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# Submicron ZnO raspberries as effective catalysts for Fries rearrangement

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*o*-Xylene-in-water emulsion droplets have been exploited as soft templates for the synthesis of submicrometer-sized raspberry-like ZnO morphologies. The optical properties, structure and morphology of the microstructures have been characterised by absorption and fluorescence spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction and selected area electron diffraction analysis. It has been found that the microstructures could act as an environmentally benign and cost-effective alternative to conventional Lewis acid catalysts for the illustrious Fries rearrangement of *o*-methylphenyl acetate to 3-methyl-4-hydroxyacetophenone, employed as the model reaction and which has been probed by NMR spectroscopic studies.

## 1. Introduction

In recent years, self-assembly of nanoscale objects has pioneered a facile strategy to design micrometer-sized hollow structures that have attracted increasing attention because of their specific morphology, fascinating properties and wide applications in physics, chemistry, biology and materials science.[1] Amongst the three different approaches currently explored to effect ordering of nanoparticles by self-assembly processes, liquid–liquid interfaces offer an important alternative scaffold for the organisation of nanoscale substances into higher-order assemblies.[2] Although catalysis is a mature field, it possesses a vital role in chemical-based industries, accounting for about a quarter of the world's gross domestic product.[3] The field of nanocatalysis has undergone an exponential growth during the past decade.[4] This is due to the fact that particles in the nanometer size regime inherently provide a high surface-to-volume ratio, making them attractive candidates for catalysis.[5] The application of transition metal oxides in the nanometer size regime in catalysis has become fascinating because they manipulate the surface activity of the metal and hence, the catalysis at the nanoscale, imperting activity and selectivity to heterogeneous catalysis.[6] The benefit of using heterogeneous catalysis is the facile recovery and recyclability of the catalyst materials and thus, meet the modern requirements for green catalysts.[7] Amongst the transition metal oxides, zinc oxide (ZnO) at the nanoscale dimension have attracted immense interest due to its direct wide band gap (3.37 eV), high exciton binding energy (60 meV) and the opportunity to vary its properties by morphological tuneability provides new chemical insights from an old material.[8] In addition to these physicochemical properties, numerous environmental advantages, such as, non-toxicity, corrosion resistance, recyclability and easy disposal of the material have encouraged its application as greener catalysts in a diverse range of catalytic and photocatalytic reactions.[8] In the early 1900s, Fries and co-worker reacted phenolic esters of acetic and chloroacetic acid with aluminum chloride and isolated a mixture of *o*- and *p*-acetyl- and chloroacetyl phenols and in general, the conversion of phenolic esters to the corresponding *o*- and/or *p*-substituted phenolic ketones and aldehydes, in the presence of Lewis or Brønsted acids has been recognized as the Fries rearrangement.[9] Different types of Fries rearrangement have been reported so far in the literature using varieties of catalyst materials. For example, Paul and colleague[10] has shown that zinc powder efficiently catalyzes the selective Fries rearrangement of acetylated phenols under microwave heating or with conventional heating in the presence of *N*,*N*-dimethylformamide and in some cases, it was seen that different products were obtained using microwave heating and conventional heating. Krishnamurthy and co-authors[11] reported a convenient way to carry out the Fries rearrangement of phenolic esters to hydroxyphenyl ketones by refluxing in nitrobenzene in the presence of Nafion-H, a solid superacidic resin sulfonic acid catalyst. Belokon and group[12] reported $TiCl_4$-catalysed Fries rearrangement *via* regioselective acylation of *p*-hydroxy [2.2] *para*-cyclophane to *o*-acylhydroxy [2.2] *para*-cyclophanes. Dupont and colleagues[13] have optimized the Fries rearrangement with methanesulfonic acid to give *p*-hydroxyacetophenone with high conversion and selectivity. However, the Fries rearrangement of aryl esters, a special case of Friedel–Craft

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acylation provides an important route for the synthesis of aromatic hydroxyl aryl ketones which are important intermediates for several pharmaceuticals, such as, paracetamol, salbutamol *etc.* However, the use of aluminium chloride can lead to violations of several principles of green chemistry through the release of hazardous substances in the environment. While the present state-of-the-art literature reveals that ZnO at the bulk or at the nanoscale has been employed as greener catalysts in Friedel–Crafts acylation, Knoevenagel condensation, Biginelli reaction, Hantzsch condensation, phospha-Michael addition, Beckmann rearrangement and so on[14] and Fries rearrangement has been carried out using a wide variety of heterogeneous media or catalysts *viz.*, scandium trifluoromethanesulfonate,[15] sulfated zirconia,[16] zeolite,[17] electron beam irradiation within a cyclodextrin inclusion complex,[18] microwave irradiation,[19] ionic liquids,[20] *etc.*; with the advancement of nanotechnology, therefore, it seems quite appealing to design the landscape of a greener chemical approach for the Fries rearrangement. In this article, we have reported a soft-templated strategy for the synthesis of microstructured zinc oxide assemblies and exploited the particles as viable alternatives to conventional Lewis acid catalysts in the Fries rearrangement of *o*-methylphenyl acetate to 3-methyl-4-hydroxyacetophenone employed as the model reaction.

# 2. Experimental

## 2.1. Reagents and instruments

All the reagents used were of analytical reagent grade. Zinc acetate dihydrate [$Zn(OOCCH_3)_2 \cdot 2H_2O$] (Sigma-Aldrich), potassium hydroxide (S. D. Fine Chemicals, India), hydrochloric acid (Qualigens' Fine Chemicals, India) were used as received. *o*-Xylene (Sisco Research Laboratories, India) and were used without further purification. Double distilled water was used throughout the course of the investigation. The temperature was 298 ± 1 K for all experiments.

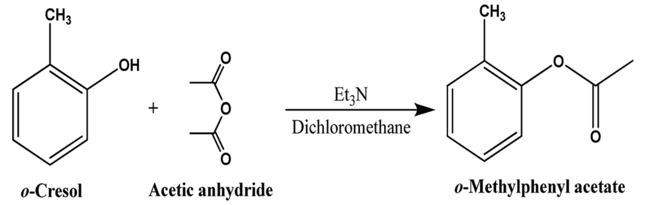
Absorption spectrum was recorded in a Lambda-750 digital UV-vis NIR spectrophotometer (PerkinElmer, England) using the solid sample accessories. Fluorescence spectrum was measured with a PerkinElmer LS-45 spectrofluorimeter equipped with a pulsed xenon lamp and a photomultiplier tube with R-928 spectral response. The spectrofluorimeter was linked to a personal computer and utilized the FL WinLab software package for data collection and processing. Scanning electron microscopic (SEM) images were recorded by using a JEOL (JSM-6360) Zeiss 1530 Gemini instrument equipped with a field emission cathode with a lateral resolution of approximately 3 nm and acceleration voltage 3 kV after sputtering the sample on a silicon wafer (approx. 6 nm). Energy dispersive X-ray (EDX) analysis was performed on a LEO 1530 field emission scanning electron microscope using an X-ray detector. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) was carried out on a JEOL JEM 2100 (JEOL, Japan) microscope operated at 200 kV. An epoxy resin (EpoFix kit, Struers) was used to prepare specimens for cross-sectional microtomed TEM imaging. Ultrathin sections, 50–70 nm in thickness, of the microstructures were cut with an Ultracut E Reichert-Jung microtome prepared at room temperature using a diamond knife (Drukker) and dropped on a silicon wafer by using a loop. Fourier transform infrared (FTIR) spectra were recorded in the form of pressed KBr pellets in the range of 400–4000 $cm^{-1}$ on a Shimadzu-FTIR Prestige-21 spectrophotometer. The powder X-ray diffraction patterns were obtained using a D8 ADVANCE BROKERaxs X-ray Diffractometer with $CuK_\alpha$ radiation ($\lambda = 1.4506$ Å); data were collected at a scan rate of 0.5° $min^{-1}$ in the range of 10–80°. The NMR spectra were recorded in BRUKER AVANCE II 400 FT-NMR spectrometer.

## 2.2. Synthesis of zinc oxide microstructures

Zinc oxide microstructures have been synthesized in a one pot reaction by hydrolysis of zinc acetate dihydrate as precursor using water and *o*-xylene as the solvent media. An amount of 0.057 g of zinc acetate dihydrate was dissolved in water/*o*-xylene mixture (9 : 1 v/v) in a double-necked round bottom flask by refluxing the mixture in a water bath at 45 °C for 45 min. After dissolving the precursor zinc acetate, potassium hydroxide solution (0.5 g KOH dissolved in 13.5 mL of water) was added to the reaction mixture. The reaction mixture was, then, kept on refluxing for another 15 min; after that, the temperature was increased to 60 °C and the refluxing was continued for another 1 h. Refluxing of the reaction mixture at higher temperature facilitates to achieve smaller size and monodispersity of the constituent ZnO particles in the microstructures. Then, the water bath was removed and the mixture was allowed to stir for 12 h at room temperature. The zinc oxide particles so obtained were retrieved by centrifugation at 10 000 rpm for 5 min and stored in the dark for 3 days before using as catalysts in the corresponding organic reaction.

## 2.3. Synthesis of the *o*-methylphenyl acetate

Synthesis of *o*-methylphenyl acetate has been carried out by following the procedure described in Vogel's text book.[21] An aliquot of 5 mmol of *o*-cresol was taken in a 50 mL double-necked round bottom flask, dissolved in 25 mL dichloromethane and the reaction mixture stirred for 15 min followed by the addition of 7.5 mmol of triethylamine. Then, acetic anhydride (10 mmol) was added dropwise and the reaction mixture was stirred for 12 h at room temperature. The completion of the reaction was monitored by thin layer chromatographic technique. After completion of the reaction, the post reaction mixture was filtered through a sintered funnel and the residue was washed with ethyl acetate (2 × 5 mL). The combined ethyl acetate was transferred to a separating funnel, washed with water (3 × 10 mL) and dried using activated $MgSO_4$. The solvent was removed in a rotary evaporator at room temperature under reduced pressure. The crude product was purified by column chromatography over silica gel (60–120 mesh) using ethyl acetate–petroleum ether as eluent to afford the desired ketone. A schematic presentation of the synthesis of *o*-methylphenyl acetate has been illustrated in Scheme 1.



Scheme 1 Schematic presentation of the synthesis of *o*-methylphenyl acetate.

# 3. Results and discussion

The ZnO microstructures have been synthesised in an one-pot reaction by alkaline hydrolysis of zinc acetate dihydrate employing *o*-xylene-in-water emulsion droplets as the soft templates. Fig. 1 shows the absorption and photoluminescence spectra of the ZnO raspberries in the solid state. The absorption spectrum of the as-prepared particles shows two maxima, one at 254 nm (4.88 eV) and the other at 294 nm (4.22 eV) that arise due to the excitonic transitions between the trapped energy states situated within the confinement region.[22] The optical band edge (band gap 4.4 eV) bears the characteristic electronic transition energy taking place to promote the electrons to the energy states in the conduction band from the valence band, including, excitonic effects. The fluorescence spectrum ($\lambda_{ex} \sim 254$ nm) of ZnO microstructures shows an UV emission band at 372 nm (3.33 eV) that arises due to the radiative recombination of a hole in the valence band and an electron in the conduction band (excitonic emission) and a broad emission in the visible that could be attributed to the presence of multiple surface defects in the microstructures.[23] Therefore, it seems that the formation of microstructures controls the various aspects of the recombination process and favours the radiative transitions from the oxygen vacancies/trap levels in the band gap to give a broad visible luminescence for the assemblies.

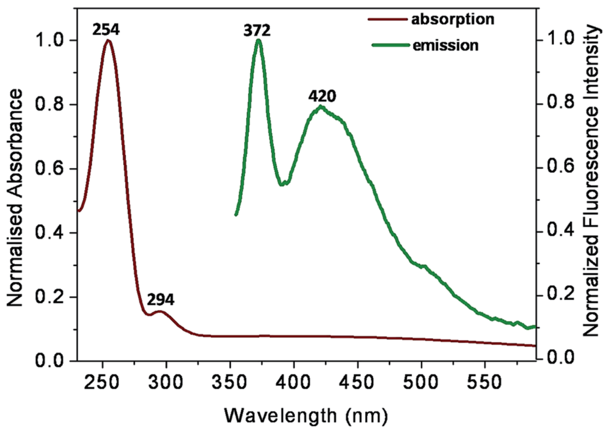


Fig. 1 Absorption and fluorescence spectra of ZnO microstructures in the solid state.

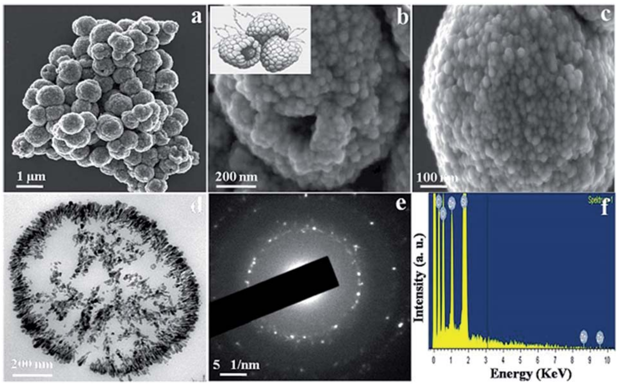


Fig. 2 (a–c) Representative scanning electron microscopic images with increased magnification; (d) microtomed transmission electron micrograph: (e) selected area electron diffraction pattern and (f) energy dispersive X-ray spectrum of the ZnO microstructures.

The morphology, composition and crystallinity of the as-prepared ZnO assemblies synthesised at the droplet interface are described in Fig. 2. Low resolution scanning electron micrograph (panel a) shows ZnO nanobuilding units are self-assembled into nearly spherical submicrometer-sized aggregates resulting in raspberries-like appearance with average diameter *ca.* 0.7 μm. Careful inspection (panel b) recognises that the assemblies possess well-defined hollow structures and there is, typically, one hole on the surface of each microsphere that appears due to adequate stabilisation of the nanoparticles at interfaces with a high degree of organizational selectivity.[24] Inset shows the photograph of raspberries showing the morphological resemblance with the particles. At higher resolution (panel c), self-assembly of the nanobuilding units on the interface as constructional base and roughened surface of the assemblies are apparent. The microtommed transmission electron micrograph of the cross-section (panel d) of the assemblies exhibit hollow interior of the microstructures bearing spherical cavity, with the thickness of the shell ranging from 40 to 100 nm. The corresponding selected area electron diffraction pattern (panel e) of the as-prepared raspberries reveals the appearance of polycrystalline-like diffraction, which is consistent with reflections (100), (002), (101), (102) and (110), corresponding to the hexagonal wurtzite phase of ZnO particles, indicating that the microstructure is an ordered assembly of small nanocrystal sub-units without crystallographic orientation.[25] The EDX spectrum (panel f) of the hollow microstructures indicates the presence of Zn elements in the composites. The signals of C, O and Si elements come from the as-prepared ZnO, acetate counterions adsorbed onto the particle surface and the silicon wafer employed for the SEM measurement.

The crystallinity and phase of the as-synthesised ZnO microstructures is shown in Fig. 3. The strong reflections shown in the pattern could be indexed to the pure hexagonal phase of Zn with a space group of $C_{6v}^4$ and cell constants $a = 3.25$ Å, and $c = 5.21$ Å (JCPDS card no. 76-0704), which suggests that the product comprises ZnO nanocrystals with the wurtzite structure.[26]

Fig. 4 shows the FTIR spectrum of the as-prepared ZnO assemblies formed at the interface of emulsion droplets. The presence of a sharp peak at 458 cm$^{-1}$ could be assigned to the stretching vibration of Zn–O bonds in the composites.[27] In

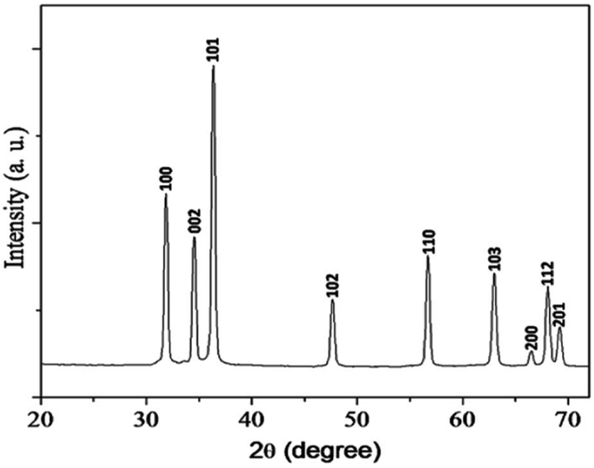


Fig. 3 X-Ray diffractogram of the as-prepared ZnO raspberries.

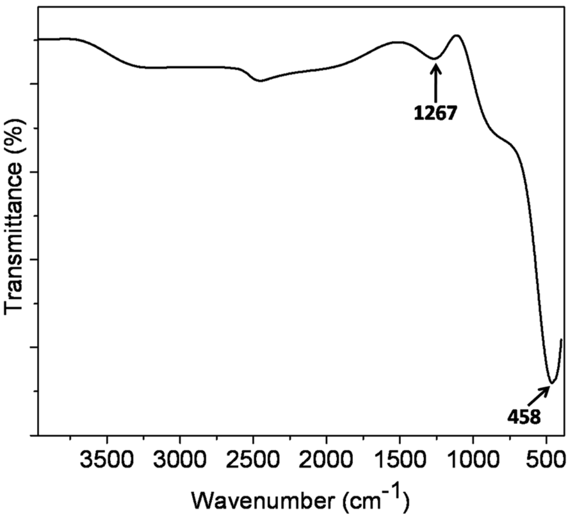


Fig. 4 FTIR spectrum of ZnO raspberries formed at the water/*o*-xylene interface.

addition, a weak absorption at around 1267 cm$^{-1}$ corresponds to C–O stretching frequency of acetate counterions adsorbed onto the metal oxide surface.[28] The absence of any other dominant peak indicates that the particles are merely naked and emphasizes the aptability of the particles for catalytic applications.

A plausible mechanism of the evolution of ZnO microstructures by alkaline hydrolysis of zinc acetate dihydrate in an immiscible liquid pair could be enunciated as follows.

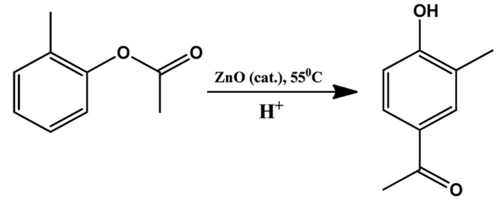
The formation of the assembly was not seen in water (boiling point 100 °C) or *o*-xylene (boiling point 144.4 °C) alone; this indicates oil-in-water emulsion droplets provide the restricted environment at the liquid–liquid interface in harnessing into raspberry-like assemblies.[29] It is now well established in the literature that a liquid–liquid interface is a non-homogeneous region, having a thickness of the order of a few nanometers.[2] The interface between two immiscible liquids, thus, offers an important scaffold for the chemical manipulation and self-assembly of the nanocrystals.[30] During the evolution, the ZnO clusters become, mainly, confined at the vicinity of the interface of the emulsion droplets and subsequently, the evolution of shell-like structure follows. When two ZnO building blocks come together, the capillary forces between them strengthen the agglomerate by van der Waals' forces. The monomers in the inner part of the droplet would diffuse to the surface due to the concentration gradient, resulting in hollow structures, and simultaneously such nanostructures would aggregate and fuse together to form nanometer- or micrometer-sized hollow spheres.[31] The resulting naked hollow spheres with accessibility of both interior and exterior having roughened surface because of their low effective density and high specific surface area possess the potential for promising applications, especially, in catalysis.

The as-prepared ZnO raspberries were employed as Lewis acid catalysts for the Fries rearrangement of aryl ester to *p*-hydroxyaryl ketone. The synthesis of the starting organic compound has been described in the Experimental section. In the catalytic reaction, 40 mg of the catalysts was dispersed with 3.5 mL of 0.1 mM *o*-methylphenyl acetate solution and the mixture was hydrolysed at 55 °C for 5 h under stirring condition. The completion of the reaction was tested by thin the catalytic reaction, 40 mg of the catalysts was dispersed with 3.5 mL of 0.1 mM *o*-methylphenyl acetate solution and the mixture was hydrolysed at 55 °C for 5 h under stirring condition. The completion of the reaction was tested by thin layer chromatographic technique and subsequently, worked up to achieve the desired product. A schematic presentation of the catalytic protocol has been described in Scheme 2.

Fig. 5 shows the $^1$H and $^{13}$C NMR spectra of the rearrangement of the ester in the presence of the catalysts. $^1$H NMR spectra (panel A) of the ester does not exhibit any characteristic NMR peak around alcoholic region, whereas, a well defined peak at $\delta$ 3.481 is seen for the product that confirms the formation of *o*-hydroxy ketone upon rearrangement.[32] Moreover, in the $^{13}$C NMR spectra (panel B), the presence of a peak at $\delta$ 169 for esteric carbon for the reactant is not seen in the product which further authenticates the rearrangement reaction under the experimental condition. A detailed analysis of the NMR spectra could be enunciated as follows:

### 3.1. *o*-Methylphenyl acetate

$^1$H (300 Hz, CDCl$_3$; Me$_4$Si at 25 °C, ppm) $\delta = 2.19$ (s, 3H, H$^6$), 2.28 (3H, H$^4$), 3.481 (s, 1H, H$^1$), 7.01 (1H, H$^2$), 7.13 (1H, H$^5$), 7.24 (1H,



Scheme 2 Catalytic protocol for Fries rearrangement in the presence of ZnO raspberries as catalysts.

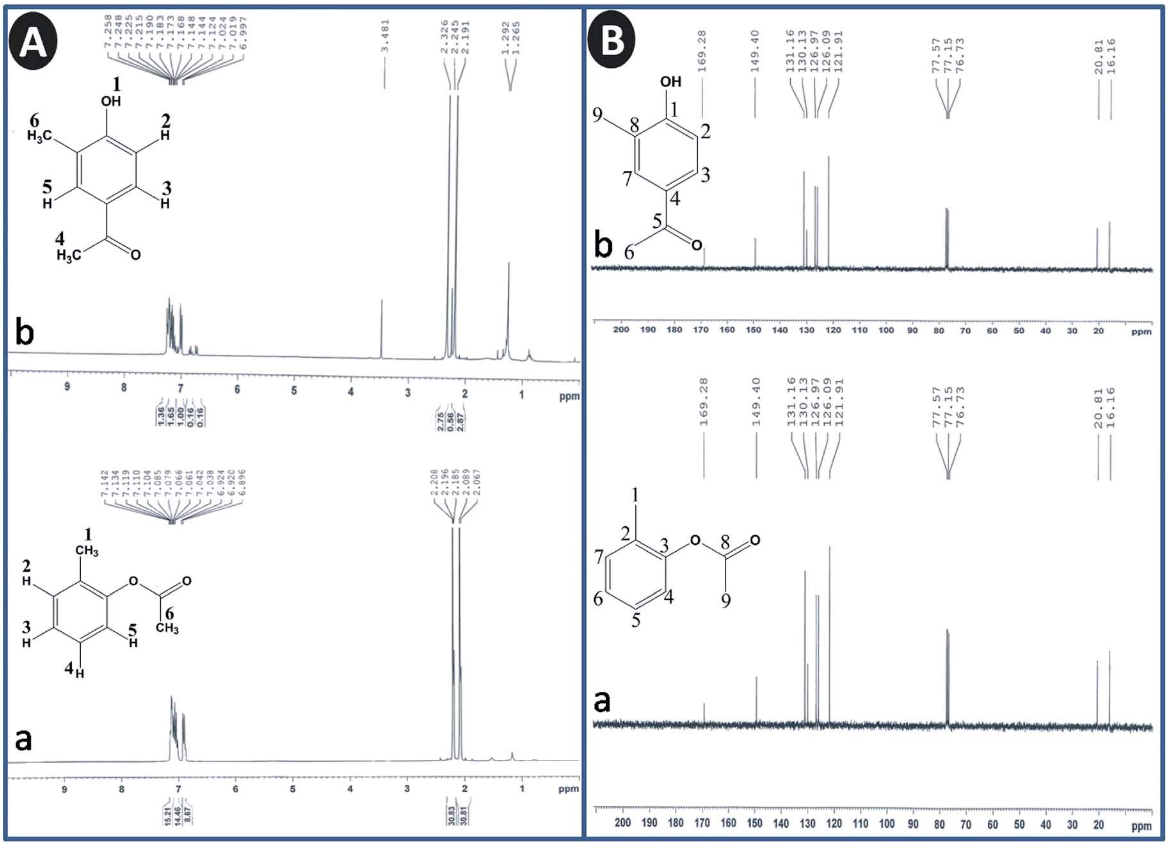


Fig. 5 (A) $^{1}$H and (B) $^{13}$C NMR spectra of *o*-methylphenyl acetate (a) before and (b) after Fries rearrangement in the presence of ZnO raspberries as catalysts.

H$^{3}$); $^{13}$C NMR, $\delta = 16.16$ (C$^{1}$), 20.81 (C$^{9}$), 121.91 (C$^{4}$), 126.09 (C$^{5}$), 126.97 (C$^{6}$), 130.13 (C$^{2}$), 131.16 (C$^{7}$), 149.49 (C$^{3}$), 169.28 (C$^{8}$).

### 3.2. *p*-Hydroxyaryl ketones

$^{1}$H (300 Hz, CDCl$_3$; Me$_4$Si at 25 °C, ppm) $\delta = 2.078$ (s, 3H, H$^{1}$), 2.196 (s, 3H, H$^{6}$), 6.913 (m, 1H, H$^{2}$), 7.047 (1H, H$^{3}$), 7.127 (1H, H$^{4}$), 7.142 (s, 1H, H$^{5}$); $^{13}$C NMR, $\delta = 16.16$ (C$^{9}$), 20.81 (C$^{6}$), 121.91 (C$^{2}$), 126.09 (C$^{3}$), 126.97 (C$^{8}$), 130.13 (C$^{7}$), 131.16 (C$^{4}$), 149.49 (C$^{1}$), 169.28 (C$^{5}$).

The proposed methodology is capable of providing the desired product in good yields (92–97%). At the end of the reaction, *p*-hydroxyaryl ketones and ZnO microstructures remain in the reaction mixture. In this reaction, submicrometer-sized ZnO assemblies act as heterogeneous catalysts which are inorganic materials. Therefore, the catalysts were separated from the reaction mixture by centrifugation or natural sedimentation at the end of the reaction and subsequent drying in air. It is observed that the assemblies could be reused up to seven cycles of operations without any apparent loss of activity and the catalytic turnover frequency is *ca.* 24.14 per gm of the catalysts. A histogram showing the yield of product for each cycle is presented in Fig. 6. Therefore, it is evident that the as-prepared ZnO raspberries could be projected as catalysts for Fries rearrangement of phenolic esters to *p*-hydroxyphenyl carbonyl compounds with industrially favourable turnover frequency.

It is well-established in the literature that Fries rearrangement is an organic reaction used to convert aryl ester to *o*- and/or *p*-hydroxyaryl-ketones using a Lewis acid catalyst involving the migration of an acyl group of phenolic ester to benzene ring.[33] In the present reaction, ZnO assemblies act as alternative to conventional Lewis acid catalysts. Therefore, the mechanism begins with coordination of the ester to the Lewis acid, followed by a rearrangement which generates an electrophilic acylium

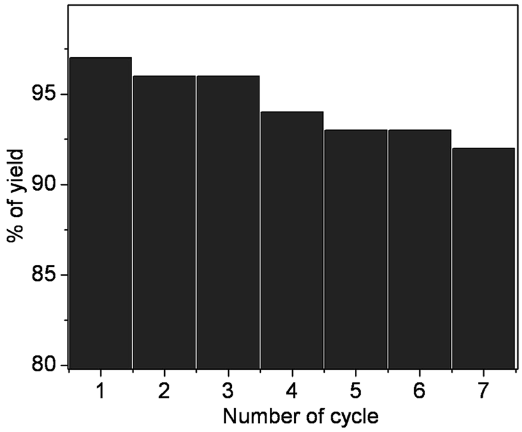
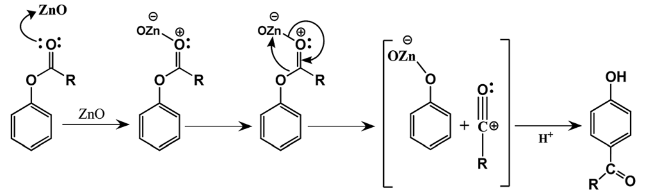


Fig. 6 Histogram showing the yield of product in different cycles of the reusability of the catalysts.



Scheme 3 Schematic representation of the reaction mechanism in the presence of ZnO as catalysts.

cation. The aromatic compound, then, attacks the alkyl cation, selectively, at the *para* position, *via* an electrophilic aromatic substitution. Deprotonation regenerates aromaticity and Brønsted acid work-up regenerate the Lewis acid catalyst provided with the *p*-hydroxyaryl ketonic product.[34] A plausible mechanism of the reaction in the presence of ZnO as catalysts is depicted in Scheme 3.

## 4. Conclusion

In conclusion, the present methodology based on the formation of *o*-xylene-in-water emulsion droplets could offer a viable platform for the synthesis of submicrometer-sized ZnO assemblies. These hollow and template-free assemblies could be envisaged as greener catalysts in Fries rearrangement for the conversion of phenolic ester to *p*-hydroxyaryl carbonyl compound with high turnover frequency. It is anticipated that the strategy of preparing hollow ZnO assemblies could be utilized as a landscape to the self-assembly of nanobuilding units of other transition metal oxides at the fluid interfaces to explore the application of these light-weight materials in nanotechnology.

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