

*Synthesis, characterization and catalytic applications
Of CeO₂- MgO nanocomposite oxide for Knoevenagel
Condensation reaction*

*A Dissertation
Submitted in partial fulfillment*

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Submitted by

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This is to certify that the dissertation entitled “*Synthesis, characterization and catalytic application of CeO₂-MgO nanocomposite oxide for Knoevenagel condensation reaction*” being submitted by **Prabhat Kumar Subudhi** to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of the degree of Master of Science is a record of bonafide research carried out by him under my supervision and guidance. I am satisfied that the dissertation has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

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Introduction

1.1 General Introduction

Metals and their oxides control the vast panorama of heterogeneous catalysis. Metal oxides generally exhibit both electron transfer and surface polarizing properties which are of direct relevance in redox as well as acid-base catalytic reactions. The redox properties of oxides have been used in catalytic purification systems for complete oxidation of toxic materials [1, 2]. The surface acid-base properties of oxides having a crucial role in the selective organic transformations. For fine chemical synthesis and selective oxidation reactions, oxide systems having redox properties have been studied [1, 2]. The physicochemical properties and the catalytic activity of metal oxide depend upon several factors. Among the different factors, the most important is the method of preparation. Many methods have been reported in the literature for the preparation of the metal oxides with desired properties. Thus, the synthesis of nanosize heterogeneous catalyst with high surface area and more number of active centers is highly desirable. MgO is an alkaline earth oxide having many advance applications in different area such as refractory material in high fire risk area, wet area, mineral insulated thermo couples, PPLN display and house furniture. MgO is also a most promising solid basic catalyst for many industrial processes as well as fine chemical synthesis [3-9]. MgO is one of the strongest solid base however, it has some limitations like low surface area, lower number of basic sites. Thus, in order to improve its catalytic activity the surface and structural modification is highly essential to tailor makes its properties suitable for catalytic applications. Cerium dioxide is a rare earth oxide which shows promising applications in environmental catalysis, redox catalysis and wet catalytic oxidation of organic pollutants [10-17]. Ceria-based oxide materials continue to be investigated for their structural and chemical

properties, reduction behavior and non-stoichiometry, oxygen storage capacity and metal-ceria interactions. With an intension to develop materials with good catalytic and surface properties we have prepared CeO₂-MgO composite oxide in this study and evaluated their catalytic activity for Knoevenagel condensation reaction.

1.2 Structure of MgO

The structural and catalytic properties of magnesium oxide have been investigated extensively [3]. Valuable information regarding the surface basic character of MgO and their involvement in the catalytic processes has been obtained from these studies. MgO is white color solid and is known to exist in rock salt crystal structure. The unit cell structure of MgO is shown in Fig. 1.1. In the face centered cubic (FCC) structure of MgO, oxide ions form a cubic close packing arrangement and all the octahedral sites are occupied by the Mg⁺² ions whereas the tetrahedral sites remain vacant. The unit cell of MgO can be considered as simple cube in which the face center positions and corners are occupied by oxide ions where as the magnesium ions occupy the edge centres and body centre position.

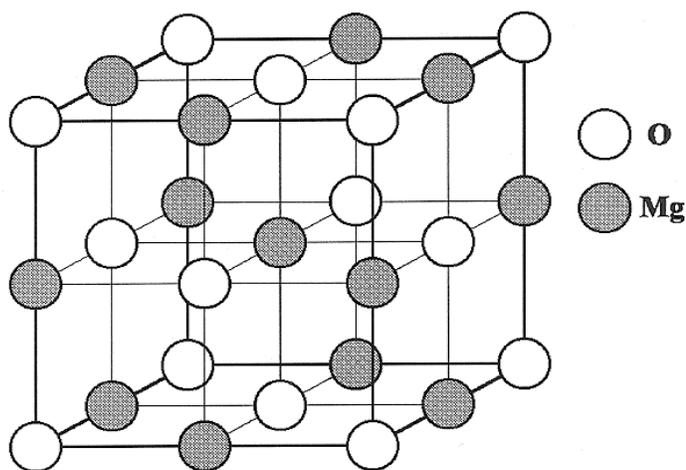


Fig. 1.1 Rock salt structure of MgO.

1.3 Structure of Ceria

The structural properties and non-stoichiometry of cerium dioxide has been investigated extensively [10, 16]. Valuable information regarding the redox property and the oxygen mobility in the lattice of ceria has been obtained from these studies. Ceria is pale yellow color solid due to $O^{2-} \rightarrow Ce^{4+}$ charge transfer and is known to crystallize in a fluorite structure (CaF_2) with a space group of $Fm\bar{3}m$. The unit cell structure of ceria is shown in Fig. 1.2. In the face centered cubic (FCC) structure of ceria, Ce^{4+} ions form a cubic close packing arrangement and all the tetrahedral sites are occupied by the oxide ions whereas the octahedral sites remain vacant. The unit cell of ceria can be considered as simple cube in which the face center positions and corners are occupied by Ce^{4+} ions. The tetrahedral sites can be visualized by dividing the cube into eight smaller cubes. The body center positions of all the smaller cubes are occupied by oxide ions and alternate corners are occupied by Ce^{4+} ions.

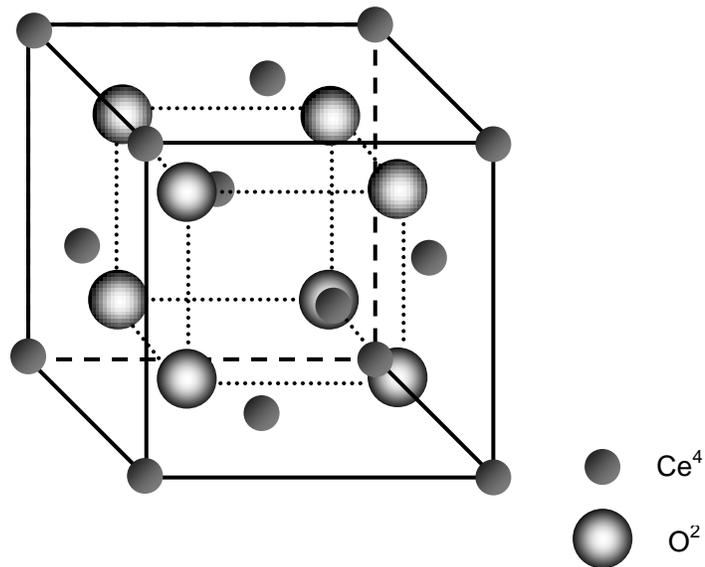


Fig. 1.2 Fluorite structure of Ceria

1.4 Ceria in Catalysis

The catalytic applications of ceria have been reviewed in literature [11-19]. The main applications of ceria in industrial catalysis are the removal of environmental pollutants such as CO, NO_x and unburned hydrocarbon (HC) originating from transport sector and also the removal of SO_x from FCC process. Ceria also plays an important role in the catalyst formulation for dehydrogenation of ethyl benzene to styrene, the removal of organic moieties from waste water by catalytic wet oxidation. Besides these catalytic applications of ceria, the surface acid-base properties of ceria have also been explored for synthetic organic transformations. Pure ceria and its combination with other oxide materials or noble metals have been employed for various catalytic processes. However, ceria has poor structural stability compared to other oxides like Al₂O₃ and SiO₂. For this reason, the main catalyst formulation consists of ceria finely dispersed on thermally stable support or thoroughly mixed with other oxides in mixed-oxide formulations.

1.5 Objectives

- ✓ To synthesize CeO₂-MgO nanocomposite oxides by gel combustion route.
- ✓ To characterize the synthesized materials by various analytical techniques such as XRD, SEM and UV-Vis to obtain complete information on the physicochemical characteristics of these materials.
- ✓ To explore the activity of the materials for Knoevenagel condensation reaction

CHAPTER 2

MATERIALS AND METHODS

2.1 Preparation of Catalyst

2.1.1 Materials

Ceric ammonium nitrate ((NH₄)₆Ce(NO₃)₃·6H₂O), magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) and citric acid monohydrate (C₆H₈O₇·H₂O) were procured from Merck, India. Double distilled water was used in synthesis procedure.

2.1.2 Preparation of CeO₂-MgO nanocomposite oxide

The CeO₂(x mol%)-MgO of different compositions were prepared using ceric ammonium nitrate ((NH₄)₆Ce(NO₃)₃·6H₂O), magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) and citric acid monohydrate (C₆H₈O₇·H₂O) as starting materials. An aqueous solution of ceric ammonium nitrate and magnesium nitrate of desired molar ratio was mixed with an equimolar amount of citric acid. Liquid ammonia was added drop wise to the solution with continuous stirring till pH 9.0 was achieved. The resulting mixture was transferred to hot air oven preheated at 110°C to remove the water which yields the corresponding precursor. The precursor was then calcined at 500°C for 2 h to obtain CeO₂-MgO mixed oxide materials. Using this procedure we have prepared pure CeO₂, MgO and CeO₂-MgO mixed oxide phases containing 5, 10, 20, 50, and 100 mol % of CeO₂.

2.2 Characterizations of Catalyst Materials

The XRD patterns of the pure CeO₂, MgO and xCeO₂-MgO composite oxide materials were recorded using a Philips PAN analytical diffractometer using Ni filtered CuKα₁ (λ = 1.5405 Å) radiation in the range of 20 – 70° at a scan rate of 2° per minute. Scanning electron micrographs of the materials were recorded on JEOL JSM-6480 LV microscope working with acceleration voltage of 15 kV. The UV-Visible absorbance spectra of the samples were recorded using Shimadzu spectrometer model 2450 with BaSO₄ coated integration sphere. Thermogravimetry analysis of the precursors was performed using Perkin-Elmer TGA-7 apparatus in air atmosphere (30 ml per min) with linear heating rate (20°C per min) from room temperature to 800°C. Melting points were measured using LABTRONICS LT-110 model and are uncorrected. ¹H NMR spectra were recorded with Bruker spectrometer at 400 MHz using TMS as internal standard. IR spectra were obtained using Perkin-Elmer IR spectrophotometer as KBr pellets.

2.3 Catalytic Studies

A mixture of benzaldehyde (1mmol), malononitrile (1mmol) and CeO₂ (10 mol%)-MgO (50 mg) were taken and ground by a mortar and pestle till it become solid (Table 1). The completion of the reaction was monitored by TLC. After the completion of the reaction, the heterogeneous catalyst was separated from the reaction mixture by dissolving in ethyl acetate. The final product was recovered from the ethyl acetate solution to give benzyldene malononitrile in 80% yield.

Mp: 82 °C, ¹HNMR (400MHz, CDCl₃): δ: 7.92 (d, 2H, Ar), 7.80 (s, 1H, CH), 7.69-7.64 (m, 2H, Ar), 7.62-7.51 (m, 1H, Ar).

CHAPTER 3

RESULTS AND DISCUSSION

3.1 XRD Study

Fig. 3.1 shows the XRD patterns of the pure CeO_2 , MgO , along with $10\text{CeO}_2\text{-MgO}$ and $20\text{CeO}_2\text{-MgO}$. The pure MgO shows well defined and intense XRD peaks with 2θ values at 36.8 , 42.8 and 62.2 degrees corresponding to the reflections from (111), (200) and (220) planes. These peaks correspond to the presence of the rock salt structure of MgO .

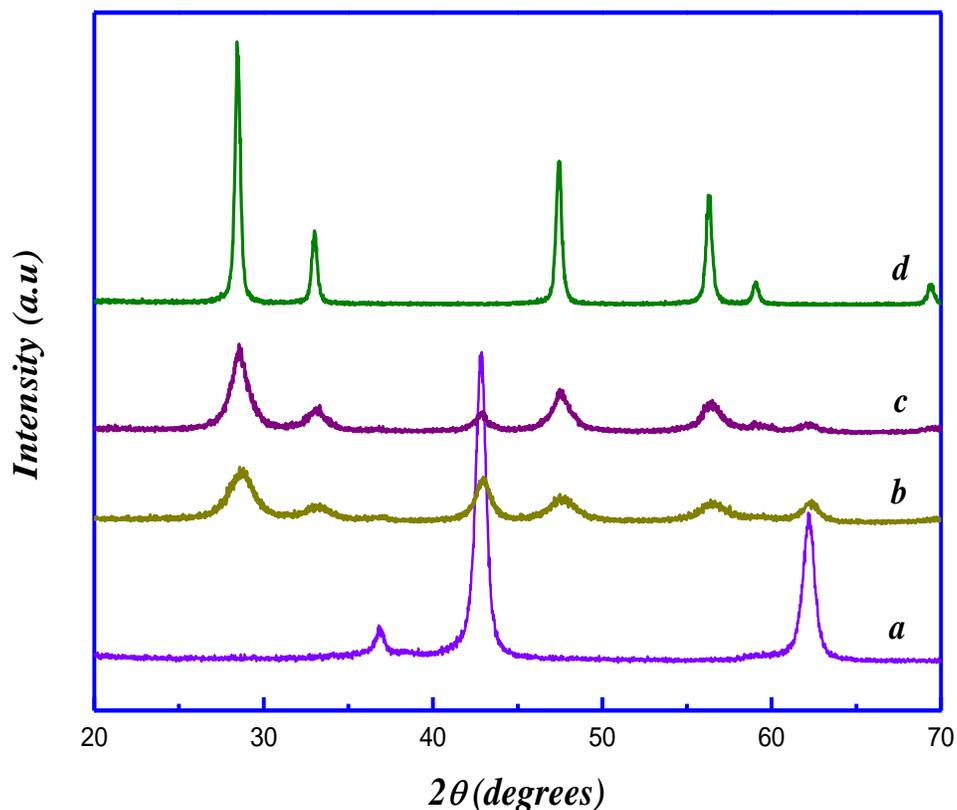


Fig. 3.1 XRD patterns of (a) MgO , (b) $10 \text{CeO}_2\text{-MgO}$, (c) $20 \text{CeO}_2\text{-MgO}$ and (d) CeO_2

Similarly, pure CeO₂ shows well defined and intense XRD peaks with 2θ values at 28.46, 33.06, 47.49 and 56.25 degrees reflections from (111), (200), (220) and (311) planes indicating the existence of fluorite structure of ceria which is agreeing with earlier reported literature [11]. Addition of 10% CeO₂ to the MgO matrix, result in significant change in the XRD patterns of MgO. The peak intensity of the MgO phase was found to decrease drastically where as a peak was observed at 28.46 corresponding to the reflection from the (111) plane of ceria particles. When the cerium content was further increased to 20% the ceria peak was found to gain intensity and prominence in the composite oxide sample. This is due to the higher X-ray scattering factor of Ce⁴⁺ ions as compared to the Mg²⁺ ions. Moreover, the composite oxide shows broadened XRD profiles as compared to the individual oxide components. The crystallite size of MgO, 10CeO₂-MgO, 20 CeO₂-MgO and CeO₂ calculated from XRD broadening profile was found to be 5, 6, 10 and 14 respectively.

3.2 UV-Vis Study

The UV-Vis spectra of the xCeO₂-MgO nanocomposite oxide materials are presented in **Fig. 3.2**. Pure CeO₂ is a semiconducting oxide which is known to show broad absorption features in the UV- region of the spectrum [11]. Crystalline cerium dioxide has a band gap of 3.1 eV and absorbs strongly in the UV region with the absorption threshold near $\lambda = 1240/E_g = 400$ nm. The synthesized pure CeO₂ in the present case shows two absorption maxima at 278 nm and 325 nm. The absorption maxima at 278 nm can be assigned to the O²⁻ → Ce³⁺ charge transfer transitions of ceria. Similarly, the absorption maxima at 325 nm can be assigned to the O²⁻ → Ce⁴⁺ charge transfer transitions of ceria nanoparticles.

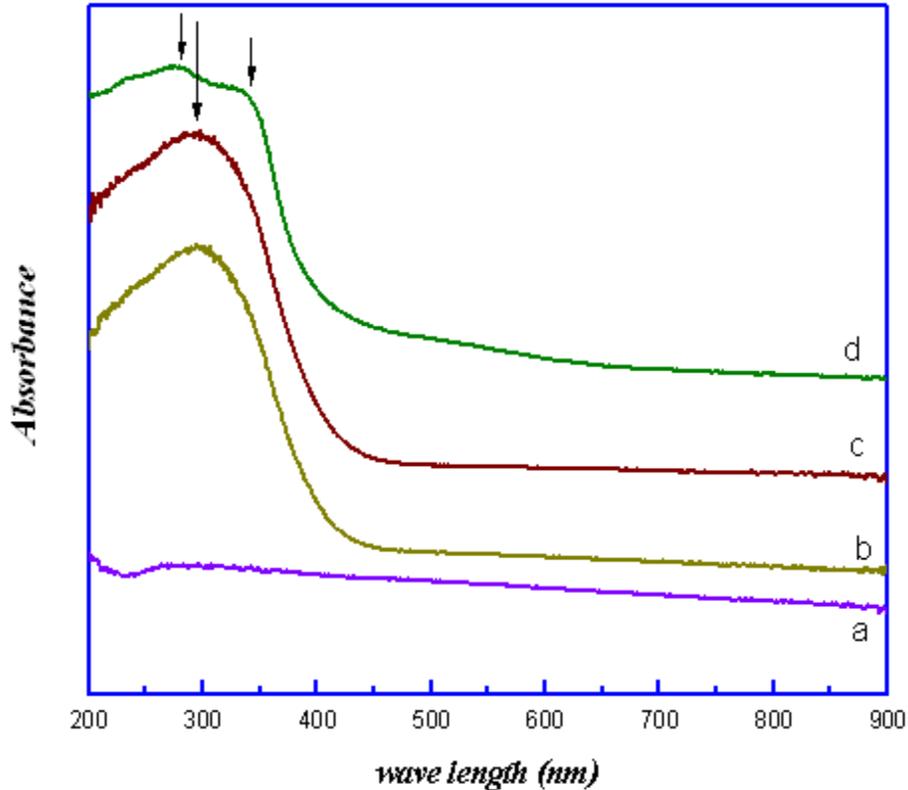


Fig. 3.2 UV-Vis patterns of (a) MgO, (b) 10 CeO₂-MgO, (c) 20 CeO₂-MgO and (d) CeO₂

The composite oxide shows absorption feature which are different from the pure ceria. The CeO₂-MgO material with ceria content (10% & 20%), a broad absorption maxima was observed at 293 nm. The 293 nm peak can be assigned to the O²⁻ → Ce⁴⁺ charge transfer transitions of ceria nanoparticles in the composite oxide. There is a significant blue shifting of the CT transition in the composite oxide suggesting the presence of ceria nanoparticles with structural disorder and defect centre in the composite oxide.

3.3 SEM Study

The scanning electron micrographs of CeO_2 and $20\text{CeO}_2\text{-MgO}$ composite oxides are presented in **Fig 3. 3**. The particles are found to be of low density and spongy in nature. There are numerous macropores present on the surface of particles. The pores are formed due to the escaping of large amount of CO_2 and H_2O gases during the decomposition. These escaping gases swelled the materials and resulted in the formation of pores.

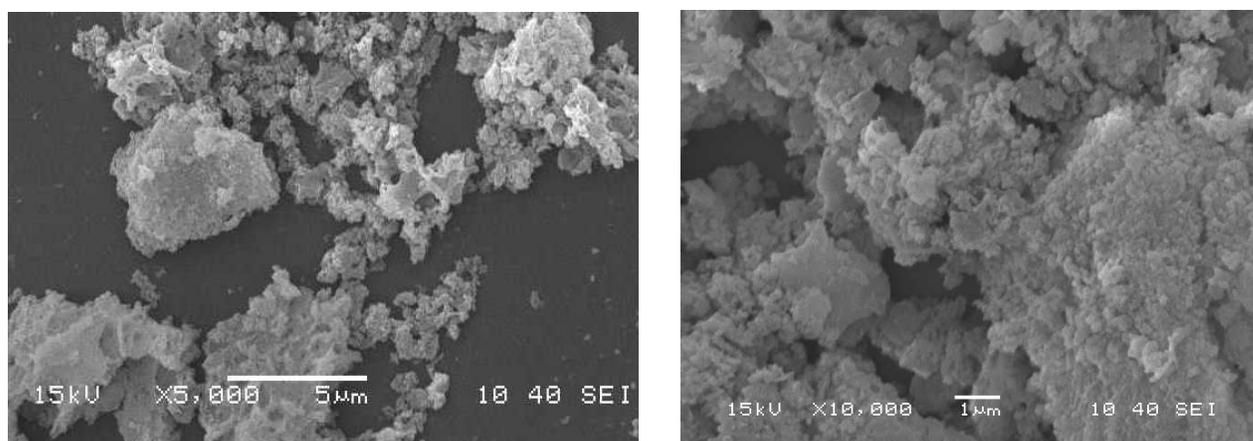


Fig. 3.3 Scanning electron micrograph of (a) MgO and (b) $20\text{CeO}_2\text{-MgO}$.

3.4 Catalytic Activity

The Knoevenagel condensation is one of the most advantageous and broadly employed reactions towards carbon-carbon bond formation in organic synthesis. The Knoevenagel condensation is the reaction between carbonyl compounds with an active methylenecompound in the presence of a base as catalyst. Homogeneous basic catalytic systems reported for this reaction in the literature are ammonia or ammonium salts, primary and secondary amines, pyridine and piperidine in different solvents [19, 20]. Keeping view towards environmental pollution

recyclability of the material and economic factor, in the recent times, much attention have been focused for the development of eco-friendly and economic processes. Hence, the use of heterogeneous catalysts for Knoevenagel condensation instead of homogeneous catalyst is highly desirable. The heterogeneous catalytic systems already reported for this reaction are alumina [21], ionic liquid/silica [22], hydroxy apatite [23], zinc oxide [24] and Si-MCM-41 [25]. With an aim to develop environmentally acceptable protocol, we have focused our attention towards Knoevenagel condensation of aromatic aldehydes with malononitrile in the presence of CeO₂-MgO as an efficient catalyst under solvent-free conditions. Initially, the reaction conditions were optimized by taking the reaction of benzaldehyde and malononitrile as the model reaction and the 20CeO₂-MgO as the catalyst under solvent free condition at room temperature (*Scheme 1*). It was observed that for a reaction involving 1 mmol of the reactant, 50 mg of the catalyst ideally suited for the efficient condensation reaction. Using 20 CeO₂ -MgO materials the applicability of the optimized protocol was examined by varying different aldehydes. The results obtained from these experiments are presented in the Table 1. A variety of aldehydes containing electron withdrawing and releasing groups reacted efficiently in the optimized protocol to give the corresponding products in high yield and purity. Overall, in this investigation we have used CeO₂-MgO composite oxide materials for Knoevenagel condensation reaction. The protocol developed in this study is advantageous in terms of simple experimentation, preclusion of toxic solvents, use heterogeneous catalyst and high yield and purity of the products.

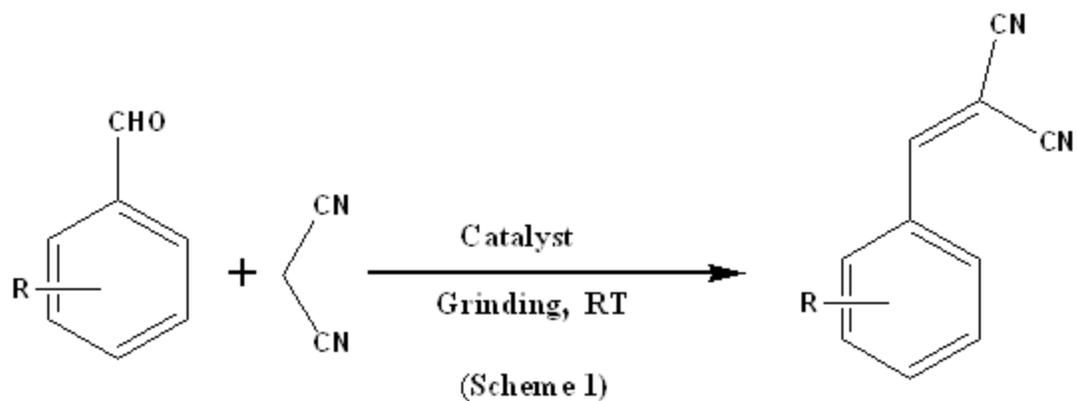


Table 1 20CeO₂-MgO catalyzed Knoevenagel Condensation reaction

Entry	X	Time	Yield (%)
1	H	25	70
2	4-Cl	20	76
3	4-OH	28	66
4	4-OCH ₃	25	77
5	4-Br	12	74
6	4-F	10	79
7	2-OH	14	76

CHAPTER 4

CONCLUSION

In this investigation we have synthesized a series of CeO₂-MgO composite oxide catalysts by gel combustion method. The composite oxides were characterized by XRD, UV and SEM techniques. The presence of well dispersed ceria nanoparticles in MgO matrix was ascertained from the XRD and UV study. SEM study indicates the material to be porous and low density in nature. The CeO₂-MgO composite oxide was used as an efficient heterogeneous catalyst for the Knoevenagel condensation of aromatic aldehydes and malononitrile. The protocol developed in this study is advantageous in terms of simple experimentation, preclusion of toxic solvents, heterogeneous catalyst and high yield and purity of the products.

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