Applied Catalysis B: Environmental 87 (2009) 230–238

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Utilization of carbon dioxide as soft oxidant for oxydehydrogenation of ethylbenzene to styrene over V_2O_5–CeO_2/TiO_2–ZrO_2 catalyst

Benjaram M. Reddy [a,b], Seung-Cheol Lee [a], Dae-Soo Han [a], Sang-Eon Park [a,*]

[a] Laboratory of Nano-Green Catalysis, Department of Chemistry, Inha University, 253 Yonghyun-dong, Incheon 402-751, Republic of Korea
[b] Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India

ARTICLE INFO

Article history:
Received 4 June 2008
Received in revised form 9 July 2008
Accepted 27 August 2008
Available online 3 September 2008

Keywords:
Carbon dioxide
Oxidative dehydrogenation
Ethylbenzene
Styrene
Vanadium oxide
Cerium oxide
Titania–zirconia
Catalyst characterization

ABSTRACT

Vanadium oxide and cerium oxide doped titania–zirconia mixed oxides were explored for oxidative dehydrogenation of ethylbenzene to styrene utilizing carbon dioxide as a soft oxidant. The investigated TiO_2–ZrO_2 mixed oxide support with high specific surface area (207 $m^2\,g^{-1}$) was synthesized by a coprecipitation method. Over the calcined support (550 °C), a monolayer equivalent (15 wt.%) of V_2O_5, CeO_2 or a combination of both were deposited by using wet-impregnation or co-impregnation methods to make the V_2O_5/TiO_2–ZrO_2, CeO_2/TiO_2–ZrO_2 and V_2O_5–CeO_2/TiO_2–ZrO_2 combination catalysts, respectively. These catalysts were characterized using X-ray diffraction (XRD), Raman, scanning electron microscopy (SEM), transmission electron microscopy (TEM), temperature preprogrammed reduction (TPR), CO_2 temperature preprogrammed desorption (TPD) and BET surface area methods. All characterization studies revealed that the deposited promoter oxides are in a highly dispersed form over the support, and the combined acid–base and redox properties of the catalysts play a major role in this reaction. The V_2O_5–CeO_2/TiO_2–ZrO_2 catalyst exhibited a better conversion and product selectivity than other combinations. In particular, the addition of CeO_2 to V_2O_5/TiO_2–ZrO_2 prevented catalyst deactivation and helped to maintain a high and stable catalytic activity.

1. Introduction

Exploitation of carbon dioxide as a soft oxidant for the commercially significant catalytic oxidative dehydrogenation (ODH) of ethylbenzene (EB) to styrene has received enormous interest recently owing to its several attractive features [1–4]. Styrene is one of the most important basic chemicals in the modern petrochemical industry [5,6]. Styrene is normally synthesized by two methods: mainly by an endothermic dehydrogenation of EB and as a co-product of propylene oxide production [5–9]. The ODH of EB is a third possibility to produce styrene employing different oxidants that gained much attention because it can be operated at a lower temperature, as it is exothermic [3,4,10–13]. The dissociation of CO_2 on the surface of an appropriate catalyst system produces an active oxygen species, which can take part in the ODH and related reactions [14,15]. Utilization of CO_2 in the ODH process, for example, can encompass several advantages such as acceleration of the reaction rate, alleviation of the chemical equilibrium and the enhancement of product selectivity [2].

As per recent studies, various catalyst systems based on mostly Fe-, Cr- or V-oxides exhibited good catalytic activity for the ODH of EB with CO_2 as the oxidant [2–4,8,16–23]. Interestingly, various supported vanadium oxide catalysts that are active and selective for selective oxidation, ammoxidation and selective catalytic reduction have also been reported to show better performance for the ODH of EB with CO_2 [19,21,23–27]. Contrary to the conventional ODH reaction that uses oxygen, a strong oxidant, the ODH of EB with CO_2 has been reported to exhibit much higher selectivity towards styrene. However, the CO_2 as an oxidant in the ODH reaction is generally believed to result in the formation of more carbonaceous deposits resulting in the fast deactivation of catalysts. Therefore, there is a need to design better catalyst systems, which can overcome the deactivation.

Although the reaction mechanism of selective oxidation or ODH is not established completely, it is widely believed that breaking of C–H bond in the hydrocarbon is the rate determining step [28], and the reaction proceeds via a Mars-Van Krevelen (redox)-type mechanism [28,29]. Further, it is generally agreed that hydrocarbon oxidation over metal oxide catalysts involves the participation of lattice oxygen species or oxygen vacancies [28,30]. Ceria is a well-known oxygen storage/release capacity (OSC) material widely employed in auto exhaust purification

---

* Corresponding author. Tel.: +82 32 860 7675; fax: +82 32 872 8670.
E-mail address: separk@inha.ac.kr (S.-E. Park).

0926-3373/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2008.08.026

three-way catalysts (TWC) owing to its high concentration of oxygen vacancies and oxygen-ion mobility character [31]. The CeO_2 containing catalysts were also reported to display good catalytic properties for oxidative conversion of propane to propylene and ethane to ethylene, and known to suppress catalyst deactivation by preventing coke formation [32,33]. Therefore, the unique combination of excellent OSC features of CeO_2 and oxidizing ability of V_2O_5 were thought to result in a good catalyst system for the title reaction. However, bulk V_2O_5 and CeO_2 are known to suffer from poor thermal stability, mechanical strength and rapid deactivation, and promote nonselective oxidations [34]. Therefore, an appropriate metal oxide support is essential to overcome those deficiencies. The combined titania–zirconia mixed oxides have attracted considerable attention recently as active catalysts as well as supports for a wide variety of reactions [35]. The significant features of TiO_2–ZrO_2 mixed oxides include a high specific surface area, profound acid–base and redox properties, a high thermal stability and strong mechanical strength [35]. The TiO_2–ZrO_2 mixed also exhibited a good catalytic activity and selectivity for the ODH of EB with CO_2 [36,37]. Therefore, a combination catalyst consisting of V_2O_5 and CeO_2 over the TiO_2–ZrO_2 support was undertaken for systematic investigation.

In this study, the TiO_2–ZrO_2 support was synthesized through a soft-chemical route by adopting a coprecipitation method, and a theoretical monolayer equivalent of V_2O_5, CeO_2 and combination of both were deposited by a wet impregnation method. The structural evolution of the prepared TiO_2–ZrO_2, V_2O_5/TiO_2–ZrO_2, CeO_2/TiO_2–ZrO_2 and V_2O_5–CeO_2/TiO_2–ZrO_2 combination catalysts was done using X-ray diffraction (XRD), Raman spectroscopy (RS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), temperature preprogrammed reduction (TPR), temperature preprogrammed desorption (TPD), BET surface area and pore size distribution methods. The catalytic performance was evaluated for the ODH of EB to styrene in the vapour phase under normal atmospheric pressure employing CO_2 as the soft oxidant.

2. Experimental

2.1. Catalyst preparation

The TiO_2–ZrO_2 (1:1 mole ratio) mixed oxide was synthesized by a coprecipitation method from $TiCl_4$ and $ZrOCl_2$ aqueous solutions by hydrolysis with ammonium hydroxide. In a typical experiment, the required quantities of zirconyl(IV) nitrate hydrate (Acros Organics, USA) and titanium(IV) chloride (Yakuri Pure Chemicals, Japan) were dissolved separately in deionized water and mixed together. To this mixture solution, dilute aqueous ammonia (DC Chemicals, Korea) was added drop wise with vigorous stirring until the precipitation was complete (pH 7–8). The resultant precipitates were aged hydrothermally for 12 h at 100 °C before filtration. The well-formed white precipitates were separated by filtration under reduced pressure and washed with deionized water until free from anion impurities. The obtained cake was oven dried at 120 °C for 12 h and finally calcined at 550 °C for 6 h in air atmosphere. On the calcined TiO_2–ZrO_2 mixed oxide support, a monolayer equivalent of V_2O_5 (15 wt.%), CeO_2 (15 wt.%) and CeO_2–V_2O_5 (7.5 wt.% + 7.5 wt.%) were deposited by adopting a standard wet impregnation method. To achieve this, the desired quantities of ammonium metavanadate (Aldrich) and ceric ammonium nitrate (TCI, Japan) were dissolved separately in deionized water to which the finely powdered support was added with continuous stirring. The excess water was evaporated on a water-bath under vigorous stirring. The resulting material was oven dried at 120 °C for 12 h and subsequently calcined at 550 °C for 6 h in air atmosphere. Some portions of the finished samples were again heated at 750 °C for 6 h to investigate their temperature stability. The rate of heating as well as cooling was always maintained at 5 °C min^{-1}.

2.2. Catalyst characterization

The BET surface area and BJH pore size distribution measurements were made by N_2 adsorption/desorption at liquid-nitrogen temperature using a Micromeritics ASAP 2020 instrument. Before analysis, samples were evacuated for 3–4 h at 250 °C in the degassing port of the instrument. Powder XRD patterns were obtained on a Rigaku Multiflex instrument using nickel-filtered Cu $K\alpha$ (0.15418 nm) radiation source and a scintillation counter detector. The intensity data were collected over a 2θ range of 2–80° with a 0.02° step size and using a counting time of 1 s per point. Crystalline phases were identified by comparison with the reference data from International Center for Diffraction Data (ICDD) files. The Raman spectra were recorded with a LabRam HR800UV Raman spectrometer (Horiba Jobin-Yvon) equipped with a confocal microscope and liquid-nitrogen cooled CCD detector at ambient temperature and pressure. The emission line at 325 nm from He–Cd laser (Melles Griot Laser) was focused on the sample under microscope. The time of acquisition was adjusted according to the intensity of Raman scattering. The SEM images were collected with a JEOL 630-F microscope. Before measurements, samples were dispersed on a steel plate surface and coated with Pt metal. The TEM images were obtained on a JEM-2010 (JEOL) instrument equipped with a slow-scan CCD camera and at an accelerating voltage of 200 kV. Samples were sonically dispersed in ethanol and deposited on a carbon coated copper grid before examination.

The TPR and TPD measurements were made on a Pulse Chemisorb 2705 (Micromeritics, USA) instrument. Before the TPR measurements, the sample was preconditioned by passing dry air (20 ml/min) at 400 °C for 2 h next the temperature was brought down to 100 °C. The TPR was run from 100 to 700 °C at a heating rate of 10 °C/min in 5% H_2 and argon gas mixture. For TPD measurements, a high purity CO_2 was adsorbed at 100 °C for 30 min and purged at the same temperature with helium gas (20 ml/min) to remove the physisorbed gas. The TPD run was then conducted from 100 to 700 °C at a heating rate of 5 °C/min.

2.3. Catalyst activity

The catalytic activity for vapor phase ODH of EB was investigated in a down flow fixed-bed stainless steel microreactor [36]. For each run, ~1.0 g of sample was loaded in the reactor. The reactor was heated to 600 °C at a rate of 2 °C/min in the flow of N_2 (20 ml/min) and kept at this temperature for 2 h and the N_2 was replaced with CO_2 gas. The catalyst pretreatment was continued at 600 °C for 30 min with CO_2 (20 ml/min) before conducting the reaction. The EB was introduced into the preheating zone of the reactor through a liquid feed pump with a constant feed rate of 9.8 mmol/h. Gaseous and liquid products were analyzed simultaneously by an on-line gas chromatograph (Younlin Instrument, Acme 6000 Series, Korea) equipped with TCD and FID. For analysis of liquid products, HP-innowax column (30 m long, 0.32 mm i.d. and 0.25 μm film thickness) was employed and for the gaseous products Porapak N 80/100 column (6 ft × 1/8 in.) was used. The main liquid products that were analyzed include styrene, benzene, toluene, benzaldehyde and acetophenone, and the gaseous products were hydrogen, methane, carbon monoxide and carbon dioxide.