

Synthesis, Characterization and Catalytic Studies of Nano Mixed Metal Oxides for Knoevenagel Condensation

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Abstract— The series of $M\text{Cr}_{1-x}\text{Ba}_x\text{O}_{3-\delta}$ ($M=\text{La}$ and Ce) nano mixed metal oxides with different mole ratios ($x= 0, 0.6$ and 1) was synthesized by sol-gel method. The structural phase, thermal behaviour, surface morphology and vibrational frequencies of catalysts were studied by XRD, TGA, SEM and FT-IR respectively. The catalytic potential of $M\text{Cr}_{1-x}\text{Ba}_x\text{O}_{3-\delta}$ ($M=\text{La}$ and Ce) were investigated by synthesis of 5-benzylidene - 2, 4-thiazolidinedione via Knoevenagel condensation using benzaldehyde and 2, 4-thiazolidinedione in ethanol: water medium. The synthesized compound was confirmed by FT-IR, NMR and GC-MS spectroscopic techniques.

Key words: Mixed oxides, Sol-gel method, 5-benzylidene-2, 4-thiazolidinedione, Catalytic potential, Organic reactions

I. INTRODUCTION

Thiazolidinediones were been found effective for preventing hyperglycemia to type 2 diabetes, Alzheimer's disease and certain cancers. 2,4-thiazolidinediones have been reported for its anti-inflammatory, neuro protective agents, anti-hyperglycemic, antifungal, antibacterial, antitubercular, antidiabetic, cardiotoxic, anticonvulsant and anti-proliferative effects. The active methylene group present in 2,4-thiazolidinedione makes it more reactive and hence many substituent's such as 5-arylidene-2,4-thiazolidinediones, at this position were prepared. Though there are several methods involving synthesis of 5-arylidene-2,4-thiazolidinediones i.e., piperidine in ethanol, piperidine and acetic acid in toluene, morpholine in acetic acid, polyethylene glycol and so on but some of these methods has its demerits causing harm to the environment. Therefore, an alternate environmentally benign method was developed for synthesis of 5-arylidene-2,4-thiazolidinediones.

In recent years nano sized mixed metal oxides are of immense importance in selecting catalysts for organic reactions. Mixed metal oxides act as solid state heterogeneous catalysts due to their temperature and heat resistant properties. Mixed metal oxides are of great use because of eco-friendliness and simplicity in synthesis. Oxidation of ethanol takes place faster when Co_4MnAl and NiMgMn mixed metal oxides are used as catalysts than zeolites. Similarly, $\text{Fe}_3\text{O}_4@\text{Nico}@\text{Ag}$ magnetic nanocatalyst served as good catalyst for the reduction reactions in the liquid phase. Iron oxide-supported copper oxide nanoparticles, prepared using simple impregnation method was found to be highly efficient catalyst in the synthesis of 4-methoxyaniline, pyrazole derivatives, and Ullmann-type condensation. Hence, these mixed metal oxides have been used for several organic transformations such as oxidation, condensation, dehydrogenation, epoxidation and photocatalytic reactions.

In the present investigation, sol-gel method was employed to synthesize La and Ce containing mixed metal oxides and was characterized by various analytical techniques like FT-IR, SEM, TG and XRD to determine their vibrational frequencies, surface morphology, thermal behavior and chemical composition of the oxides respectively. This study also presents the catalytic activity of mixed metal oxides via Knoevenagel condensation and their end products obtained were characterized using various spectroscopic techniques.

II. EXPERIMENTAL DETAILS

A. Materials

$\text{LaN}_3\text{O}_9.6\text{H}_2\text{O}$ (HIMEDIA), $\text{CrN}_3\text{O}_9.9\text{H}_2\text{O}$ (HIMEDIA), barium nitrate (Fischer Scientific), $\text{CeN}_3\text{O}_9.6\text{H}_2\text{O}$ (SDFCL), $\text{C}_6\text{H}_8\text{O}_7.7\text{H}_2\text{O}$ (Fischer Scientific), ethylene glycol (Fischer Scientific), thiourea (Fischer Scientific), Chloroacetic acid (LOBA Chemie), ethanol (Changshu Yangyuan Chemicals), benzaldehyde (RANKEM), dil HNO_3 , con HCl, deionised water.

1) Catalyst Preparation

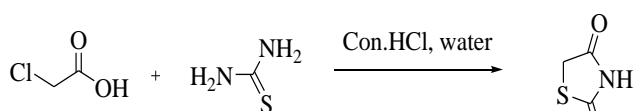
All pure single and mixed oxides were prepared by sol gel method following the procedure as mentioned in literature. Citric acid, Lanthanum, Cerium were taken in the 3:1 ratio and different mole ratios of Cr and Ba in the compounds are shown in Table I.

Sample Code	Ratios of Cr and Ba in the compound		
	M (La and Ce)	Cr	Ba
LCBO-1	1	1	0
LCBO-2	1	0.4	0.6
LCBO-3	1	0	1
CCBO-4	1	1	0
CCBO-5	1	0.4	0.6
CCBO-6	1	0	1

Table 1: Different mole ratios of Cr and Ba in the compounds

B. Synthesis of 2, 4-thiazolidinedione

In a 250ml three necked flask was placed a solution containing 56.4g of chloroacetic acid in 60 ml of water and 45.6g of thiourea dissolved in 60 ml of water. The mixture was stirred for 15 min to form a white precipitate accompanied by considerable cooling. To the contents of the flask, was then added slowly 60 ml of concentrated HCl from a dropping funnel. The flask was then connected with a reflux condenser and gentle heat applied to effect complete solution. Thereafter the reaction mixture was stirred and refluxed for 8-10 hr at 100-110°C. The mixture was cooled and product was filtered and washed with water to remove traces of hydrochloric acid. The product was purified by recrystallization from ethyl alcohol. The yield was 85%, m.p. 123-25°C.



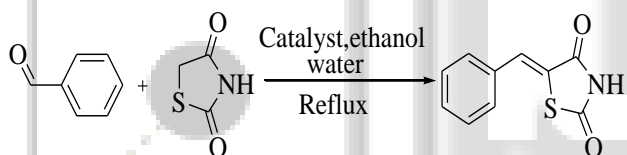
Scheme1 General reaction for synthesis of 2,4 - thiazolidinedione

C. Typical reaction procedure for synthesis of 5-Arylidene-2,4-Thiazolidinediones via Knoevenagel condensation¹⁴

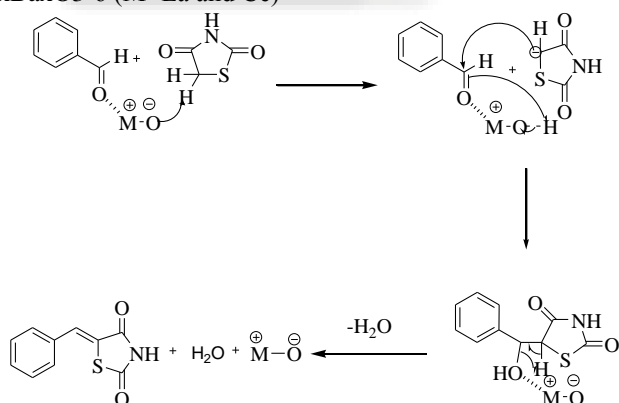
A mixture of 5 mmol benzaldehyde, 2, 4-thiazolidinedione and the catalyst were mixed in 20ml equimolar quantities of absolute ethanol and water in a 100 ml round bottom flask. This was loosely capped and heated in an oil bath at a temperature of 75°C. The progress of the reaction was monitored by TLC [Hexane: Ethyl acetate(7:3)]. After completion of the reaction, the solvent was evaporated to give a crude product for LCBO-2 and CCBO-5 good yields was purified by recrystallization.

Sample code	Reaction Time	Product Yield	Melting Point(°C)
LCBO-1	90mins	No reaction	-
LCBO-2	90mins	90%	242
LCBO-3	90mins	No reaction	-
CCBO-4	90mins	No reaction	-
CCBO-5	90mins	94%	246
CCBO-6	90mins	No reaction	-

Table 2: Synthesis of 5-benzylidene-thiazolidine-2,4-dione, catalyzed by LCBO-2 and CCBO-5 in ethanol: water at 75°C



Scheme 2: Knoevenagel reaction catalyzed by MCr1-xBaxO3-delta (M=La and Ce)



Scheme 3: Possible mechanism for Knoevenagel reaction catalyzed by MCr1-xBaxO3-delta (M=La and Ce)¹⁴

III. RESULTS AND DISCUSSION

A. Characterization of Catalysts

1) Powder X-Ray Diffraction Studies

The powder XRD patterns of LCBO-2 and CCBO-5 are shown in Fig. 1. The XRD patterns of LCBO-2 was compared and studied with the reported XRD patterns of LaCrO₃ and LaBaO_{3-delta}. The LaCrO₃ (JCPDS- 75- 0441) is simple cubic system with 'a' value 3.880Å and LaBaO_{3-delta}

(JCPDS -42- 1500) is an orthorhombic system with a = 10.66Å, b = 12.64Å and c = 3.703Å. The XRD pattern of LCBO-2 is not reported but it matches with the XRD patterns of LaCrO₃ and LaBaO_{3-delta} with slight variation. This is due to the presence of Cr and Ba present in LaCr_{1-x}Ba_xO_{3-delta}. Similarly the XRD pattern of CCBO-5 was compared and studied with the reported XRD patterns of CeCrO₃ and CeBaO_{3-delta}. The CeCrO₃ (JCPDS-75- 0289) is a cubic system with 'a' value 3.890Å and CeBaO_{3-delta} (JCPDS -22- 0074) is an orthorhombic system with a = 8.779Å, b = 6.214Å and c = 6.236Å. The XRD pattern of CCBO-5 is not reported but it matches with the XRD patterns of CeCrO₃ and CeBaO₃ with slight variation. This is due to the presence of Cr and Ba present in CeCr_{1-x}Ba_xO₃. The characteristic peaks corresponding to MCr_{1-x}Ba_xO_{3-delta} (M=La and Ce) confirms the presence of mixed metal oxide as a single phase in the compounds. Therefore, the uniqueness of these XRD patterns is a proof that the compounds LCBO-2 and CCBO-5 is of novel nature.

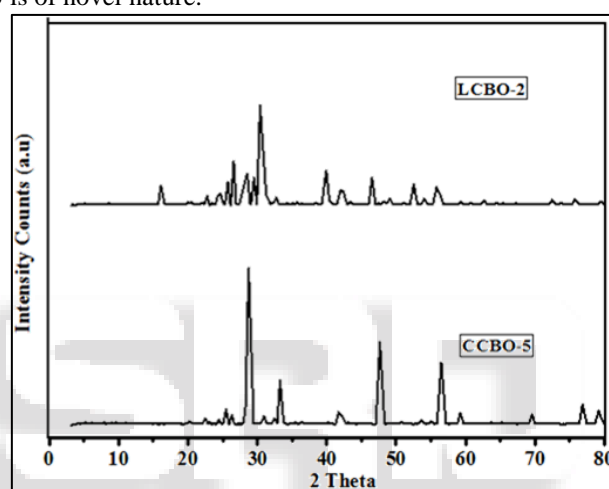
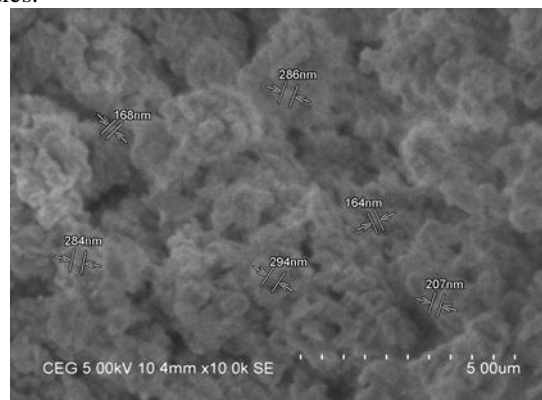


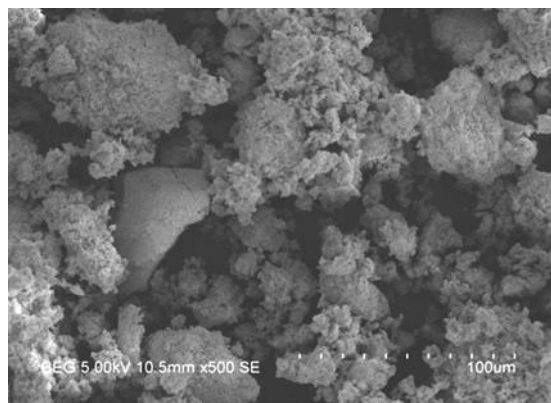
Fig. 1: XRD patterns of LCBO-2 and CCBO-5 compounds

2) Scanning Electron Microscopy (SEM)

On comparing the catalytic activity of mixed metal oxides from LCBO-1 to 3 and CCBO- 4 to 6, LCBO -2 and CCBO-5 exhibited higher catalytic activity and thereby the surface morphology of these two catalysts were studied. The SEM micrographs of LCBO-2 and CCBO-5 are shown in Fig.2. The particle size of LCBO-2 is found to be 160-300 nm whereas the particle size of CCBO-5 is 130-270 nm. Among LCBO-2 and CCBO-5, a larger grain size, decrease in particle size and a well-developed porosity is observed in CCBO-5 which plays a very important role in catalytic studies.



LCBO-2



CCBO -5

Fig. 2: SEM micrographs of LCBO-2 and CCBO-5 compounds

3) FT-IR Spectroscopy

The FT-IR spectra of LCBO-1 to LCBO-3 and CCBO-4 to CCBO-6 (Fig.3 and Fig.4) compounds exhibit a common broad band near 3400 cm^{-1} due to the OH stretching vibrations of free and hydrogen-bonded hydroxyl groups and an absorption at 1630 cm^{-1} is assigned to the deformative vibration of water molecules which is most probably due to water adsorption during the compaction of the powder specimens with KBr_{30,31}. The metal-oxygen stretching frequencies are in the range of 400–1000 cm^{-1} . The frequencies at 496.97 & 651.52; 858.54 & 873.84; 936.03 cm^{-1} corresponds to La-O, Ba-O and Cr-O in the compound. The frequencies at 413.54 & 635.34; 871.66 & 898.86; 934.68 cm^{-1} corresponds to Ce-O, Cr-O and Ba-O bonds which are existing as mixed metal oxides. On comparing the FT-IR spectrums of the compounds, it is evident that the bands near 3400 cm^{-1} and 1600 cm^{-1} indicates that the adsorption of water on the surface is more in LCBO-2 and CCBO-5 than in other compounds^{30,31}.

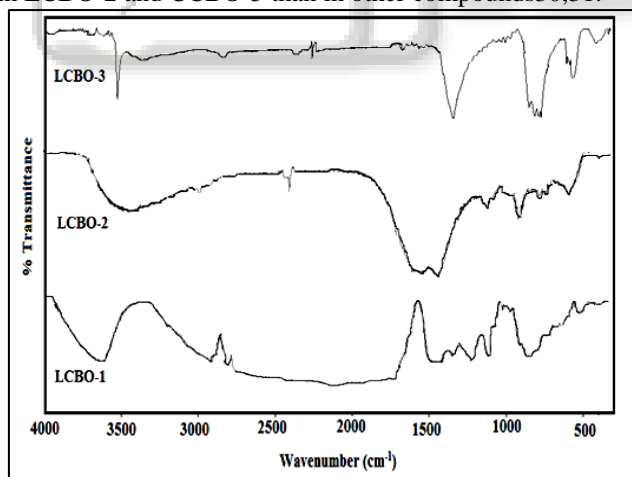


Fig. 3: FT-IR Spectra of LCBO-1 to LCBO-3 compounds

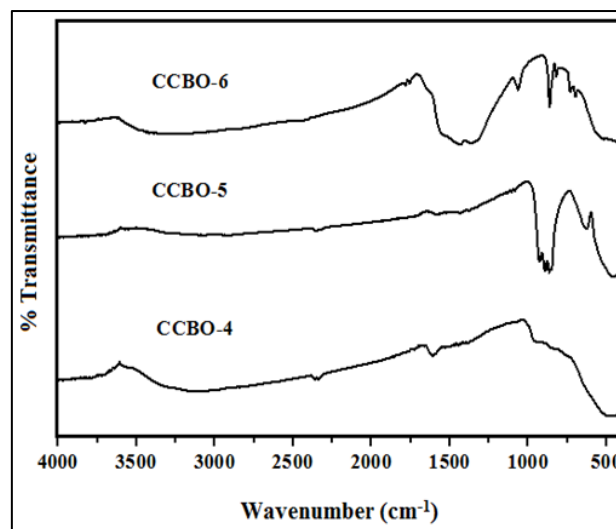


Fig. 4: FT-IR spectra of CCBO-4 to CCBO-6 compounds

4) Thermo Gravimetric Analysis (TGA)

Thermal analysis was done for LCBO-2 and CCBO-5 compounds before sintering the sample in order to study the complete decomposition of impurities present in the compound. It is shown in Fig.5, that the study of the thermograms of the compounds gives an idea for fixing the sintering temperature. It has been found that the compounds were stable above 750°C and hence, the sintering temperatures of the compounds were chosen as 800°C.

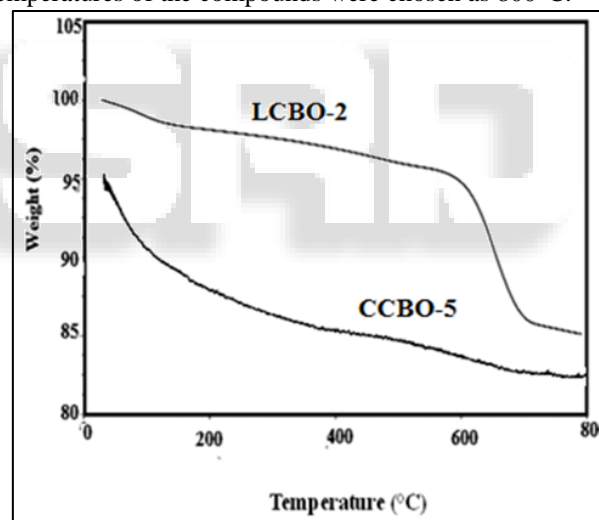


Fig. 5: Thermograms of LCBO-2 & CCBO-5 before sintering

B. Characterization of 5-benzylidinthiazolidine-2,4-dione

1) Analytical and Spectral Data Representation

5-Benzylidinthiazolidine-2,4-dione using LCBO-2: %; m.p 242°C; IR (KBr cm^{-1}): 1702, 1704 (C=O stretching), 2926 (aromatic stretching), 768, 698 (C-H bending), 1672, 1643 (C=C stretching vibrations within phenyl ring); ¹HNMR (DMSO-d₆, δ /ppm): 8.24 (1H, s, -NH), 7.61 (1H, s, C-H), 7.23 (5H, m, aromatic protons); MS (m/z, (relative abundance, %)): 235.26

5-Benzylidinthiazolidine-2,4-dione using CCBO-5: %; m.p 246 °C; IR (KBr cm^{-1}): 1702, 1704 (C=O stretching), 2928 (aromatic stretching), 768, 698 (C-H bending), 1672, 1643 (C=C stretching vibrations within phenyl ring); ¹HNMR (DMSO-d₆, δ /ppm): 8.68 (1H, s, -

NH), 7.58 (1H, s, C-H), 7.23 (5H, m, aromatic protons); MS (m/z, (relative abundance, %)): 235.26

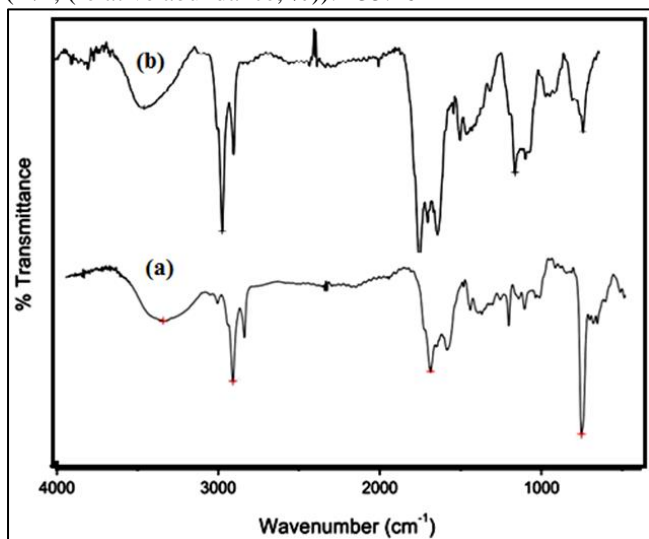


Fig. 6: FT-IR Spectra of 5-benzylidene-thiazolidine-2,4-dione in the presence of catalyst LCBO-2 b) CCBO-5

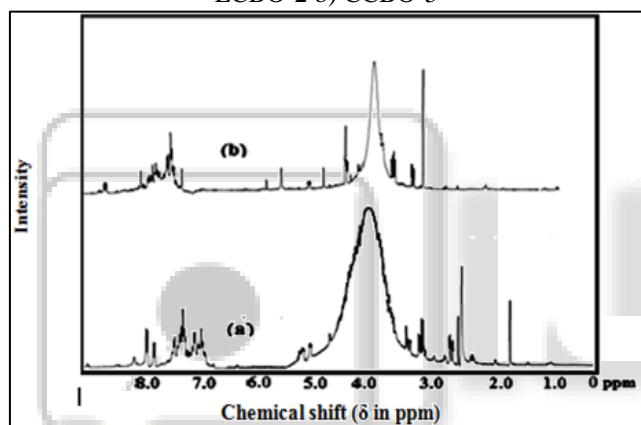


Fig. 7: ¹H NMR spectrum of 5-benzylidene-thiazolidine-2,4-dione LCBO-2 b) CCBO-5

IV. CONCLUSION

The catalytic potential of the catalysts were explored using the synthesis of 5-benzylidene-thiazolidine-2,4-dione. FT-IR spectroscopic studies showed the formation of 5-benzylidene-thiazolidine-2,4-dione with their characteristic vibrational frequencies and the corresponding ¹H NMR chemical shift values of the same using LCBO-2 and CCBO-5 were matched with the literature. The results revealed that, the LCBO-2 and CCBO-5 catalysts exhibited excellent catalytic performance in the condensation of benzaldehyde and 2,4-thiazolidinedione. The melting point of the compound matched with the literature with good yield for CCBO-5 than LCBO-2 which reveals very good application towards catalytic property in organic synthesis via Knoevenagel condensation

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