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Low temperature vapor phase selective oxidation of ethylbenzene over $Ce_{1-x}Mn_xO_2$ nanocubes

A. Selvamani [a], M. Selvaraj [a], P. Santhana Krishnan [a], M. Gurulakshmi [b], K. Shanthi [a,*]

[a] Department of Chemistry, Anna University, Chennai 600 025, India
[b] Department of Chemistry, Madras Christian College (Autonomous), Tambaram, Chennai 600 059, India

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ABSTRACT

The $Ce_{1-x}Mn_xO_2$ nanocatalysts (x = 0, 0.25, 0.50, 0.75 and 1.0 mol. ratio) were synthesized by precipitation method using a different precursor salt. The effect of morphology with exclusive (1 0 0) plane was examined for the selective oxidation of ethylbenzene into acetophenone with maximum selectivity. The physico-chemical properties of synthesized catalysts were characterized using various techniques. The incorporation of Mn^{n+} into ceria lattice and the presence of (1 0 0) plane were confirmed by XRD and HRTEM analysis. The XRD patterns of $Ce_{1-x}Mn_xO_2$ catalysts were analyzed using the Rietveld refinement method to calculate the lattice parameters. Surface area and pore size distribution of the catalysts were analyzed from N_2 sorption study. XPS and DR–UV–vis spectra confirm the presence of Ce^{3+} and Mn^{2+} in the ceria lattice. Further, the presence of Mn^{2+} in $Ce_{1-x}Mn_xO_2$ framework was confirmed from ESR technique. H_2-TPR study revealed the oxygen storage capacity (OSC) of the catalysts. 3D flower-like and cubic morphology of ceria nanoparticles were confirmed from FESEM and HRTEM images, and the composition values of the elements present in the catalysts were calculated using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The catalytic activity was tested for vapor phase selective oxidation of ethylbenzene using oxygen as an oxidant at low temperature (463 K). The key reaction parameters were varied to study the stability, activity and selectivity of catalysts. The study concluded that suitable amount of manganese ion content in ceria is essential for selective oxidation of ethylbenzene at low temperature (463 K). Cubic structure $Ce_{0.25}Mn_{0.75}O_2$ nanocatalyst with specific (1 0 0) plane is found to be the most suitable catalyst for high conversion and selectivity toward acetophenone under the given reaction conditions.

1. Introduction

In synthetic organic chemistry, oxidation of alkyl aromatics is an important process for the introduction of functional groups [1,2]. The oxidation of alkyl C—H bond in the aromatics into their corresponding carbonyl compounds is a significant process for the industrial manufacturing, pharmaceutical and commercial applications [3,4]. Predominantly, oxidation of ethylbenzene is an industrially important process because of the formation of acetophenone [5–9], those added value chemical properties make the wide applications such as a basic units in pharmaceutical products, resins, alcohols, esters, aldehydes and tear gas, and also used as the solvent for cellulose ethers [10,11]. Lewis acids have been frequently used for the oxidation of ethylbenzene [4,12,13] and also some of the homogeneous catalysts were used with oxidant

and various solvents; the use of such oxidants and solvents may cause the various environment issues [12]. Liquid phase oxidation of ethylbenzene to acetophenone was reported over various homogeneous transition metals as catalysts (viz. Co, Mn, Cu, or Fe) using air as an oxidant [14,15]. The oxidation of ethylbenzene using H_2O_2 as oxidant over 8-quinolinolato manganese (III) complexes in water–acetone medium containing ammonium acetate and acetic acid as solvents has been reported by Lu et al. [5]. Zr-K-OMS-2 catalyst with TBHP as oxidant in the presence of acetonitrile solvent exhibited ethylbenzene conversion of about 60% with 98% of acetophenone [16], and Co/MCM-41 catalyst showed 26% conversion with 85% selectivity [17]. Rebelo et al. [18] have also reported the ethylbenzene with 64% conversion and 75% selectivity to acetophenone. Several reports on the selective oxidation of ethylbenzene to acetophenone using mixed metal oxide catalysts with t-butyl hydroperoxide (TBHP) as oxidant were also found in the literature [7,11,19]. The use of solvents and oxidants interrupts the product analysis and recovery of the catalysts [7,20,21]. The selective oxidation of organic compounds utilizing air as a primary oxidant

* Corresponding author. Tel.: +91 44 22358654.
E-mail address: kshanthiramesh@yahoo.com (K. Shanthi).

represents an eco-friendly technology for industrial application *via* green chemistry.

In order to increase the conversion, selectivity and easy handling of the products, heterogeneous catalytic process has been performed instead of homogeneous catalysts [22–25]. In particular, low temperature vapor phase selective oxidation reaction using air as an oxidant plays a vital role in industrial application due to the absence of hazardous solvents, oxidants and low energy consumption [26]. In recent decades, researchers are interested in the development of heterogeneous catalysts for the various oxidation reactions using nanoparticles, which had more advantage than conventional catalysts owing to their extremely small size and high surface area to volume ratio [21,27]. Ceria nanoparticles are potentially used for the oxidation of hydrocarbons and carbon monoxide due to the existence of Ce^{4+} and Ce^{3+} redox equilibrium associated with high oxygen storage capacity (OSC) [28–30]. It is found from the literature that among these two oxidation states Ce^{3+} may favor the selective oxidation reaction due to availability of lone pair electron. However, pure ceria posses low thermal stability, and leads to low oxygen storage capacity. In-order to improve the thermal stability and catalytic behavior of the catalyst, the transition metals are incorporated into ceria lattice [31,32]. In addition to the well-known particle size effect would make it into better catalytic activity [33,34], also the oxygen storage capacity of the catalysts is closely related to its morphology and exposure active planes [35,36]. The current study focuses on the synthesis of manganese ions incorporated ceria nanoparticles, and on effect of morphological impact associated with exclusive (1 0 0) plane for low temperature vapor phase selective oxidation of ethylbenzene in the presence of oxygen as oxidant.

2. Experimental

2.1. Material

Ce(NO$_3$)$_3$·6H$_2$O (Alfa Aesar), Mn(OAc)$_2$·4H$_2$O (Aldrich), cetyltrimethylammonium bromide (CTAB) (Sigma) and urea (Thomas-Baker) were used as the source materials for the synthesis of flowerlike ceria and manganese ions incorporated nanocubes. Ethylbenzene (Merck) was used as the reactant for vapor phase selective oxidation reaction.

2.2. Preparation of Ce$_{1-x}$Mn$_x$O$_2$ nanocubes

The manganese ions incorporated nanocubes (Ce$_{1-x}$Mn$_x$O$_2$) are synthesized by precipitation method using urea as follows [37,38]; the precursors Ce(NO$_3$)$_3$·6H$_2$O (10 mmol) and Mn(OAc)$_2$·4H$_2$O (10 mmol) are taken in equal ratio and dissolved in 100 ml triple distilled water (Solution A). Cetyltrimethylammonium bromide (10 mmol) was dissolved in 100 ml triple distilled water and stirred for an hour to form a clear solution (Solution B). The solution A was added drop wise into solution B and stirred for 1 h to form a homogeneous solution followed by the addition of 80 mmol of urea. The solution was stirred continuously for another 3 h to obtain complete homogeneous solution. The solution was then subjected to heat treatment under reflux condition at 393 K for 24 h with constant stirring; it was then allowed to cool and age for 24 h at room temperature. The resulting white precipitate was washed with triple distilled water followed by absolute ethanol. The precipitate was then dried at 333 K for 24 h and calcined at 673 K for 3 h. The calcined sample is denoted as Ce$_{0.50}$Mn$_{0.50}$O$_2$ nanocubes. The same synthesis procedure was adopted for other ratios such as 0.25, 0.75 and 1.0 mol. ratio. Pure ceria nanoparticles with flowerlike morphology were prepared by the procedure reported earlier
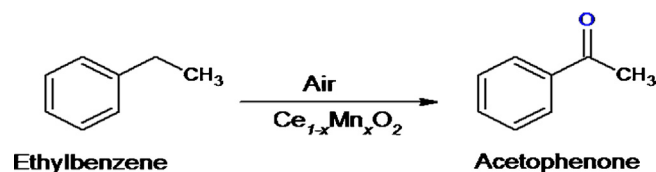
Scheme 1. Oxidation of ethylbenzene to acetophenone.

[31,36]. Further, MnO$_2$ catalyst is also synthesized by the same procedure using manganese acetate as the precursor.

2.3. Catalysts characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a PANalyticalX'pert PRO diffractometer equipped with CuKα = 1.54 Å as the radiation source. The samples were scanned in the 2θ range of 5–80° with the step scan of 0.02 Å and count time of 5 s at each point. XRD patterns of the Ce$_{1-x}$Mn$_x$O$_2$ catalysts were analyzed using the Rietveld refinement method with the FULLPROF program to calculate the lattice parameters, the Thompson-Cox-Hastings pseudo-Voigt function was adopted and the background was fitted with the 6-coefficient polynomial function. The lattice parameter, scale factor, background, *etc.* were refined. The diffuse reflectance ultraviolet visible spectral (DR–UV–vis) analysis was carried out on Shimadzu (UV-2450) instrument. The surface area of the samples was obtained using ASAP-2020 porosimeter from Micromeritics Corporation (Norcross, GA, USA) instrument. Prior to analysis, the samples were degassed at 573 K for 6 h in nitrogen atmosphere. FTIR spectra were recorded on a PerkinElmer FTIR spectrophotometer using KBr technique. The pellet was scanned at 4 cm^{-1} resolution in the range of 4000–400 cm^{-1}. The morphology of the prepared samples was analyzed by field emission scanning electron microscopy (FESEM), and images were taken with the Hitachi SU6600 FESEM at an operating voltage of 2–5 kV. The elemental compositions of synthesized catalysts were obtained by inductively coupled plasma–optical emission spectroscopy (ICP-OES) on a PerkinElmer Optima 5300 DV equipped with a concentric nebulizer and cyclonic spray chamber. The oxygen storage capacities (OSC), active sites, and reduction temperature of the samples were analyzed from H$_2$-TPR technique using ChemBET TPR/TPD Chemisorptions analyzer instrument. Oxidation states of manganese ion in the synthesized catalysts were identified using ESR spectra recorded on a BrukerESP 300 spectrometer. The magnetic field was calibrated with a Varian E-500 gauss meter. The microwave frequency was measured by a Hewlett-Packard HP 5342A frequency counter. High-resolution transmission electron microscopy (HRTEM) images were recorded using TECNAI-G2 (model T-30) S-twin HRTEM with a field emission gun operating at 300 kV. Oxidation state of constituent ions was identified by XPS spectra acquired using M/s. Omicron Nanotechnology (GmbH, Germany) with XM1000 monochromatic Al Kα source ($h\nu$ = 1486.6 eV) operated at 300 W (20 mA and 15 kV) and a hemispherical electron energy analyzer.

2.4. Oxidation of ethylbenzene

Oxidation of ethylbenzene was carried out in a fixed bed down flow quartz reactor with CO$_2$ free air at atmospheric pressure in the temperature range of 423–523 K (Scheme 1). About 0.5 g catalyst was placed in the center of the reactor supported on either side with a thin layer of quartz wool and ceramic beads, and the reactor was heated to required temperature using a temperature programmed furnace. The catalyst was activated at 873 K for 4 h. The reactant was fed into the reactor using a syringe infusion pump and the products were collected in the receiver flask