

Preparation of Mg-doped Ce-Zr Solid Catalysts and Their Catalytic Potency for the Synthesis of 5-Arylidene-2,4-Thiazolidinediones *via* Knoevenagel Condensation

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ABSTRACT

A series of Mg-doped Ce-Zr mixed oxides with different molar ratios were prepared by a simple co-precipitation method. The surface characterization of these materials were investigated by means of XRD, FT-IR, SEM-EDS, CO₂-TPD and BET techniques. The catalytic activity of the prepared materials was tested by synthesizing of 5-arylidene-2,4-thiazolidinedione derivatives *via* a Knoevenagel condensation using aromatic aldehydes and 2,4-thiazolidinedione in ethanol:water medium. The best catalytic activity was obtained with Ce₁Mg_{0.6}Zr_{0.4}O₂. The particle size or crystallite size was estimated using the Debye-Scherrer equation. Addition of MgO to the Ce-Zr mixed metal oxides affected both particle size and catalytic activity.

KEYWORDS

Mg-doped Ce-Zr oxide, surface characterization, co-precipitation, 5-arylidene-2,4-thiazolidinedione.

1. Introduction

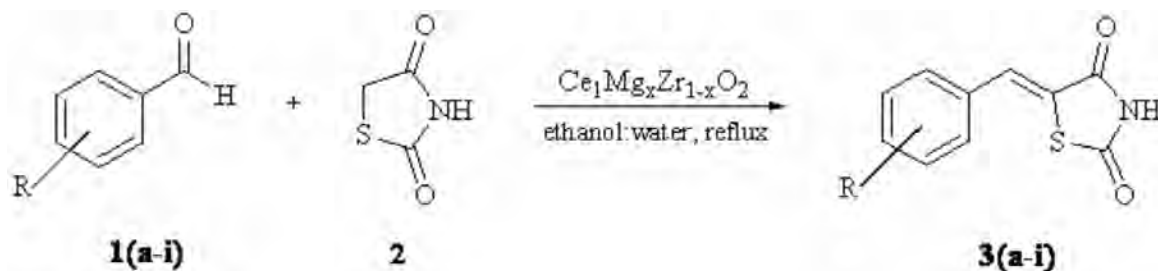
The synthesis of thiazolidinedione (TZD) represents a class of chemical products with interesting pharmacological and biological activity which includes antibacterial,¹ antifungal,² and antidiabetic,³ cardiotoxic⁴ and anticonvulsant activity.⁵ Also, 2,4-TZD and its derivatives have a remarkable anti-proliferative effect on vascular smooth muscle.⁶ 2,4-TZD has an active methylene group and so is very reactive.⁷ For this reason, many substituents at this position have been prepared. A series of 5-arylidene-2,4-TZDs are under clinical trials as potential phospholipase A2 inhibitors, dual COX-2/5-LOX inhibitors and inflammatory agents.⁸ As a result of their importance from a pharmacological, industrial and synthetic point of view, there has been increasing interest in the development of efficient methodologies for the synthesis of 5-arylidene-2,4-thiazolidinediones. Generally, 5-arylidene-2,4-TZDs are prepared by condensation of aromatic aldehydes with 2,4-TZD, i.e. piperidine in EtOH,⁹ NaOAc in DMF-AcOH¹⁰, ethylenediammonium acetate in MeOH,¹¹ piperidine and acetic acid in toluene,¹² morpholine in AcOH,¹³ polyethylene glycol¹⁴, etc. Each of the above methods has its own merits. Some of these methods are limited in terms of poor yields, longer reaction times, difficult workup procedures, effluent pollutions and use of expensive catalysts and solvents that are harmful to the environment. Accordingly, there is a need to develop alternative methods for the synthesis of 5-arylidene-2,4-thiazolidinedione under environmentally benign conditions. Recent synthesis and development of nanosized catalytic materials are of paramount interest in designing and selecting catalysts. They reduce the toxic waste and by-products arising from chemical processes.¹⁵ The main advantage of using a heterogeneous catalyst is that, being a solid material, it is easy to separate from the gas or liquid phase reactants and products. Mixed metal oxides, as

solid heterogeneous catalyst, are potentially useful because of their eco-friendliness and ease of synthesis. The use of mixed metal oxide catalyst offers several advantages such as, they are active over a wide range of temperatures and are more heat resistant. Mixed metal oxides represents one of the most important and widely used solid state catalysts, either as active phase or supports. Metal oxides and mixed metal oxides may be applied both for their acid/base and redox properties and constitute the largest family of heterogeneous catalysts.^{16–19} They have been used in various organic transformations such as oxidation, dehydrogenation, condensation, epoxidation and photocatalytic reactions.^{20–27}

Much work has been done on the design of solid acid heterogeneous catalysts and less effort has been taken to develop heterogeneous base catalysts.²⁸ Several solid bases have been reported as being effective. These include zeolites,²⁹ alkali metals supported on alumina (Na/NaOH/ γ -Al₂O₃),³⁰ clay minerals,³¹ hydrotalcites (HDT)³² metal oxides such as magnesium oxide (MgO) and mixed metal oxides for example, magnesium-lanthanum mixed oxide.³³ Among the solid bases, magnesium oxide (MgO) exhibits excellent catalytic activity and has recently been studied the most.³⁴ Also, the type of support plays an important role in the catalytic properties and for a given reaction the activity and selectivity of the catalyst can be improved by the use of an appropriate support. Because of their high thermal stability, ceria and zirconia oxides are often used as supports.³⁵ Considering these aspects, we have decided to study the catalytic role of magnesium oxide in mixed metal oxides.

In this paper we continue our efforts, in the synthesis, characterization and catalytic application of mixed metal oxide as solid heterogeneous catalysts for fine chemical synthesis under green conditions.³⁶ Here we report, the synthesis, characterization and catalytic application of a series of mixed metal oxides containing cerium (IV), magnesium (II) and zirconium (IV). Nanosized

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Scheme 1

Knoevenagel reaction catalyzed by $Ce_1Mg_xZr_{1-x}O_2$ solid catalyst.

powdered solid solutions with different molar ratios were prepared by simple co-precipitation. Their catalytic activity in the synthesis of 5-arylidene-2,4-thiazolidinedione *via* Knoevenagel condensation was investigated.

2. Results and Discussion

The catalytic activity was examined using a liquid phase Knoevenagel condensation (Scheme 1) reaction between aromatic aldehydes and 2,4-thiazolidinedione. Initially, 4-chlorobenzaldehyde and 2,4-thiazolidinedione were used as a model reaction using pure and mixed metal oxides in ethanol:water medium. Reaction time and yield of the products were studied. The results obtained are summarized in Table 1. Catalytic activity results reveals that the pure ZrO_2 and CeO_2 - ZrO_2 mixed oxides exhibited negligible activity during the synthesis of 5-arylidene-2,4-thiazolidinediones. Pure MgO was also employed for the same reaction; however the results obtained are not satisfactory. Insertion of MgO additive in the mixed oxides increases the catalytic activity of the catalysts to give excellent yields of the products; probably due to the involvement of strong acidic and basic sites.^{37–39} Interestingly, among these different mixed metal oxides, $Ce_1Mg_{0.6}Zr_{0.4}O_2$ exhibits very good catalytic activity for the synthesis of various 5-arylidene-2,4-thiazolidinediones. This might be due to the small particle size (Table 4), which provides high surface area for reaction adsorption and hence exhibiting high catalytic activity. Therefore, it was further used as a catalyst to prepare the various derivatives of 5-arylidene-2,4-thiazolidinedione (Table 2). A variety of different substituted aromatic aldehydes possessing an electron donating ($-CH_3$, $-OCH_3$, $-OH$) and electron withdrawing groups (NO_2) offered

Table 1 The synthesis of 5-arylidene-2,4-thiazolidinedione catalyzed by $Ce_1Mg_xZr_{1-x}O_2$ in ethanol medium.

Mixed metal oxide	Time/min	Yield ^a /%
ZrO_2	180	25
CeO_2 - ZrO_2 (1:1)	180	30
$Ce_1Mg_{0.2}Zr_{0.8}O_2$	120	30
$Ce_1Mg_{0.4}Zr_{0.6}O_2$	120	40
$Ce_1Mg_{0.6}Zr_{0.4}O_2$	90	92–96
$Ce_1Mg_{0.8}Zr_{0.2}O_2$	160	55
CeO_2 -MgO (1:1)	180	40
MgO	120	45

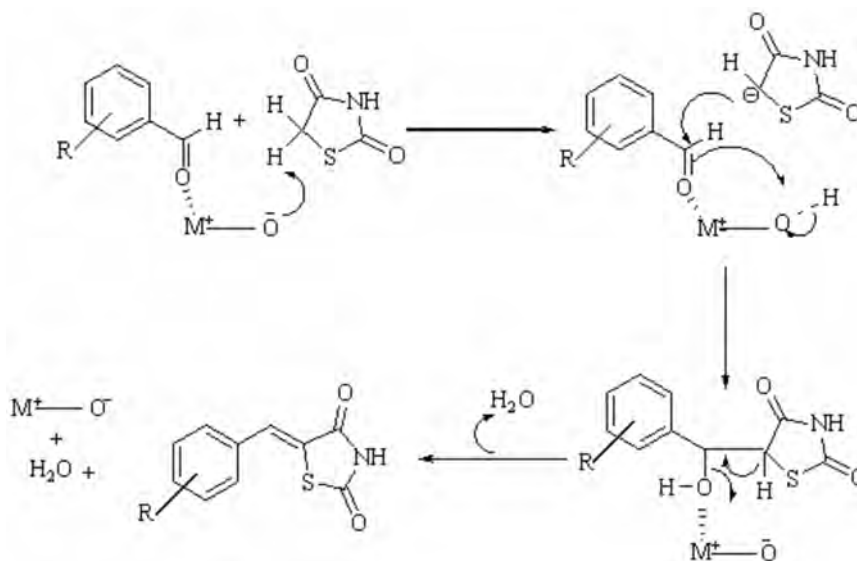
Reaction condition: the amount of catalyst, 0.2 g; 4-chlorobenzaldehyde (5 mmol) and 2,4-thiazolidinedione (5 mmol), 20 mL ethanol:water.

^a Yield refers to the isolated products.

good yields (90–96 %) and reactions were completed within 90–100 min. in ethanol:water medium (Table 2).

We believe that, $Ce_1Mg_xZr_{1-x}O_2$ possesses both acidic and basic sites (M^+-O^- , $M =$ Metal cation), which helps to increase the speed of the reaction and thereby giving excellent yields. A plausible mechanism is given in Scheme 2.

The recovery and reusability of the catalyst was examined, as it is important from industrial point of view. The catalyst was separated, washed with n-hexane, dried at 60 °C and activated at 120 °C for 1 h before each catalytic run. The reusability of catalyst was investigated for the reaction of 4-chlorobenzaldehyde and 2,4-thiazolidinedione for three cycles with almost constant activity (Table 2, entry 3e). This has prompted us to perform the



Scheme 2

Plausible mechanism for Knoevenagel reaction catalyzed by $Ce_1Mg_xZr_{1-x}O_2$ solid catalyst.

Table 2 The synthesis of 5-arylidene-2, 4-thiazolidinedione catalyzed by $Ce_{1-x}Mg_xZr_{0.4}O_2$ in ethanol:water at 75 °C.

Product	R	Time/min	Yield ^a /%	M.P./°C
3a	H	90	96	242 ^[9]
3b	2-OH	100	90	279–280 ^[9]
3c	4-OH	110	92	283–285 ^[9]
3d	4-OCH ₃	90	92	238–239 ^[9]
3e	4-Cl	90	96 (96,96,94) ^b	267–268 ^[9]
3f	4-N(CH ₃) ₂	95	94	282–283 ^[9]
3g	3-NO ₂	95	94	183–184 ^[9]
3h	4-OH,3-OCH ₃	90	90	198–200 ^[9]
3i	3-OH, 4-OH	100	92	263–264 ^[9]

Reaction condition: the amount of catalyst, 0.2 g; aldehyde (5 mmol) and 2,4-thiazolidinedione (5 mmol), 20 mL ethanol:water.

^a Yield refers to the isolated products.

^b Yield after consecutive cycles.

condensation reactions under mild conditions. In this case also, yields were excellent.

3. Conclusion

In summary, we have prepared, by simple co-precipitation, a series of mixed metal oxides with general formula $Ce_{1-x}Mg_xZr_{0.4}O_2$. The catalytic activity of these materials were explored using the synthesis of 5-arylidene-2,4-thiazolidinedione derivatives. Catalytic activity results revealed that, the $Ce_{1-x}Mg_xZr_{0.4}O_2$ catalyst exhibited excellent catalytic performance in the condensation of various aromatic aldehydes and 2,4-thiazolidinedione. It is postulated that the smaller particle size and high specific surface area of this catalyst resulted in excellent yields within 90–100 min. Additionally, we believed that insertion of magnesium oxide in the mixed metal oxide increases the catalytic activity for the synthesis of 5-arylidene-2,4-thiazolidinedione. Furthermore, the addition of magnesium oxide to mixed metal oxides decreases the particle size and helps to generate a nanosized catalytic material. Finally, we conclude that, the present proposed method is also very good alternative method for the synthesis of biologically important compound of the type 5-arylidene-2,4-thiazolidinedione. These catalysts are relatively non-toxic, environmentally safe and easy to recover and reuse.

4. Experimental

4.1 Catalyst Preparation

All the chemicals used were of synthesis grade reagents (Merck) and obtained from commercial suppliers and used as such.

A series of $Ce_{1-x}Mg_xZr_{0.4}O_2$ mixed metal oxides were prepared by a simple co-precipitation method. An aqueous solution containing the required quantities of ammonium ceric nitrate, magnesium nitrate and zirconyl nitrate was prepared in deionized water. To this mixture 20 mL 5 % polyethylene glycol (PEG-400) (structure-directing agent) was with constant stirring. This solution was hydrolyzed using 1:1 aqueous ammonia with vigorous stirring until the solution reached pH = 9. A yellowish precipitate so formed, was allowed to digest at 60 °C in an electric oven for 24 h. The resulting precipitate was filtered, washed with deionized water and dried at 120 °C for 12 h. Finally, the dried powders were calcined at 500 °C for 1 h in atmospheric air. All pure single and mixed oxides were prepared by following same procedure.

4.2 Catalyst Characterization

The prepared mixed metal oxides were characterized by XRD, FT-IR, SEM-EDS, CO₂-TPD and BET techniques. The X-ray

powder diffraction patterns of the catalysts were recorded on a Bruker D8 advance X-ray diffractometer using CuK α radiation ($\lambda = 0.154$ nm). The IR spectra were recorded on an FT-IR spectrometer (JASCO, FT-IR/4100) Japan, using dry KBr as standard reference in the range of 4000–500 cm⁻¹. To study the morphology of CMZO (1:0.6:0.4), SEM analysis was carried out with a JEOL; JSM-6330 LA operated at 20.0 kV and 1.0000 nA. The elemental composition of the metal in the $Ce_{1-x}Mg_xZr_{0.4}O_2$ catalyst was determined using energy dispersive spectrophotometer (EDS). Brunnauer–Emmett–Teller (BET) surface area and Temperature programmed desorption (CO₂-TPD) measurements were carried out on a Quantachrome CHEMBET 3000 and CHEMBET 3000 TPR/TPD instrument, respectively.

4.2.1 X-ray diffraction (XRD) Results

In order to understand the phase symmetry of the prepared powdered materials, a systematic study on the XRD was undertaken. Fig. 1(a) shows the XRD pattern for pure ZrO₂ powder, calcined at 500 °C for 1 h in air. Sharp peaks were obtained at ($2\theta = 30^\circ, 35^\circ, 50^\circ, 54^\circ, 60^\circ, 62^\circ$) corresponding to the tetragonal structure of ZrO₂. Fig. 1(h) shows the XRD pattern of pure MgO powder, calcined at 500 °C for 1 h in air. Sharp peaks were obtained at ($2\theta = 36^\circ, 42^\circ, 62^\circ, 74^\circ, 78^\circ$) corresponding to the planes (111), (200), (220), (311), (222) indicating the cubic structure of MgO which was found to be highly crystalline in nature. Fig. 1(b–f) shows the XRD patterns of a series of mixed oxides with different molar ratios for the $Ce_{1-x}Mg_xZr_{0.4}O_2$ system. The peaks were apparently broad, due to smaller particle size and poor crystallinity. Intense, sharp peaks were obtained at ($2\theta = 28^\circ, 33^\circ, 47^\circ, 51^\circ, 57^\circ, 59^\circ, 77^\circ$) corresponds to the planes (111), (200), (220), (221), (311), (222), (322), (331) indicating the formation of cubic solid solutions.⁴⁰ The identified XRD phases are in good agreement with Alifants and Kim.^{40,41} Also, the X-ray powder diffraction pattern shows clear shifts. It confirms that the cubic structure of mixed metal oxide system is retained with addition of MgO into the Ce-Zr lattice. From this it was concluded that, the magnesium oxide is well incorporated in the cubic structure of ceria-zirconia lattice forming nanosized catalytic material.

4.2.2 Fourier Transform-Infrared Spectroscopy (FT-IR)

The FT-IR spectra of a series of mixed metal oxides, calcined at 500 °C for 1 h in air, are shown in Fig. 2. From the IR spectrum, it was observed that each sample (a–h) had a peak in the range 3200–3500 cm⁻¹ due to the hydroxyl group adsorbed on the surface of the mixed metal oxide which helps to generate the Bronsted acidic sites. All the oxides also had peaks in the range of 1500–1600 and 1410–1446 cm⁻¹ due to the deformation mode of

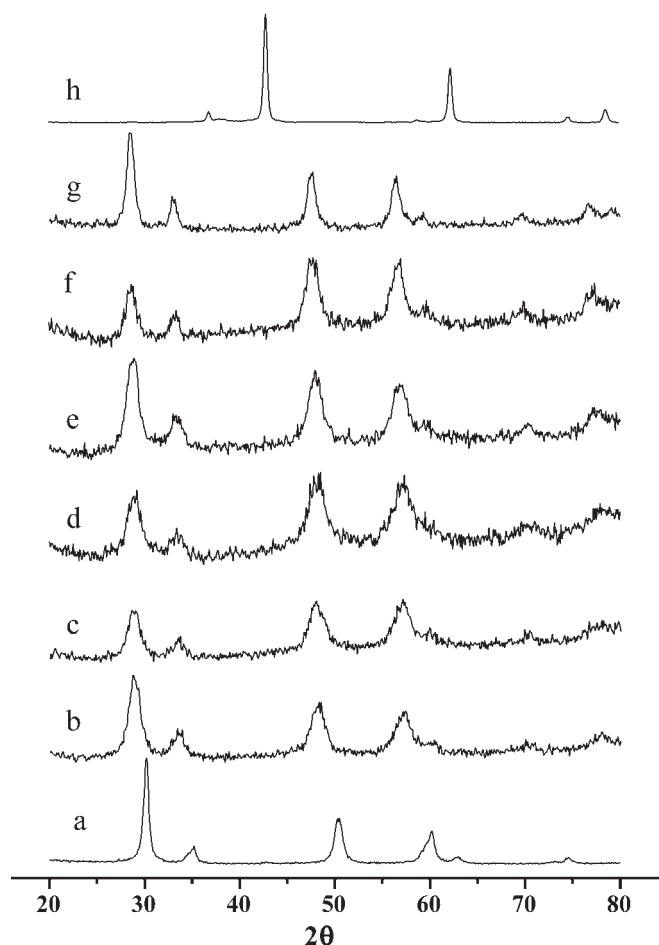


Figure 1 XRD patterns of series of (a) pure ZrO_2 , (b) CeO_2-ZrO_2 (1:1), (c) $Ce_1Mg_{0.2}Zr_{0.8}O_2$, (d) $Ce_1Mg_{0.4}Zr_{0.6}O_2$, (e) $Ce_1Mg_{0.6}Zr_{0.4}O_2$, (f) $Ce_1Mg_{0.8}Zr_{0.2}O_2$, (g) CeO_2-MgO (1:1) and (h) MgO calcined at $500\text{ }^\circ\text{C}$.

surface hydroxyl group.⁴² As shown by the IR spectrum of each sample, the peaks in the range of $1010\text{--}1079\text{ cm}^{-1}$ are assigned to the M-O-M bonding ($M = Ce, Mg, Zr$).

4.2.3 Scanning Electron Microscopy (SEM)

To study the morphology of the series of $Ce_1Mg_xZr_{1-x}O_2$ mixed metal oxides, SEM analyses were performed. The SEM micrographs are shown in Fig. 3. Figure 3(a) and (b) show the SEM images of pure ZrO_2 and CeO_2-ZrO_2 materials, respectively. These indicate that these materials are homogeneous agglomerations of particles and are irregular in shape. Also, Fig. 3(c–f) represents the SEM images of (c) $Ce_1Mg_{0.2}Zr_{0.8}O_2$, (d) $Ce_1Mg_{0.4}Zr_{0.6}O_2$, (e) $Ce_1Mg_{0.6}Zr_{0.4}O_2$, and (f) $Ce_1Mg_{0.8}Zr_{0.2}O_2$ materials. SEM images of (c) and (d) show some cracks on the surface. This might be due to the removal of water during the heat treatment or calcinations process. It was also observed that some porosity is generated (Fig. 3(e) and (f)). It may be due to the addition of 5 % PEG as structure-directing agent, which certainly allows the alteration in the particle size and morphology. It can be noted from the SEM micrograph, all three metal oxides are strongly interacted and highly dispersed on their surfaces. Similarly, Fig. 3(g) and (h) represent $CeO_2:MgO$ (1:1) and pure MgO , respectively.

4.2.4 Energy Dispersive Spectroscopy (EDS)

The elemental composition of $Ce_1Mg_{0.6}Zr_{0.4}O_2$ is shown in Fig. 4. The elemental distribution of Ce, Mg, Zr, O is (22.53 %), (2.75 %), (11.09 %), and (63.63 %), respectively.

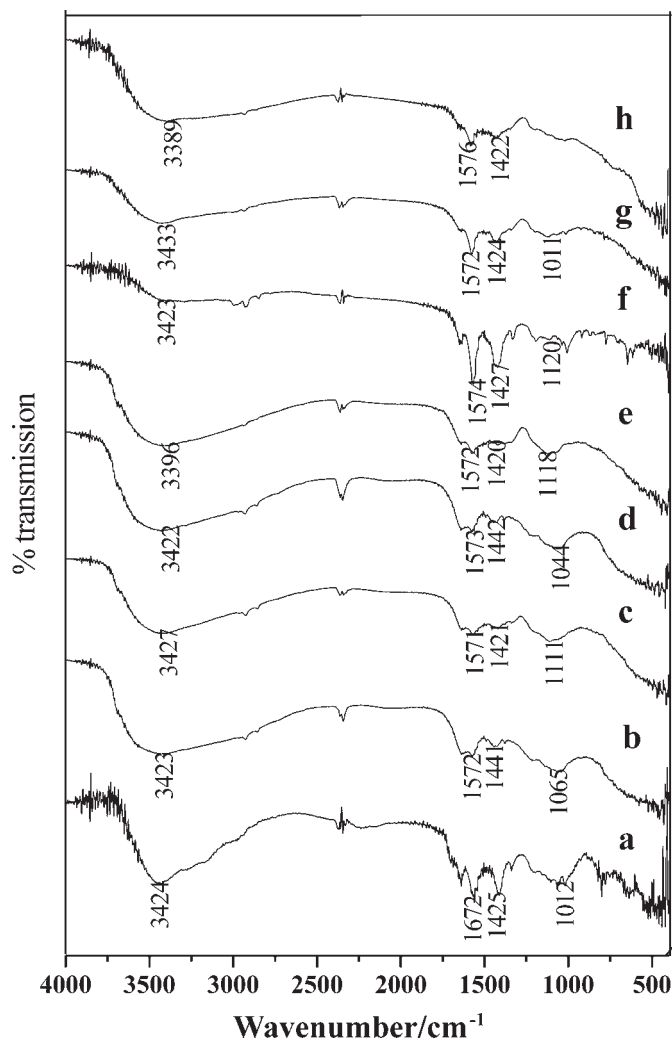


Figure 2 FT-IR spectra of series of (a) pure ZrO_2 , (b) CeO_2-ZrO_2 (1:1), (c) $Ce_1Mg_{0.2}Zr_{0.8}O_2$, (d) $Ce_1Mg_{0.4}Zr_{0.6}O_2$, (e) $Ce_1Mg_{0.6}Zr_{0.4}O_2$, (f) $Ce_1Mg_{0.8}Zr_{0.2}O_2$, (g) CeO_2-MgO (1:1) and (h) pure MgO calcined at $500\text{ }^\circ\text{C}$.

4.2.5. BET and CO_2 -TPD Results

The total basicity and specific surface area of $Ce_1Mg_{0.6}Zr_{0.4}O_2$ were calculated from CO_2 -TPD and BET measurements. The results obtained are shown in Table 3.

Table 3 CO_2 -TPD and BET analysis.

Sr. no.	Catalyst	Total basicity	Surface area
1	$Ce_1Mg_{0.6}Zr_{0.4}O_2$	0.487 mmol/g	53.54 m^2/g

4.2.6. Estimation of Particle Size using the Debye-Scherrer Equation

Generally the particle size of solid material can be estimated from X-ray line broadening and FWHM values by using Debye-Scherrer equation.

$$T = 0.94 \lambda / \beta \cos \theta,$$

where, T = particle size, λ = wavelength, θ = diffraction angles, and β = FWHM (full width half maximum). Particle sizes of the series of mixed metal oxides are shown in Table 4, which indicates that the pure zirconium oxide (ZrO_2) and magnesium oxide (MgO) are crystalline in nature (from XRD) and their particle sizes are larger (9.78 and 8.94 nm), respectively. Additionally, the addition of MgO to $Ce-Zr$ unit results in a decrease

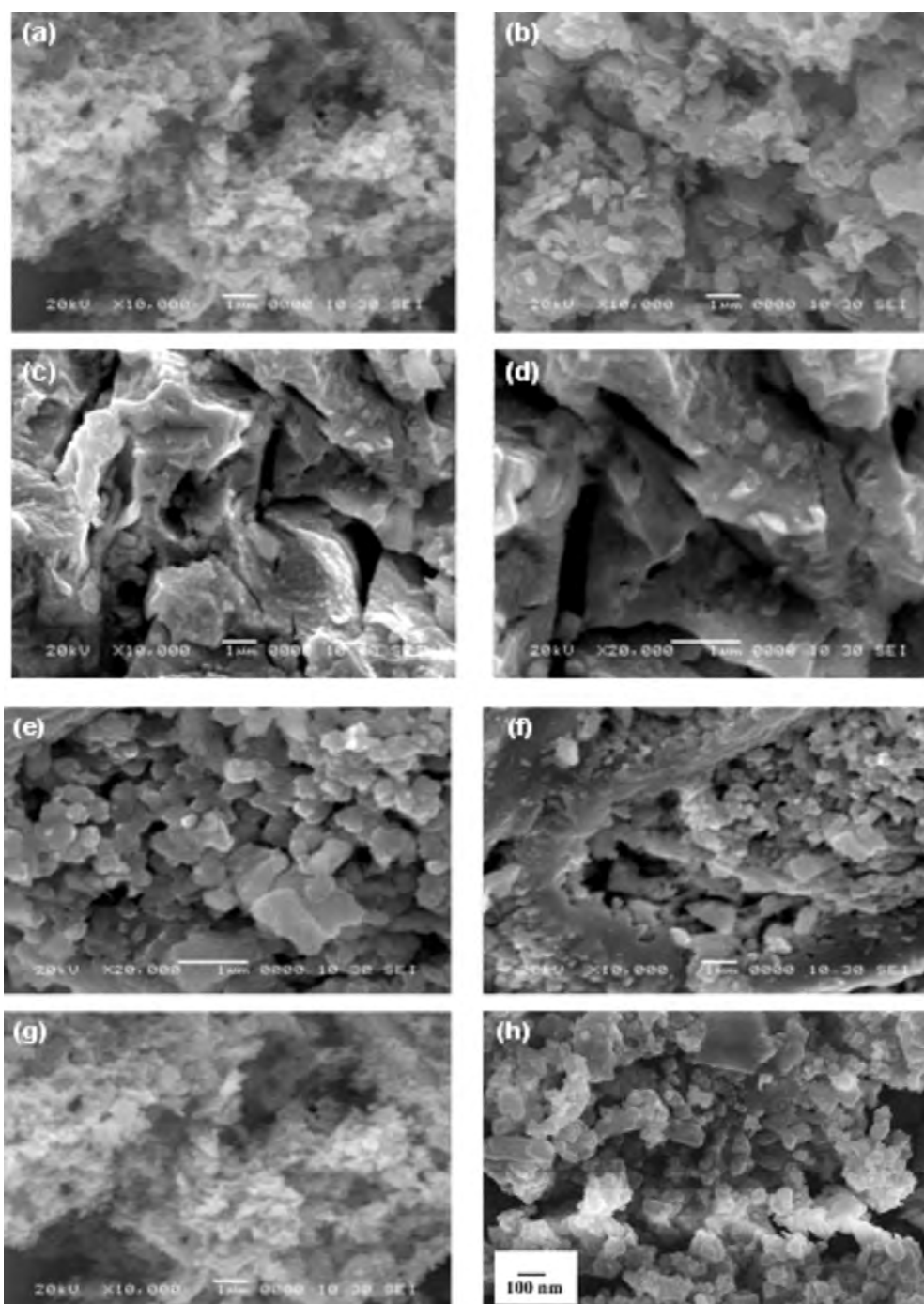


Figure 3 SEM images of (a) pure ZrO_2 , (b) $\text{CeO}_2\text{-ZrO}_2$ (1:1), (c) $\text{Ce}_1\text{Mg}_{0.2}\text{Zr}_{0.8}\text{O}_2$, (d) $\text{Ce}_1\text{Mg}_{0.4}\text{Zr}_{0.6}\text{O}_2$, (e) $\text{Ce}_1\text{Mg}_{0.6}\text{Zr}_{0.4}\text{O}_2$, (f) $\text{Ce}_1\text{Mg}_{0.8}\text{Zr}_{0.2}\text{O}_2$, (g), $\text{CeO}_2\text{-MgO}$ (1:1) and (h) pure MgO calcined at 500°C .

in particle size (6.74 to 5.41 nm) compared to their pure form and the smallest particle size was obtained for $\text{Ce}_1\text{Mg}_{0.6}\text{Zr}_{0.4}\text{O}_2$ (5.41 nm). Therefore, the addition of MgO , to the mixed metal oxide, decreases the particle size and helps to generate nanosized, solid, mixed metal oxide catalytic material.

4.3 Typical Reaction Procedure

A mixture of aldehydes **1** (5 mmol) and 2,4-thiazolidinedione **2** (5 mmol) and $\text{Ce}_1\text{Mg}_x\text{Zr}_{1-x}\text{O}_2$ (0.2 g) were mixed in (20 mL) equimolar quantities of absolute ethanol and water, in a 100 mL round bottom flask. This was loosely capped and heated in an oil bath at a temperature of 75°C . The progress of the reaction was monitored by TLC [hexane:ethyl acetate (7:3)]. After completion of the reaction, the solvent was evaporated to give a crude product,

Table 4 Preparation series of mixed metal oxides by simple co-precipitation method and estimated particle sizes.

Entry	Mixed metal oxide	Particle size/nm
1	ZrO_2	9.78
2	$\text{CeO}_2\text{-ZrO}_2$ (1:1)	6.64
3	$\text{Ce}_1\text{Mg}_{0.2}\text{Zr}_{0.8}\text{O}_2$	6.74
4	$\text{Ce}_1\text{Mg}_{0.4}\text{Zr}_{0.6}\text{O}_2$	6.57
5	$\text{Ce}_1\text{Mg}_{0.6}\text{Zr}_{0.4}\text{O}_2$	5.41
6	$\text{Ce}_1\text{Mg}_{0.8}\text{Zr}_{0.2}\text{O}_2$	6.14
7	$\text{CeO}_2\text{-MgO}$ (1:1)	9.51
8	MgO	8.94

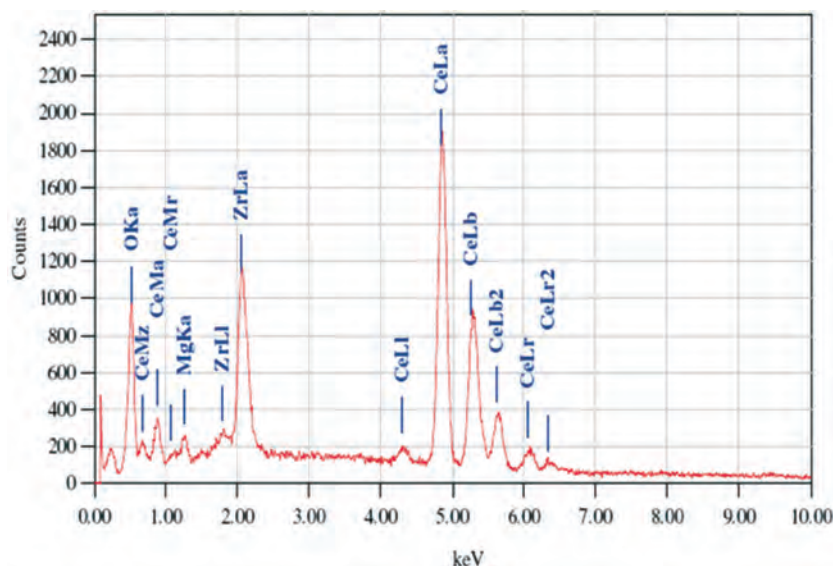


Figure 4 EDS Spectrum of $\text{Ce}_1\text{Mg}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst calcined at 500 °C.

which was purified by recrystallization. The required starting material, i.e. 2,4-thiazolidinedione⁴³ was prepared in an eco-friendly way, by the reaction of thiourea with monochloroacetic acid in water.

4.3.1 Spectroscopic Data of Selected Isolated Compounds

3a: ¹HNMR ($\text{CDCl}_3/\text{DMSO}-d_6$): 8.27 (1H, s, NH), 7.86 (1H, s, CH), 7.26 (5H, m, aromatic protons). MS *m/z* (%): 206 (M+1).

3d: ¹HNMR ($\text{CDCl}_3/\text{DMSO}-d_6$): 3.73 (3H, s, OCH_3), 7.26 (4H, m, aromatic protons). MS *m/z* (%): 236 (M+1).

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