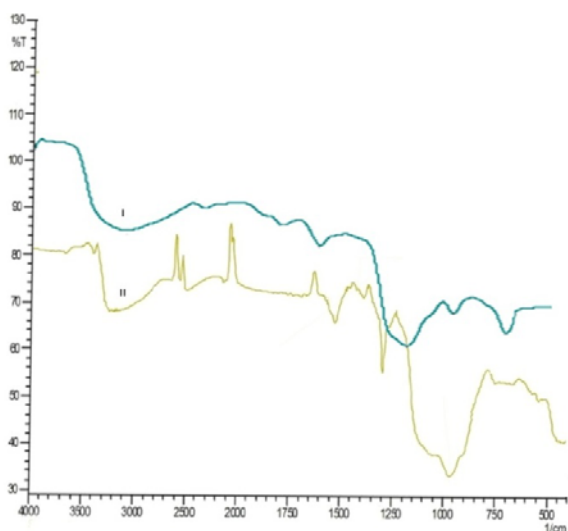
The presence of Nd in silica matrix of fly ash is confirmed by XRD analysis of NdFA catalyst **(Fig. 1b),** which shows that the catalyst calcined at 800˚C for 4h had sharp peaks that are characteristic of neodymium silicates. The initial structure of the developed phase may be described by reflections centered about 30.7˚, 36˚, 39˚, 42.9˚ [14].

FTIR spectra of raw fly ash and NdFA catalyst are shown in **Fig. 2**. The FT-IR spectrum of raw fly ash (FA) show a broad band in –OH region (3700–3000 cm^{-1}) which is attributed to surface -OH groups, characteristics of silica and the water molecules adsorbed on the surface **(Fig. 2(I))**. The broadness of the band reflects strong hydrogen bonding between the

hydroxyl groups as reported earlier [9]. An intense band in the range 1000–1300 cm^{-1}, corresponding to the valence vibrations of the silicate oxygen skeleton also appeared.
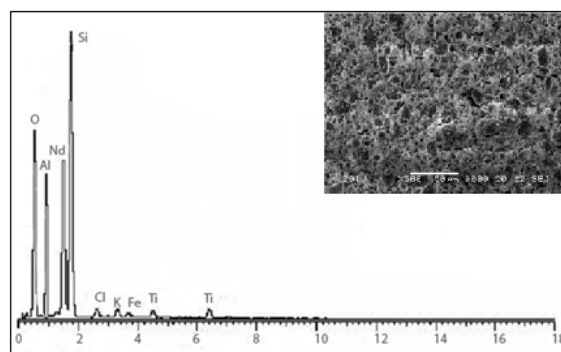
The absorption band of the valence oscillations of the Si-O-Si groups in quartz appears with a main absorption maximum at 940 cm^{-1}, but with an incorporation of Nd in silica framework of fly ash **(Fig. 2(II))** this band shifts toward the higher wave number side (950 cm^{-1}) in the case of NdFA catalyst. The presence of this band of neodymium silicates appearing around 950 cm^{-1} may be explained by the absorption due to asymmetric stretching vibration of Si–O–Nd bond [15]. However, Duhan and Aghamkar [16] reported that asymmetric stretching vibration of Si–O–Pr appears at 900 cm^{-1}. The shifting of the Si–O–Nd peak towards higher spatial frequency appears to be a consequence of the larger ionic radius of Nd than Pr.

SEM images of NdFA catalyst in **Fig. 3**, shows dense particles with a distribution of varying particle size. In the image rod like or quasi spherical shape, cube or square like shapes are found that are due to the presence of Neodymium. Irregular clusters are also found [17].


Fig. 3: SEM-EDX of NdFA catalyst.

Thermogravimetric analysis of the prepared catalyst shows weight loss of 1% below 300 °C corresponding to the loss of water. The curve presented in **Fig. 4** shows a major weight loss of 4 wt.% between 500 and 650 °C which may be ascribed to the decomposition of metal ion, loaded on the surface as in the case of silica supported lanthanide catalyst.

Fig. 2: FTIR spectra of (I) Fly ash (II) NdFA catalyst.

The EDX spectrum is showing the microchemistry of the catalyst. The elements detected are Si-19.44%, Al-9.62%, O-61.12%, Nd-8.57%, K-0.20%, Fe-0.47%, Ti-0.21%. Presence of Nd (Nd-8.57%) in the catalyst also confirms the incorporation of Nd on fly ash surface.
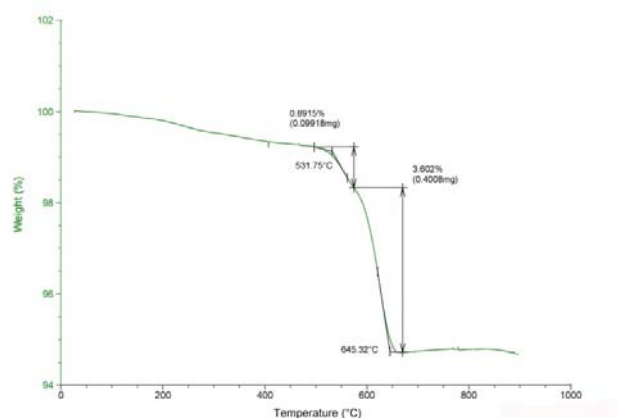
Fig. 4: TGA of NdFA catalyst.

NdFA shows high catalytic activity for condensation of 4-methoxybenzaldehyde with 2-hydroxyacetophenone resulting in a 87% conversion of 4-methoxybenzaldehyde where as FA due to the absence of any Lewis acidity on the surface does not catalyze the condensation reaction. The reaction conditions such as reaction temperature, time and molar ratios of reactants were optimized in order to achieve maximum conversion of 4-methoxybenzaldehyde.

The effect of reaction temperature was studied to optimize the reaction temperature. The reaction for condensation of 4-methoxybenzaldehyde was carried out at temperatures ranging from 30 °C to 150 °C for 4 h. The effect of temperature on the condensation activity of NdFA is given in **Table 1**. It can be

seen that the conversion of 4-methoxybenzaldehyde has a maximum efficiency of 87% at 120 °C.

Table 1: Conversion (%) of 4-methoxybenzaldehyde with NdFA catalyst at different temperatures.

Temperature (°C)	Conversion % of 4-methoxy benzaldehyde[b]	Yield (%)
30	56	81
60	59	89
90	67	89
120	87	91
150	87	91

Reaction conditions: Time = 4h; substrate/catalyst ratio = 10; molar ratio = 1:1.

The optimum reaction time required, achieving maximum conversion of 4-methoxybenzaldehyde was carried out at 120 °C for different time intervals ranging from 30 min to 6 h. The conversion of 4-methoxybenzaldehyde gradually increases with time giving 87% after 4 h as seen in **Table 2** and remains constant till 6 h.

Table 2: Conversion (%) of 4-methoxybenzaldehyde with NdFA catalyst at different time.

Time (h)	Conversion % of 4-methoxybenzaldehyde	Yield (%)
0.5	64	79
1	72	81
2	81	87
4	87	91
6	87	91

Reaction conditions: Temperature = 120°C; Time = 4h; substrate/catalyst ratio = 10; molar ratio = 1:1.

The used NdFA catalyst from the reaction mixture was filtered, washed with acetone and re-generated by heating at 350 °C for 2 h. The regenerated catalyst was used for the next reaction cycles under similar reaction conditions as first cycle.

Conclusion

In the present study, an efficient, recyclable and cost effective solid acid catalyst has been synthesized by loading neodymium ion on. The characterization of the catalyst confirmed the loading of rare earth metal Nd^{+3} ions on activated fly ash surface. The prepared NdFA catalyst possesses significant amounts of Lewis acidity responsible for the high conversion of 87% for 4-methoxybenzaldehyde giving predominantly chalcones as product, which is an important precursor for the synthesis of Naproxen an anti-inflammatory drug. Higher conversions and higher selectivities for desired products make the NdFA the most suitable catalyst for industrial scale production of chalcones.

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