Journal of Molecular Catalysis A: Chemical 408 (2015) 41–47

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Modulated heterogeneous Fenton-like activity of 'M' doped nanoceria systems (M = Cu, Fe, Zr, Dy, La): Influence of reduction potential of doped cations

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ARTICLE INFO

Article history:
Received 31 May 2015
Received in revised form 13 July 2015
Accepted 14 July 2015
Available online 19 July 2015

Key words:
Ceria nanoparticles
Fenton-like oxidation
Redox potential
Oxygen vacancy

ABSTRACT

In this communication, we investigate the Heterogeneous Fenton-like oxidation of methylene blue in model waste water over ceria based nanocatalysts. Modification of ceria nanoparticles with oxides of Fe, Cu, Zr, La and Dy is carried out via wet impregnation and deposition precipitation methods. The synthesized catalytic systems are well characterized by X-Ray Diffraction technique, Electron microscopy (TEM &SEM), Raman spectral study, FTIR spectroscopy, UV-DR Spectra and BET surface area analysis. Among the prepared catalysts, copper oxide modified ceria system is found to be the most effective for the mineralization of methylene blue. It is concluded that oxygen vacancies and Ce^{3+} ions in the catalyst have prominent role in deciding the performance of M/CeO_2 catalysts in Fenton-like oxidation reactions. Besides this, the decisive role of redox potential of the doped metal ions on the efficiency of nanoceria in Fenton-like oxidation has also been examined for the first time in literature. A correlation between redox potential of doped metal ions and the oxidation activity is also established.

1. Introduction

Cerium oxide (CeO_2, also called ceria) is an active and wonderful multifunctional rare earth oxide which claims promising applications in various fields. It is a low energy gap semiconductor with facile redox functioning between Ce^{3+} and Ce^{4+}, which significantly differentiates ceria from other rare earth oxides. Other fine features of ceria are its superior chemical and physical stability, high oxygen vacancy and mobility, which are characteristic of the fluorite type metal oxides. Unique properties of ceria implicate its role in miscellaneous fields like catalysis, electrochemistry, material science, biological fields and medicinal fields[1–4]. As a major component in three way automotive exhaust catalyst system, ceria plays an outstanding role in pollution abatement also [5]. Fabrication of ceria into nano dimension generates fascinating properties compared to coarsened bulk ceria due to the quantum confinement effect that accounts for its unusual oxygen storage capacity, and hence the low temperature redox ability [6]. In nanostructures, the clustering of oxygen vacancies occurs on the surface of the particles, where cerium exists as Ce^{3+}. Hence nanoparticles can be designated more correctly as $CeO_{(2-x)}$. Indeed, the oxygen storage capacity of the system has been coupled directly to the concentration of oxygen vacancies at the surface of nanoparticles. The performance of nanoceria can be effectively tuned by the addition of various transition and lanthanide metal ions, where the lattice changes occurred during the modification affect / tune the catalytic efficiency. In the present study, cerium oxide based catalysts have been adopted as a Fenton-like catalyst for the degradation of organic contaminant in waste water.

Removal of organic pollutants from industrial waste water is a hot research area today. Stable organic dye molecules are prominent in their contribution towards water pollution. These dyes and pigments not only give colour to water but also suppress the reoxygenation ability of water, thereby posing threat to humans. Researchers have devoted intensive efforts to find out a benign route for the removal of stable dye contaminants. Various techniques are adopted as protective measures to this effect include adsorption, chemical coagulation, electrochemical route, degradation by strong oxidizing agents etc. [7–10]. Pure adsorption is a preferred route, which is investigated and adopted globally for waste water treatment. But our focus is on complete mineralisation and effortless reusability of the used catalysts. Recently, advanced oxidation processes (AOPs) have got great attention in this area due to its attractive features such as cheap and readily available materials, ease of operation as well as efficient degradation. Among these, Fenton oxidation is one of the well-known AOPs, that have been dis-

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http://dx.doi.org/10.1016/j.molcata.2015.07.018
1381-1169/

cussed much. Fenton's reagent, Fe^{2+}/H_2O_2, which is widely used in advanced oxidation processes offers promise for the treatment of polluted water. Oxidation of organic moieties is affected by the highly active hydroxyl radicals generated by Fenton's reagent by the reaction,

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-.$$

Fenton-like reaction system, (Fe^{3+}/H_2O_2), is also proven to be an efficient system for the mineralization of organic pollutants in waste water [11]. Recently, the role of ceria in this area has been brought to limelight by the researchers. The use of redox cycle between cerous (Ce^{3+}) and ceric ions (Ce^{4+}) has been extended to the oxidation of organic pollutants using ceria as a Fenton like catalyst. Ceria is the only rare earth metal oxide that can exhibit a Fenton-like oxidation activity. Heckert et al. have reported the homogeneous Fenton- like activity over cerium salts for the mineralization of organic particulates in aqueous solutions [12]. The difficulties associated with recyclability and removal of the catalyst holds back its commercial application for waste water treatment. As an ambient catalytic reaction, a heterogeneous Fenton -like oxidation on pure and modified ceria nanoparticles was attempted by researchers due to its merits over homogeneous catalysis [13,14]. In depth investigations of ceria/H_2O_2 Fenton- like system revealed that the production of hydroxyl radicals mainly depends on the nature of the oxide surface. Cai and co-workers have reported that the degradation rate of the organic pollutant via Fenton-like reaction improves as Ce^{3+} content increases, even at ambient conditions [15]. For instance, researchers have noticed the increase in the Ce^{3+} content in ceria system when loaded with noble metals which improves the Fenton-like reactivity of ceria [16].

The specific objective of the current investigation is to examine the activity M/CeO_2 systems for the removal of Methylene blue (MB) through heterogeneous Fenton-like oxidation. Herein, ceria nanoparticles have been synthesized via simple ammonia precipitation route, and are modified with the oxides of transition metals and lanthanide metals. The well characterized catalysts are combined with the green oxidising agent hydrogen peroxide to achieve almost complete mineralisation of the dye through heterogeneous Fenton- like oxidation route. The influence of doped ions on Ce-H_2O_2 Fenton-like system is examined and a correlation is established between the activity and oxygen vacancy of the catalysts. The decisive role of redox potential of the doped metal ions on the oxidation efficiency of nanoceria in Fenton-like oxidation has also been examined for the first time.

2. Experimental

2.1. Preparation of catalysts for dye mineralization

Ceria nanoparticles were synthesized by simple homogeneous precipitation method from aqueous cerium nitrate hexahydrate (Sigma–Aldrich purity 99.9%) solution with dilute ammonia (SRL, extra pure) following the reported procedure [17]. Ceria supported catalyst systems were prepared through wet impregnation and deposition precipitation methods from corresponding aqueous salt precursors. The amount of dopants has been fixed to be 20% by weight in the modified ceria. The samples were dried at 110 °C for about 24 h and calcined in an air oven at 500 °C for 2 h. The material was sieved to obtain particles of size <75 microns.

2.2. Characterization methods

The calcined ceria sample and the modified analogues were well characterized by adopting the following techniques. The micro structure of the samples was traced by SEM–JSM 848 instrument and Philips CM 200 transmission electron microscope (TEM). Rigaku Miniflex 600 diffractometer equipped with a rotating anode was used to obtain Powder X-ray diffraction (XRD) pattern of the samples using Cu*Kα* radiation. Scherrer's method of analysis was used for the calculation of the average crystallite size of the prepared systems from the broadening of the most intense XRD peak. The surface area of the prepared systems was obtained through BET method through nitrogen adsorption study using Micromeritics Gemini surface area analyser. Jasco V-550 spectrophotometer served the purpose of recording the DR UV–vis spectra in the range 200–800 nm with $BaSO_4$ as reference. Raman scattering measurement was performed using LabRam HR-Horiba Jobinyvon spectrometer to study the structural characteristics and the oxygen vacancy levels in each system.

2.3. Fenton-like activity study

The catalytic efficiency of the prepared ceria systems was studied by examining the Fenton-like oxidation of methylene blue. In a typical experiment, 20 ml of a known concentration (0.0138 g/250 ml) of MB solution (pH ~ 9.6) was mixed with 20 mg of the catalyst in a sealed vessel and injected I ml H_2O_2 to the mixture. Similarly, seven parallel reactions were carried out to study the degradation activity at selected time intervals. The reaction temperature was fixed as 27 °C. The treated solution was centrifuged after regular intervals of time to remove the solid catalyst. The progress of the degradation was followed by quantitative analysis method using UV Visible Spectrophotometer. The decrease in absorbance of methylene blue in the treated solution after regular intervals of time at 660 nm is an indication of removal efficiency. The efficiency of the reaction was quantified using the following equation $\%\text{Degradation} = \left(1 - \frac{C_t}{C_0}\right) \times 100$, where C_0 and C_t are the initial methylene blue content and the retained methylene blue in solution after particular intervals of time respectively.

3. Results and discussions

3.1. Characterization of nanostructured ceria

The following characterization techniques give the fundamental structural information regarding nanoceria. From the microscopic analysis, the morphology and particle size of ceria nanoparticles are revealed. Scanning electron microscopic image (Fig. 1a) reveals the surface morphology and the extent of porosity present in the system, which indicated considerable agglomeration of individual particles. The average particle size measured from the transmission electron microscopic analysis is 8–9 nm, with truncated octahedral shape,as identified from Fig. 1b. The Raman spectrum reveals a single intense peak at 465 cm^{-1} which is the characteristic vibrational mode (F_{2g}) of the fluorite type structure (Fig. 1c). This band arises from the symmetric stretching vibration of the oxygen atoms around cerium ions. A weak broad band around 600 cm^{-1} was noticed on enlarging the concerned area.

3.2. Characterisation of M/CeO_2 systems

Strong intense bands are observed in the Fourier Transform Infrared spectra of ceria based nanostructures at 3435 cm^{-1}, 1630 cm^{-1} and below 700 cm^{-1} (Fig. 2). The diffuse band observed at 3417 cm^{-1} account for the ν (O—H) mode of 'H'-bonded water molecules on the catalyst surface. Strong broad band observed below 700 cm^{-1} corresponds to δ (Ce—O—Ce) vibrational mode in the system [18]. The IR absorption at 848 cm^{-1} signifies the metal—oxygen bond, and the OH bending modes of physisorbed water are observed around 1630 cm^{-1}[19]. All the supported