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Article

Catalytic properties of nanosized zinc aluminates prepared by green process using *Opuntia dillenii* haw plant extract

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ABSTRACT

Various nanosized zinc aluminate (ZnAl_2O_4) samples were prepared by a conventional and a microwave method both with and without using *Opuntia dillenii* haw plant extract, and were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), high resolution scanning electron microscopy (HRSEM), energy dispersion scanning (EDX), temperature dependent conductance measurements, thermoelectric power measurements, ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy, and photoluminescence spectroscopy. The formation of a pure ZnAl_2O_4 phase was confirmed by XRD and FT-IR. A change in morphology from nanosized plates to nanosized sheets with, respectively, the conventional and microwave heating methods was clearly shown by HRSEM. UV-Vis diffusion reflectance spectroscopy measured the band gaps of ZnAl_2O_4 nanosized plates and nanosized sheets as 3.5 and 3.9 eV, respectively. The synthesized ZnAl_2O_4 was single crystalline and has three photoluminescence emissions at 482, 528, and 540 nm. ZnAl_2O_4 nanosized sheets prepared by the microwave method showed higher catalytic activity for the oxidation of benzyl alcohol (85% conversion) than ZnAl_2O_4 nanosized plates prepared by the conventional method (60% conversion).

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1. Introduction

Transition metal oxides represent a broad class of materials that have been studied extensively for their interesting catalytic, electronic, and magnetic properties. They have a wide range of applications for their optical properties [1] and are used in solar cells [2]. They are commonly used in semiconductor and sensor technology as well as in heterogeneous catalysis [3–5]. Zinc aluminate (ZnAl_2O_4) with a spinel structure is of interest due to a combination of desirable properties such as high mechanical resistance, high thermal stability, low temperature sinterability, low surface acidity, fast diffusion, and high quantum yields. ZnAl_2O_4 is widely used as an electronic, ceramic,

catalytic material and is emerging as one of the best wide band gap semiconductor ($E_g = 3.8$ eV) for various optoelectronic applications [6–8]. In order to provide materials with the desired physical and chemical properties, the preparation of nano-structured ZnAl_2O_4 by different routes has become an essential part of research and development. There are many experimental procedures, including co-precipitation [9], sol-gel [10], hydrothermal [11], and pyrolysis of layered double hydroxide precursors [12], which have been developed for the preparation of ZnAl_2O_4 . These methods demand expensive materials and also generate toxic organic/inorganic intermediates. They involve laborious synthesis procedures. Nowadays, a restricted category of organic substances, e.g., citric acid, urea,

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glycine, oxalylhydrazide, carbohydrazide, tetraformtriazine, *N,N'*-diformylhydrazine, and hexamethylenetetramine have been used in combustion reactions as high temperature flame fuels [13]. Compared to the above methods, the microwave method has the advantages of cost-effectiveness, low processing temperature, shorter reaction time, and high purity and homogeneity of the final product [14].

Currently, there is a growing need to develop the synthesis of environmentally benign nano-materials that are free from toxic chemicals in the synthesis. Hence, biosynthetic methods employing plant extracts have drawn attention as a simple and viable alternative to chemical procedures. Bioremediation of toxic metals that makes use of microorganisms such as bacteria, plant extracts, and yeast by detoxification occurs by the reduction of the metal ions/formation of metal oxides [15]. These plants have been used in many medical applications and contains vitamins B1, B6, E, and A and also appreciable amounts of maleic, malonic, succinic, tartaric, and oxalic acid [16].

Nowadays, plant extracts have been used as both reducing and gelling agent for the synthesis of nano-materials [17]. The *Opuntia dillenii haw* plant extract is found mainly in the southern parts of India. Further determination of the sugars in the extract showed that 8%–10% of hexoses and 0.98% of pentoses are present. The major components of an *Opuntia dillenii haw* plant extract consist of a mixture of mucilage and pectin. Pectin is the most abundant polysaccharide from *Opuntia dillenii haw*. The plant extract plays not only a role as a fuel, but it also has a chemical coordinating action by capturing the involved metal ions in the amylose helix of the extract in well-defined sites and impeding the separation of ZnAl_2O_4 . The synthesis strategy described here provides a facile, environmentally benign and low cost approach for the synthesis of ZnAl_2O_4 spinel. There has been a report on ZnAl_2O_4 nanosized particles prepared by using sucrose as a chelating agent [18]. Therefore, sucrose should also act as an effective agent to prepare nanosized particles of ZnAl_2O_4 .

Synthesis using the *Opuntia dillenii haw* extract provides a simple, efficient, and green route for the synthesis of nanosized materials. The slow reduction along with the shape-directing effects of the constituents of the *Opuntia dillenii haw* extract plays a key role in the formation of nanosized structured metal oxides [19,20]. Ongoing efforts are devoted to improving soft chemical methods, which are considered efficient routes, to tailor the sizes and shapes of the nanosized metal oxide. An appealing aspect of this research field is the non-polluting and controlled synthesis of oxide materials at low cost and using natural compounds as raw materials and also as the active ingredients in the formation of nanosized metal oxide particles. A facile, cheap, and green approach is provided in the present study for the synthesis of ZnAl_2O_4 , which is a simple, fast, and economical combustion method using a plant extract, and it affords nanosized metal oxides with tunable sizes and morphologies.

In the present work, we report for the first time the synthesis of nanosized ZnAl_2O_4 by a microwave method using metal nitrates and an *Opuntia dillenii haw* (*O. dillenii haw*) plant extract

solution as the precursors. The prepared nanosized materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), high resolution scanning electron microscopy (HRSEM), energy dispersive X-ray analysis (EDX), diffuse reflectance spectroscopy (DRS), and photoluminescence (PL) spectroscopy. ZnAl_2O_4 samples prepared by the conventional and the microwave heating method both with and without using the plant extract were tested for their catalytic activity for the oxidation of benzyl alcohol.

2. Experimental

2.1. Preparation of *Opuntia dillenii haw* plant extract

Four grams of thoroughly washed *Opuntia dillenii haw* leaves (collected from local agricultural fields in Chennai, Tamil Nadu) were finely cut, and the gel obtained was dissolved in 12 ml of deionized water and stirred for 45 min to obtain a clear solution. The resulting extract was used as the *Opuntia dillenii haw* plant extract solution.

2.2. Preparation of ZnAl_2O_4 by conventional (CH) and microwave heating (MH) methods

$\text{Zn}(\text{NO}_3)_2$ (99%, Merck Chemicals, India) and $\text{Al}(\text{NO}_3)_3$ (98%, Merck Chemicals, India) were dissolved in deionized water and then mixed with the *Opuntia dillenii haw* extract solution under constant stirring for 5 h at room temperature until a clear transparent solution was obtained. The molar ratio of Zn/Al was kept at 1:2. The solution was dried in an air oven at 120 °C for 3 h. The powders were then sintered at 400 °C at a heating rate of 5 °C/min for 3 h in a muffle furnace and the sample obtained was labeled as ZnAC_1 (prepared by conventional heating).

The above clear transparent solution was placed in a domestic microwave oven (2.45 GHz, 800 W) for 10 min. Initially, the solution boiled and underwent dehydration followed by decomposition with the evolution of gases. This vaporized the solution and it left behind a solid, which was labeled as ZnAM_1 (prepared by microwave heating).

For comparison purpose, the ZnAl_2O_4 samples were also prepared without using the plant extract by both conventional and microwave heating and were labeled as ZnAC_2 and ZnAM_2 , respectively. By using the microwave, a temperature of 400 °C was created inside the oven [21], and hence no pretreatment was necessary for the microwave treated samples. From the XRD, FT-IR, and EDX results, it was confirmed that only the ZnAl_2O_4 phase was formed without any other impurity, which in turn also confirmed the complete removal of the template for the microwave treated sample.

Metal nitrate salts and the plant extract (used in the mixture) were chosen by considering the total reducing and oxidizing agent valences of the raw materials. These were quantified in equivalence of NO_x reduction (N_2O to N_2). At low temperatures and as a pure phase, fully crystallized ZnAl_2O_4 was obtained from both the compositions during the microwave method without the need for further calcination at higher tem-

perature. This is due to the fact that the heating mechanism in a microwave oven is fundamentally different from the heating in a conventional furnace. Thermal conduction in the conventional furnace takes place through radiation and the convectional heating is by the transfer of thermal energy to inside the sample. However, microwave heating involves the absorption of the microwave field followed by the conversion of electromagnetic energy into the thermal energy. In this technique, there is no thermal conduction process involved. The heat is generated internally within the sample [22].

2.3. Characterization of ZnAl_2O_4 nanosized structures

The structural studies were carried out using a Philips X'pert diffractometer for $2\theta = 10^\circ$ – 80° using $\text{Cu } K_\alpha$ radiation at $\lambda = 0.154$ nm. A Perkin Elmer infrared spectrophotometer was used for the determination of the surface functional groups. Morphological studies and EDX analysis were performed using a JOEL JSM6360 high resolution scanning electron microscope. The samples were coated with gold by a gold sputtering device for better visibility of the surface morphology. Electrical conductance was studied by making samples in pellet form employing a pressure of about 1 GPa at room temperature. The measurements were made from 120 to 300 °C by the two-probe method. The pellets were well polished, and the two surfaces of each pellet were coated with silver paste to ensure electrical contacts. The samples were electrically connected to a dc power supply and a Keithley 614 digital electrometer in series. The activation energy of the samples was calculated by using the Arrhenius expression $I = I_0 \exp(-E_a/kT)$, where I is the current, E_a is the activation energy, k is the Boltzmann constant, and T is the temperature.

The thermopower or Seebeck coefficient of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material. The p- or n-type semiconductivity of the composites was confirmed by measuring the thermoelectric force of the composites. The thermoelectric or Seebeck coefficient (θ) of the composites was calculated using the formula $\theta = \Delta E / \Delta T$, where ΔE is the thermo-emf produced across the sample due to the temperature difference ΔT [23].

The diffuse reflectance UV-Visible spectra (DRS) of the nanosized materials were recorded using a Cary100 UV-visible spectrophotometer. The emission properties were recorded using a Varian Cary Eclipse fluorescence spectrophotometer.

The N_2 adsorption-desorption isotherms of the samples were measured using an automatic adsorption instrument (Quantachrome Quadrawin gas sorption analyzer) for the determination of surface area and total pore volume.

2.4. Catalytic test

The oxidation of benzyl alcohol was carried out in a batch reactor operated under atmospheric conditions. H_2O_2 (10 mmol) was added along with 1 g of the nanosized zinc aluminate (ZnAC_1 , ZnAC_2 , ZnAM_1 , and ZnAM_2). The contents were heated to 80 °C in an acetonitrile medium for 10 h in a

three-necked round-bottom flask equipped with a reflux condenser and thermometer. The oxidized products after the catalytic reaction were collected and studied using an Agilent GC. The column used for the study was DB wax column (capillary column) of length 30 mm, and He was used as the carrier gas.

3. Results and discussion

3.1. XRD studies

To study the crystallization process and for phase identification, powder XRD analyses were performed on the various ZnAl_2O_4 samples. As shown in Fig. 1, the absence of the characteristic peaks of ZnAl_2O_4 over ZnAC_2 and ZnAM_2 samples confirmed that the ZnAl_2O_4 phase was not formed, but ZnAl_2O_4 cubic phase was present in ZnAC_1 and ZnAM_1 catalysts.

The observed diffraction peaks over ZnAC_1 samples at $2\theta = 18.96^\circ$, 31.21° , 36.77° , 44.35° , 55.65° , 59.34° , and 65.23° are associated with the (111), (220), (311), (400), (422), (511), and (440) planes, respectively. These planes are associated with the d -spacing values of 4.67, 2.86, 2.44, 2.02, 1.63, 1.55, and 1.43 Å, respectively, which can be readily assigned to the cubic phase of ZnAl_2O_4 (JCPDS file no. 74-1138). No peak of any other phase was detected. Over ZnAM_1 catalyst, the observed diffraction peaks at $2\theta = 19.23^\circ$, 31.79° , 36.78° , 44.71° , 55.01° , 59.54° , and 65.16° are associated with the (111), (220), (311), (400), (422), (511), and (440) planes, respectively. These planes are associated with d -spacing values of 4.66, 2.85, 2.43, 2.02, 1.65, 1.55, and 1.42 Å, respectively, which is assigned to the cubic phase of ZnAl_2O_4 (JCPDS file no. 71-0968).

Further observations revealed that both ZnAC_1 and ZnAM_1 prepared using the plant extract had sharp peaks, indicating good crystallinity. The diffraction peaks for ZnAM_1 were slightly broadened due to the smaller crystallite size, which may be due to the fact that ZnAl_2O_4 was prepared in a short time of 10 min by means of a domestic microwave oven operated at 2.45 GHz and 800 W without any post-annealing. Furthermore, no other crystalline diffraction peaks were present in the XRD pattern, indicating the formation of highly pure ZnAl_2O_4 . The average crystallite sizes for ZnAC_1 and ZnAM_1 calculated using Scherrer formula were 7.4 and 6.2 nm, respectively.

Fig. 1. XRD patterns of various ZnAl_2O_4 samples.

tively. Thus by using the microwave method, the average crystallite size of the nanosized zinc aluminate was reduced.

3.2. FT-IR results

Figure 2 shows the FT-IR spectra of different ZnAl_2O_4 samples. The characteristic spinel bands of ZnAl_2O_4 were not observed over ZnAC_2 and ZnAM_2 . This confirmed the absence of the formation of ZnAl_2O_4 . However, ZnAC_1 and ZnAM_1 samples exhibited a common broad band near 3500 and 1600 cm^{-1} , which is due to the $-\text{OH}$ stretching vibrations and deformative vibration of water molecules. A broad band at 3465 cm^{-1} can be attributed to the stretching vibration of $-\text{OH}$ groups in the brucite-like layers and interlamellar water molecules. The broadening of the band was attributed to hydrogen bond formation. The band observed near 1643 cm^{-1} was assigned to the bending vibration of interlayer water molecules [25], which was probably due to the water absorption by the samples during the compaction of the powder specimen with KBr [26].

The spectra of all the samples showed a peak at 1300 cm^{-1} assigned to the $\text{Al}-\text{O}$ stretching vibration. The metal-oxygen stretching frequencies in the range $400\text{--}1000\text{ cm}^{-1}$ are related to the nanosized ZnAl_2O_4 [27]. The absorption peaks of ZnAC_1 underwent a red shift for H_2O (from 3505 to 3495 cm^{-1} and from 1634 to 1630 cm^{-1}) and became weaker compared with ZnAM_1 , indicating a reduction in the degree of binding of H_2O on the surface of larger crystallites, which was due to less atoms/surface for binding with H_2O molecules [27,28].

The metal oxygen stretching frequencies in the range of $500\text{--}900\text{ cm}^{-1}$ are associated with the vibrations of aluminum-oxygen and metal-oxygen-aluminum bonds for ZnAC_1 and ZnAM_1 . Two sharp bands observed at 924 and 525 cm^{-1} are characteristic of ZnAl_2O_4 spinels. Thus, it was confirmed that for ZnAl_2O_4 formation, plant extract is needed during the preparation from the nitrate mixture using urea as the fuel.

3.3. HR-SEM studies

The morphologies of the nanosized ZnAl_2O_4 samples were investigated by HR-SEM. Figure 3(a, b) shows the formation of nanosized plates for ZnAC_1 , and Fig. 3(c, d) shows the for-

Fig. 2. FT-IR spectra of various ZnAl_2O_4 samples.

Fig. 3. HR-SEM images of ZnAl_2O_4 samples. (a, b) ZnAC_1 ; (c, d) ZnAM_1 ; (e) ZnAC_2 ; (f) ZnAM_2 .

mation of nanosized sheets for ZnAM_1 . Thus, it is clear that the morphology and nanosized structures can be varied based on the method of preparation [29]. In the present study, the change in morphology from nanosized plates to nanosized sheets was obtained by changing the method of preparation from conventional to microwave heating. Figure 3(e, f) shows the HRSEM images of ZnAC_2 and ZnAM_2 , which clearly showed that there was no defined or specific morphology formed, and hence it confirmed the absence of ZnAl_2O_4 phase formation.

In the case of ZnAM_1 , the hot spots formed due to the microwave irradiation of the powder surface stimulate particle aggregation in specific preferential directions to form the nanosized sheets morphology. Generally, in a conventional heating system, energy is transmitted to the constituents from the surface through convection, conduction, and radiation of heat. In contrast, in a microwave heating system, there is heating inside the materials, which then spreads to the surface [30,31]. Zinc aluminate is an excellent microwave adsorptive material and hence it readily heats up to the desired temperature much faster than in the conventional heating method. The observed slight difference in particle size value as estimated from XRD and HRSEM may be due to some structural disorder and strain in the lattice that resulted from the different ionic radii and/or clustering of the nanosized materials [32].

The presence of pure ZnAl_2O_4 was confirmed by EDX shown in Fig. 4. It showed that both ZnAC_1 and ZnAM_1 prepared by conventional and microwave heating, respectively, were composed of Zn, Al, and O, indicating the presence of the pure ZnAl_2O_4 phase without any other impurity, in agreement with the XRD analysis. The peaks at $2.1\text{--}2.2\text{ keV}$ in the EDX spectra

Fig. 4. EDX spectra of ZnAC1 (a) and ZnAM1 (b) samples.

were due to gold, which was coated on the samples before recording the SEM image.

3.4. Electrical conductance studies

To test the ohmic contact of the electrodes, room temperature electrical conductance measurements of the samples were carried out. The temperature dependence of electrical conductance carried out in the temperature range 120–300 °C suggested that the current increased with the increase in temperature (T). From the Arrhenius plot of $\ln(I/I_0)$ vs $1/T$, the activation energy was calculated to be 0.24 eV for ZnAC₁ and 0.21 eV for ZnAM₁. The result also confirmed that the samples were semiconductors. The activation energy for electrical conduction in polycrystalline materials generally involves the combination of the energy required to raise the carriers from the dominant levels to their corresponding transport bands and the energy required to create the carriers from the dominant levels [33].

3.5. Thermoelectric power (TEP) measurements

The potential difference ΔV across the pelleted sample due to a temperature difference ΔT was measured. The cations on the A site as well as those on the B site contribute to the Seebeck coefficient, which showed n-type conduction for both the samples where the electrons are the majority charge carriers.

3.6. DRS studies

The optical diffuse-reflectance spectral properties of the prepared nanosized ZnAl₂O₄ samples were studied by DRS. As shown in Fig. 5, over ZnAC₂ and ZnAM₂ prepared without plant extract there was no optical absorption edge observed, indicating the absence of the formation of ZnAl₂O₄. As for ZnAC₁ and ZnAM₁ samples, the maximum reflectance of 98% was observed in the range of 290–520 nm due to absorption by the ZnAl₂O₄ nanosized material. DRS gives the direct band to band (valance band to conduction band) transitions from which the band gap can be calculated. For analysis purposes, the diffuse-reflectance (R) of the sample [34,35] can be related to

Kubelka-Munk function $F(R)$ by the relation $F(R) = (1-R)^2/2R$.

The energy intercept of a plot of $[F(R) \times hv]^2$ versus hv gives E_g for a direct allowed transition when the linear region is extrapolated to the zero ordinate. The optical absorption edge was observed at a wavelength of 380 nm, which corresponds to the band gap energy of 3.5 eV for ZnAC₁. The observed band gap energy of the ZnAM₁ was 3.9 eV corresponding to a wavelength of 360 nm. These results showed that the band gap energy of ZnAl₂O₄ prepared by the microwave method using the plant extract had shifted to a higher energy value. This increase in the band gap may be associated with the decrease in oxygen content due to the microwave heating.

3.7. PL studies

A photoluminescence spectrum is used to determine defect related transitions and oxygen vacancies. The density of defects and surface states may change with the formation conditions, morphology, and size of the crystallites. It is therefore interesting to examine the different defect energy levels. As shown in Fig. 6, ZnAC₂ and ZnAM₂ prepared without the plant extract do not show any significant emission peak, thus showing the absence of formation of ZnAl₂O₄. For ZnAC₁ and ZnAM₁ samples prepared using the plant extract, emission peaks were observed at ~ 482, 528, and 540 nm, which were due to in-

Fig. 5. Diffuse reflectance spectra of ZnAl₂O₄ samples. (1) ZnAC₂; (2) ZnAC₁; (3) ZnAM₂; (4) ZnAM₁.

Fig. 6. Photoluminescence spectra of ZnAC₂ (1), ZnAC₁ (2), ZnAM₂ (3), and ZnAM₁ (4) samples.

tra-band gap defects like oxygen vacancies. These defects provide donor levels near the conduction band edge of the zinc aluminates. However, the emission peaks were considerably blue shifted to 492, 530, and 545 nm for ZnAM₁ due to the reduction in the average crystallite size, which was in good agreement with the XRD data. The wavelength of ZnAM₁ was longer (blue shift more) than that of ZnAC₁ because of the reduction in the crystallite size (ZnAC₁ 7.4 nm and ZnAM₁ 6.2 nm), which in turn is responsible for quantum confinement effect [36].

There was a significant increase in the intensity of the signal at 530 and 545 nm for ZnAM₁. This may be due to an increase in the surface defect sites of ZnAl₂O₄. During microwave heating, heat is generated internally within the material instead of originating from external heating sources, and hence an inverted temperature gradient is produced. The interionic distance between the two species is the determining factor for the efficiency of the observed energy transfer process. The emission spectra of both ZnAC₁ and ZnAM₁ also showed emission peaks between 480 and 540 nm generated by the lattice host ZnAl₂O₄ [37,38].

3.8. N₂ adsorption isotherms

The N₂ adsorption isotherm values at −196 °C for ZnAC₁ and ZnAM₁ are given in Table 1. The ZnAC₁ sample possessed a surface area of 41.87 m²/g, whereas for ZnAM₁, it was increased considerably to 66.54 m²/g. The pore volume of ZnAC₁ and ZnAM₁ were 0.16 and 0.12 cm³/g, respectively. Similarly, the average pore diameter of ZnAM₁ was increased to 97.33 Å, but for ZnAC₁, it was only 94.19 Å. During the reaction process, molecular dipoles were induced to oscillate by the microwave.

Table 1

BET surface area, average pore diameter, and pore volume of ZnAl₂O₄ samples prepared using the plant extract.

Sample	BET surface area (m ² /g)	Average pore diameter (Å)	Pore volume (cm ³ /g)
ZnAC ₁	41.87	94.19	0.16
ZnAM ₁	66.54	97.33	0.12

The oscillation caused a higher rate of molecular collision, which in turn generated more heat. Therefore, the temperature distribution was homogeneous and transferred to the material's interior, leading to an explosion reaction followed by the vigorous evolution of gases to form nanosized zinc aluminates. Also, during the microwave process, the heating is usually achieved within a few minutes, which gives rapid phase formation and a fine particle size. Also, in microwave synthesis, the reaction time is short and the equipment is not complex, making this technique very attractive. Therefore, it is possible to control both kinetic and thermodynamic factors of the chemical reactions using microwave in the combustion process. Hence, this microwave method offers several advantages like forming a chemically homogeneous composition, simple reaction process, low energy loss, inexpensive, nontoxic, high production efficiency and high purity products [39].

3.9. Catalytic oxidation of benzyl alcohol

The catalytic oxidation of benzyl alcohol was studied using ZnAl₂O₄ nanosized plates and nanosized sheets to investigate its performance as a catalyst. One gram of prepared nanosized ZnAC₁ and ZnAM₁ along with the oxidant H₂O₂ (10 mmol) in an acetonitrile medium was placed in a batch reactor. The contents were heated at 80 °C for 10 h. When the oxidized product was analyzed using GC, the conversion of benzyl alcohol reached a maximum of 85% for ZnAM₁, whereas for ZnAC₁, the conversion was only 60% with 100% selectivity. In our previous studies, we have reported the preparation of nanosized copper aluminate spinel by a modified sol-gel method using ethylenediamine, in which the conversion of benzyl alcohol to benzaldehyde was 100% [40]. In the present work, *Opuntia dillenii* haw plant extract was used to prepare nanosized ZnAl₂O₄, and the performance of the ZnAl₂O₄ catalysts were compared with those of the earlier catalysts [41–43] in Table 2. The result showed that the present ZnAl₂O₄ catalyst gave a higher yield with good selectivity for benzaldehyde as compared to the previous ones. Also, the method of preparation in the present study is very simple and economic.

Table 2

Comparison of the catalysts prepared in the present study with those reported in the literature for oxidation of benzyl alcohol.

Catalyst	Conversion (%)	Selectivity (%)
ZnAC ₁	60.0	100
ZnAM ₁	85.0	100
[Cu((Benzyl) ₂ Bzo[14]aneN ₆)] ²⁺ -NaY ^a [41]	74.5	100
	75.7	100
	74.2	100
[Cu(Me ₄ (NO ₂) ₂ Bzo[14]tetraeneN ₄)]-NaY ^a [42]	82.3	100
	83.1	100
	81.0	100
[Cu(Me ₄ [16]aneN ₈)](ClO ₄) ₂ ^a [43]	53.5	92
	56.5	98
	50.1	95

^a Conditions: benzyl alcohol 5 ml, benzene 10 ml, H₂O₂/benzyl alcohol (molar ratio) = 2, 70 °C, 10 h, and the concentrations were determined using internal standard procedure.

Table 3

Effect of oxidant and catalyst on the catalytic oxidation of benzyl alcohol.

Entry	Catalyst	Oxidant	Yield (%)
1	ZnAC ₁	—	3.0
2	ZnAM ₁	—	4.5
3	—	H ₂ O ₂	2.5
4	ZnAC ₂	H ₂ O ₂	0.8
5	ZnAM ₂	H ₂ O ₂	1.0

Reaction conditions: catalyst ZnAl₂O₄ 1 g, benzyl alcohol 10 mmol, acetonitrile 10 mmol, H₂O₂ 10 mmol, 80 °C, 10 h.

In the absence of the oxidant, ZnAC₁ showed 3.0% yield of benzaldehyde, and ZnAM₁ showed 4.5% of yield (Table 3). In the absence of a catalyst, only 2.5% yield of benzaldehyde was obtained using the oxidant H₂O₂. Thus, it was confirmed that both the catalyst and the oxidant were important to give high yield. The samples prepared without the plant extract gave very low yields of benzaldehyde, i.e., ZnAC₂ and ZnAM₂ gave only 0.8% and 1.0% of benzaldehyde as the product. Hence, the plant extract is important in forming the nanosized ZnAl₂O₄ phase, which in turn is active for the catalytic oxidation reaction.

A comparison of the data also indicated the differences between the three complexes and the zinc aluminate and their performance in the benzyl alcohol-to-benzaldehyde oxidation. Transition metal complexes always exhibit low activity and selectivity. They are also difficult to separate from the reaction medium, which makes their reuse difficult, and it contaminates the reaction products. A heterogeneous catalyst like zinc aluminate is non-toxic and environmentally friendly and has excellent catalytic performance.

3.10. Reusability studies

The reusability performance of ZnAC₁ and ZnAM₁ for 5 cycles of batch oxidation reaction is illustrated in Fig. 10. After the catalytic reaction, ZnAC₁ or ZnAM₁ was filtered and washed

Fig. 10. Reusability of ZnAC₁ (a) and ZnAM₁ (b) catalysts in the oxidation of benzyl alcohol.

with ethanol several times, then dried at 120 °C in an air for 4 h to remove the ethanol. It was used for five consecutive runs under identical conditions. In these runs, the conversions and selectivities remained at almost the similar level to that of the first run. ZnAl₂O₄ was found to have no appreciable loss of activity in the recycle tests. Thus, it was proved that the catalyst has a stable structure during the catalysis.

4. Conclusions

Zinc aluminate spinel samples were prepared using conventional heating (ZnAC₁) and microwave heating (ZnAM₁) using an *Opuntia dillenii* haw extract solution and compared with the ZnAC₂ and ZnAM₂ prepared without using the plant extract. Microwave heating achieved the same results within a shorter time compared to the conventional heating method. The average crystallite size for ZnAC₁ and ZnAM₁ prepared using the plant extract was 7.4 and 6.2 nm, respectively. The formation of the ZnAl₂O₄ phase was confirmed by XRD, SEM, and FT-IR results. The room temperature electrical conductivity studies confirmed that the prepared nanosized zinc aluminates are semiconductors. The activation energy was 0.24 and 0.21 eV for ZnAC₁ and ZnAM₁, respectively. TEP results showed that both the samples exhibit n-type conduction with electrons as the major charge carriers. Absorption bands in the visible region showed band gap values of 3.5 and 3.9 eV, respectively, for ZnAC₁ and ZnAM₁. The nanosized zinc aluminates were used as a catalyst for the conversion of benzyl alcohol with a conversion efficiency of 60% for ZnAC₁ and 85% for ZnAM₁. Hence a simple, rapid bio-synthetic green method using *Opuntia dillenii* haw has been developed to synthesize ZnAl₂O₄ nanosized structures with tunable optical and better catalytic properties.

References

- [1] Kim D K, Zhang Y, Kehr J, Klason T, Bjelke B, Muhammed M. *J Magn Magn Mater*, 2001, 225: 256
- [2] O'Regan B, Gratzel M. *Nature*, 1991, 353: 737
- [3] Stobbe E R, de Boer B A, Geus J W. *Catal Today*, 1999, 47: 161
- [4] Tzing W S, Tuan W H. *J Mater Sci Lett*, 1996, 15: 1395
- [5] Bouropoulos N, Tsiaoussis I, Pouloupoulos P, Roditis P, Baskoutas S. *Mater Lett*, 2008, 62: 3533
- [6] Kumar K, Ramamoorthy K, Koinkar P M, Chandramohan R, Sankaranarayanan K. *J Nanoparticle Res*, 2007, 9: 331
- [7] Phani A R, Passacantando M, Santucci S. *Mater Chem Phys*, 2001, 68: 66
- [8] Moreno E M, Zayat M, Morales M P, Serna C J, Roig A, Levy D. *Langmuir*, 2002, 18: 4972
- [9] Valenzuela M A, Jacobs J P, Bosch P, Reijne S, Zapata B, Brongersma H H. *Appl Catal A*, 1997, 148: 315
- [10] Valenzuela M A, Bosch P, Aguilar-Rios G, Montoya A, Schifter I. *J Sol Gel Sci Technol*, 1997, 8: 107
- [11] Zawadzki M, Wrzyszczy J. *Mater Res Bull*, 2000, 35: 109
- [12] Zou L, Li F, Xiang X, Evans D G, Duan X. *Chem Mater*, 2006, 18: 5852
- [13] Dhak D, Pramanik P. *J Am Ceram Soc*, 2006, 89: 1014
- [14] Manikandan A, Judith Vijaya J, John Kennedy L, Bououdina M. *Ceram Int*, 2013, 39: 5909
- [15] Mann S. *Nature*, 1993, 365: 499

Graphical Abstract

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Catalytic properties of nanosized zinc aluminates prepared by green process using *Opuntia dillenii* haw plant extract

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ZnAl_2O_4 is prepared by using the *Opuntia dillenii* haw plant extract. Structural and optical properties are studied. Higher conversion and better selectivity for benzyl alcohol is achieved.

- [16] Abd El-Razek F H, Hassan A A. *Aust J Basic Appl Sci*, 2011, 5: 356
- [17] Galati E M, Pergolizzi S, Miceli N, Monforte M T, Tripodo M M. *J Ethnopharmacol*, 2002, 83: 229
- [18] Khaledi A G, Afshar S, Jahromi H S. *Mater Chem Phys*, 2012, 135: 855
- [19] Satoh E, Ishii T, Shimizu Y, Sawamura S-I, Nishimura M. *Exp Biol Med*, 2001, 226: 577
- [20] Boubekri R, Beji Z, Elkabous K, Herbst F, Viau G, Ammar S, Fiévet F, von Bardeleben H J, Mauger A. *Chem Mater*, 2009, 21: 843
- [21] Selvam N C S, Manikandan A, Kennedy L J, Vijaya J J. *J Colloid Interface Sci*, 2013, 389: 91
- [22] Thomas P, Sathapathy L N, Dwarakanath K, Varma K B R. *Bull Mater Sci*, 2007, 30: 567
- [23] Patil L A, Patil D R. *Sens Actuators B*, 2006, 120: 316
- [24] Becheri A, Dürr M, Lo Nostro P, Baglioni P. *J Nano particle Res*, 2008, 10: 679
- [25] Klopogge J T, Frost R L. *J Solid State Chem*, 1999, 146: 506
- [26] Vijaya J J, Kennedy L J, Sekaran G, Nagaraja K S. *Mater Res Bull*, 2008, 43: 473
- [27] Foster M, Furse M, Passno D. *Surf Sci*, 2002, 502-503: 102
- [28] Lu J S, Yang H B, Liu B B, Zou G T. *Mater Res Bull*, 1999, 34: 2109
- [29] He Y J. *Mater Lett*, 2006, 60: 3511
- [30] Ortega Y, Fernández P, Piqueras J. *J Cryst Growth*, 2009, 311: 3231
- [31] Thostenson E T, Chou T W. *Composites Part A*, 1999, 30: 1055
- [32] Serpone N, Lawless D, Khairutdinov R. *J Phys Chem*, 1995, 99: 16646
- [33] Manikandan A, Judith Vijaya J, John Kennedy L, Bououdina M. *J Mol Struct*, 2013, 1035: 332
- [34] Sundaram R, Raj E S, Nagaraja K S. *Sens Actuators B*, 2004, 99: 350
- [35] Amaranatha Reddy D, Murali G, Vijayalakshmi R P, Reddy B K, Sreedhar B. *Cryst Res Technol*, 2011, 46: 731
- [36] Liu J Y, Lu Y M, Liu J, Yang X Y, Yu X B. *J Alloys Compd*, 2010, 496: 261
- [37] Hao Y F, Meng G W, Ye C H, Zhang X R, Zhang L D. *J Phys Chem B*, 2005, 109: 11204
- [38] Barros B S, Melo P S, Kiminami R H G A, Costa A C F M, Sá G F, Alves S Jr. *J Mater Sci*, 2006, 41: 4744
- [39] Monticone S, Tufeu R, Kanaev A V. *J Phys Chem B*, 1998, 102: 2854
- [40] Kumar R T, Suresh P, Selvam N C S, Kennedy L J, Vijaya J J. *J Alloys Compd*, 2012, 522: 39
- [41] Salavati-Niasari M, Davar F. *Inorg Chem Commun*, 2006, 9: 304
- [42] Salavati-Niasari M. *J Mol Catal A*, 2006, 245: 192
- [43] Salavati-Niasari M, Ganjali M R, Norouzi P. *Transition Met Chem*, 2007, 32: 1