Molecular Catalysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Molecular Catalysis

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

Role of oxygen vacancy in cobalt doped ceria catalyst for styrene epoxidation using molecular oxygen

Shahid Hassan[a], Rawesh Kumar[b], Ankur Tiwari[a], Weiyi Song[c], Lennart van Haandel[d], Jai Krishna Pandey[e], Emiel Hensen[c,*], Biswajit Chowdhury[a,*]

[a] Department of Applied Chemistry, Indian Institute of Technology (ISM), Dhanbad, Jharkhand, India
[b] Department of Chemistry, NIT, Jamshedpur, India
[c] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, 18#, Fuxue Road, Chang Ping, Beijing 102249, China
[d] Laboratory of Inorganic Materials Chemistry, Schuit Institute of Catalysis, PO Box 5 13, 5600 MB, Eindhoven, The Netherlands
[e] Central Institute of Mining and Fuel Research (CIMFR), Dhanbad, India

ARTICLE INFO

Keywords:
Oxygen vacancy
Cobalt
Ceria
Styrene epoxidation

ABSTRACT

The oxygen vacancy formation and refillment of oxygen vacancy by molecular oxygen are the key steps of catalyst redox cycle towards styrene epoxidation reaction. Well dispersed, Isomorphically substituted and energetically favorable cobalt based redox cycle in ceria lattice caused lower oxygen formation energy, oxygen adsorption energy and activation energy than pure ceria for the reaction ensuring excellent catalytic activity. DFT studies show that inclusion of cobalt in ceria leads to lower the oxygen removal energy. Oxygen vacancy formation resulted into the rise of the spin magnetic moment of cobalt to 2.70 μB indicating reduction of Co^{+3} to Co^{+2} as well as fall of oxygen adsorption energy. A mechanistic proposal is presented in which Co^{3+}/Co^{2+}, Ce^{4+}/Ce^{3+}, oxygen vacancies are involved in adsorption, activation reaction of oxygen and styrene on the surface of the catalyst. The Co(4)-CeO_2 catalyst also demonstrated reactivity towards stilbene, cyclooctene under similar reaction condition. The catalyst was regenerated up to three cycles.

1. Introduction

Formation of the oxygen vacancy during the active oxygen supply from catalyst surface to the substrate and subsequent refillment of oxygen vacancy by oxidant/molecular oxygen/air are the key steps of catalytic cycle for an oxidation reaction [1]. In the former step catalyst is reduced and substrate is oxidized while in later step reduced catalyst is re-oxidized. The density functional theory (DFT) calculation showed that among many redox couple CeO_2/Ce_2O_3, TiO_2/Ti_2O_3, $V_2O_5/VO_2/V_2O_3$ and MoO_3/MoO_2; CeO_2/Ce_2O_3 have least reduction energy of CeO_2/Ce_2O_3 couple about 0.2 eV compared to others [2]. The high oxygen storage capacity of ceria along with quick switching of Ce^{4+}/Ce^{3+} redox cycle [3–5] had brought most of the attention of catalyst community for an oxidation reaction [6–8]. Further, doping of lower valent cations in ceria is a common strategy for tuning reducibility and the oxygen storage capacity of the ceria which increases its catalytic performance at low temperature [9,10] due to lattice contraction-expansion [11] and electron deficit centre [12]. If both the dopant and the support have enriched redox chemistry, oxygen vacancy can be formed by reduction of support or dopant or both.

Several catalysts were reported for styrene epoxidation reaction using conventional oxidant such as H_2O_2 or TBHP Among different homogeneous complexes 12-molybdophosphoric acid [13], oxovanadium complexes [14,15], vanadium doped catalysts [16,17], manganese porphyrin [18], manganese salen complex [19], and manganese schiff bases [20], were found more effective for styrene epoxidation reaction. In the case of heterogeneous catalysts there are wide reports in the literature. Several iron based catalysts [21–25], titanosilicates [26,27], gold or gold nanoparticle deposited titanosilicates [28–32] and lanthanum containing catalysts [33] were reported as a good catalyst for styrene epoxidation reaction.,The oxidation reaction using molecular oxygen is the atom efficient pathway to get styrene epoxide from styrene. The silver, yttrium, copper containg catalyst were very much active for styrene epoxidation reaction using molecular oxygen [34–37]. Apart from those Mg or Co, Al containing binary layered double hydroxides [38,39], cobalt doped catalyst systems [40–48], were used effectively in styrene epoxidation reaction. Although, there are many reports dealing with ceria as the support for oxidation reaction [49–51], there are relatively few works focusing on the role of the oxygen vacancy (O_v) in doped ceria lattice for an

* Corresponding authors.
E-mail addresses: e.j.m.hensen@tue.nl (E. Hensen), biswajit_chem2003@yahoo.com (B. Chowdhury).

https://doi.org/10.1016/j.mcat.2018.01.025
Received 30 September 2017; Received in revised form 3 January 2018; Accepted 20 January 2018

epoxidation reaction using molecular oxygen as an oxidant [52–54]. As cobalt based catalyst system [54–56] was found more promising than other catalyst system [5] for the epoxidation of various olefins, in the present study we have selected cobalt as a dopant in the ceria lattice for styrene oxidation using molecular oxygen as an oxidant. It is hypothesized that the creation of oxygen vacancy by doping of cobalt in the CeO_2 lattice will facilitate adsorption of molecular oxygen in the $Co_xCe_{1-x}O_2$ (111) surface rendering activation of molecular oxygen for enhancing the catalytic activity towards styrene epoxidation reaction. To proceed for establishing the hypothesis CeO_2, Co(4)-CeO_2 (Co = 4 mol%), Co(8)-CeO_2 (Co = 8 mol%) and Co(12)-CeO_2 (Co = 12 mol%) were prepared and investigated for styrene epoxidation reaction at atmospheric condition. The most active catalyst in terms of productivity was characterized by XRD, N_2 physisorption, FESEM, HRTEM, XPS and TPR techniques. The activity of Co(4)-CeO_2 (Co = 4 mol%) was further optimized by varying solvent, the temperature and the oxygen flow. Interesting correlation could be drawn from the catalytic activity, catalyst characterization and theoretical studies demonstrating the role of oxygen vacancy towards styrene epoxidation reaction.

2. Experimental procedure

2.1. Chemicals and reagents

Cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$ (99.9%)) was obtained from Sigma-Aldrich and used without further purification. Triethanolamine (TEA, 99%), cobalt nitrate hexahydrate($Co(NO_3)_3{\cdot}6H_2O$) were supplied by Acros Organics and Tetraethylammonium hydroxide (TEAOH, 20% aqueous solution) was obtained from Merck Germany. All solutions were prepared using milli-Qwater (resistivity 18.2 MΩ × cm).

2.2. Preparation of cobalt doped CeO_2

Cobalt doped cerium oxide was prepared by a non-hydrothermal sol–gel method as described in our previous work [8]. In this procedure, a solution of $Ce(NO_3)_3{\cdot}6H_2O$ (99.9%, Aldrich) was added to a mixture of triethanolamine (TEA, 99%, Acros Organics) and water under stirring at the room temperature. After complete addition of the cerium nitrate solution, cobalt nitrate hexahydrate was added in solid form to the solution under constant stirring. The mixture was stirred for 10 min after which tetraethylammonium hydroxide (TEAOH, 20% aqueous solution, Merck Germany) was added dropwise under constant stirring resulting gel wih the molar composition TEA: $Ce(NO_3)_3{\cdot}6H_2O$:H_2O: $Co(NO_3)_3{\cdot}6H_2O$: TEAOH = 0.2:0.1:1.1:(0.004-0.008-0.012): 0.1. This mixture was kept for 24 h under continuous stirring at room temperature. The prepared gel was dried at 383 K for 24hin a static air oven. Finally, the dried material was collected and calcined at 973 K for 10 h with a heating rate of 1 °C min^{-1}in a muffle furnace (Thermocraft USA).

2.3. Catalyst characterization

The N_2 adsorption-desorption isotherms were measured at liquid nitrogen temperature (77 K) with a QuantachromeNova-3200e. The samples were outgassed at 573 K for 6 h. The surface area was determined by the Brunauer-Emmett-Teller (BET) equation. The average pore size distributions were calculated using the BJH (Barrett – Joyner – Halenda) model. XRD characterization was done in an X-ray diffractometer (Rigaku, Ultima IV) using Cu K_α radiation as the X-ray source (40 kV, 20 mA). The peaks were identified by a search and match technique using X'PertHighScore Plus software and the JCPDS database. The average CeO_2 crystallite size was estimated from the (111) diffraction peak at 2θ ~ 28.6° using the Scherrer equation.

Energy dispersive X-ray spectroscopy (EDX) was carried out using a field emission scanning electron microscope (FESEM Supra 55, Carl Zeiss, Germany) equipped with an energy dispersive spectrometer (Oxford Liquid Nitrogen free SDD X MAX 50 EDS) detector. The HRTEM investigation was done on JEOL JEM 2100 microscope operated at 200 KV acceleration voltage using Lacey carbon coated Cu grid of 300 mesh size.

The TPR profile of the samples was recorded with Chemisorb 2750 (Micrometrics, USA) instrument equipped with a TCD detector. The TPR experiments were carried out by reducing the catalyst samples using a gas mixture of 10% H_2 in Ar with a flow rate of 20 mL/min. The temperature was increased from ambient temperature to 973 K at a rate of 10 K min^{-1} under a flow of 10% H_2 in Ar and the hydrogen consumption was monitored by observing the change in the TCD signal. XPS measurements were carried out with a Thermo Scientific K-Alpha, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminium anode (Al Kα = 1486.6 eV) operating at 72W and a spot size of 400 µm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was 2×10^{-9} mbar and during measurement 3×10^{-7} mbar argon because of the charge compensation dual beam source. The fraction of Ce^{3+}/Ce^{4+} in the samples was calculated from the peak areas.

3. Styrene epoxidation reaction

The catalytic activity of the catalyst for styrene epoxidation reaction was carried out in 50 cm^3 two necked round bottle fitted with reflux condenser and oxygen nozzle under atmospheric pressure at 373 K for 4 h under 600 rpm agitation speed. Properly dried 0.2 g catalyst (30–60 µm mesh size) was added to mixture of 10 mmol styrene (Acros Organic), 20 mL DMF (99.8%, Merck, India) as solvent and 0.2 mL dodecane (99%, Acros Organics) as internal standard in round bottle. Then oxygen was bubbled in the reaction mixture through the nozzle at a flow rate of 50 $cm^3 min^{-1}$. The products were analyzed by gas chromatography (CIC-India Model No 2010) using a SE-30 column and an FID detector. The details of the GC analysis conditions are given in the supporting information. The separated catalyst was washed with acetone (4–5 times), dried at 353 K overnight in air, and used again in recycle experiments. The TOF was calculated on the basis of mole of styrene converted per mole of cobalt.

3.1. DFT calculation

To investigate the role of oxygen vacancies towards the styrene epoxidation reaction, DFT calculation has been done on the most stable (111) termination of $Co_xCe_{1-x}O_2$ surface. The stabilization energy of the cobalt doped ceria was measured by changing the number of oxygen vacancies on the doped oxides. The energy of adsorption of oxygen molecule to the vacant site of doped oxide has also been calculated theoretically. Finally, reaction energy was calculated for clean ceria surface and doped ceria surface considering the styrene molecule as well as adsorbed oxygen molecule.

4. Results

4.1. Preliminary catalytic activity results

The catalytic activities of CeO_2 and differently cobalt loaded Co-CeO_2 catalyst for styrene epoxidation reaction using molecular O_2 was evaluated and presented in Table 1. The pure CeO_2 was almost inert in the reaction whereas cobalt doped CeO_2 showed high catalytic activity towards the styrene epoxidation reaction using molecular oxygen as an oxidant. On increasing the cobalt loading from 4 to 12 mol%, a decrease in styrene conversion (i.e. 26.31-19.41%) and styrene oxide selectivity (i.e. 57.29-47.50%) is observed. To investigate the physicochemical properties, the best catalyst Co(4)-CeO_2 was characterized by XRD, N_2-