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MoO_3 Nanoclusters Decorated on TiO_2 Nanorods for Oxidative dehydrogenation of ethane to ethylene

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ABSTRACT

Preparation of metal oxide supported nanostructure appears to be interesting and challenging because of the well-defined morphology and highly accessible active sites responsible for catalysis. Here we present an easy approach to synthesize a novel hybrid material composed of highly dispersed MoO_3 nanoclusters on TiO_2 nanorods of diameter 80–150 nm and length between 1–1.5 μm. These hybrid nanostructure catalysts exhibited excellent oxidative dehydrogenation activity for the conversion of ethane to ethylene with an ethylene yield of 50.7% in the presence of O_2. The result shows markedly high synergy between the surface Mo^{+6} and ultrathin TiO_2 nanorods, which selectively activates the C—H bond of ethane for the production of ethylene.

1. Introduction

The demand for light olefins, serve as feedstock for the synthesis of a wide variety of chemicals, is increasing contentiously. Ethylene is one of the main building blocks in the petrochemical industry and used as a feedstock for numerous processes like the production of ethylene oxide, ethylbenzene, a precursor to ethylene glycol and styrene, etc. Global annual ethylene production is increasing gradually in ethylene production over the last 25 years and over 143 million tons per annum (mtpy) of ethylene are produced and used in 2013, worldwide [1,2]. Based on the abundant accessibility of the light hydrocarbon; ethane is mainly derived from natural gas or naphtha cracking. Naphtha cracking in the presence of steam remains the major source of ethylene globally [3,4], but the high endothermicity of this process consumes a lot of energy and produces a heavy amount of coke. The industrial method for the production of ethylene is referred to steam cracking, which is a very energy intensive process and required extremely high temperature (>800 °C). Also, the process produced CO_2 (1.5-3 tons of CO_2 per ton of ethylene produced) [4–6], a greenhouse gas is the main disadvantage of this process. Moreover, the restrictions for COx, NO_x emission will drive the investors toward energy-efficient and environmentally friendly production of ethylene in the near future. Compared to the conventional steam cracking method of dehydrogenating alkanes to olefins and current catalytic dehydrogenation processes, oxidative dehydrogenation (ODH) could reduce costs, lower greenhouse-gas emissions, and save energy [5–7]. Therefore, oxidative dehydrogenation (ODH) of ethane can be considered as environmentally benign in contrast to the other available processes. The associated capital and operational cost can be reduced by eliminating the need for a furnace and decoking shutdowns, lowering operating temperatures, reducing material demands and using a greater proportion of the alkanes in the olefin conversion process. Besides, only 48–50% yield can be obtained in the existing steam cracker[8], and for ODH process, a maximum yield of 45–60% can be achieved [9]. In this context, oxidative dehydrogenation of ethane has grown much interest as the potential alternative to produce high ethylene yield compare to any other processes. Considerable effort has been made on ODH of ethane with Ni, Mo and W based catalyst over group 5 metals [10–17]. These results also suggest that the catalyst support can affect ODH performance.

Materials with controlled size, shape, composition and internal structural assemblies from different synthetic strategies have been extensively studied [18], because it allows the properties of nanocrystals to be tailored, thus enhancing their application for nano-reactors, drug delivery, gas sensors, catalyst, energy stor-

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age, photons adsorbent materials and biomedical research [19–23]. Shape-controlled TiO_2 nanomaterials have attracted considerable research interest because of their enormous potential application as catalytic support materials, photocatalyst, and solar cell application, intercalated electrodes for Li-ion batteries and as super capacitors [24–28]. Although, over the past decade, a large number of synthesis methods have been applied to fabricate TiO_2 nanostructures; including sol-gel method, template-assisted method, seed growth method and hydrothermal processes [29–32], but the preparation of TiO_2 nanostructure with controlled shape and size are still a challenge for the researchers. There are several reports of the preparation of nanostructured TiO_2, (a comparison can be found in Table S1; in supporting information) but most of the preparation methods involve the use of hazardous inorganic acids such as HF, HCl etc. and the question of reproducibility not been claimed in most of the cases [33,34]. In contrary, support materials in nanometer range have presented improved physical and chemical properties compare to their bulk counterpart[35] and have been proven to be beneficial, especially in catalysis [36–38]. Therefore, the precise modification of surfaces of those supported nanomaterials by changing the shape and size could facilitate the control tuning of the catalytic properties [39]. Nanoclusters (of <1 nm) have approximately □50% atom located on the external surface and have their valence and co-ordination sphere not fully saturated, and hence they show very high activity in catalysis [40]. The preparation of nanoclusters supported on nanocrystalline metal oxide remains a challenge for the catalysis researchers [41,42]. We report a simple preparation of highly dispersed MoO_3 nanoclusters supported on TiO_2 nanorods. The preparation method is very simple and large quantity (up to 20 g) material can be obtained in a single batch.

In this work, we demonstrate a simple method for the preparation of highly dispersed MoO_3 nanoclusters supported on TiO_2 nanorods, and it was found that the material is highly active for the oxidative dehydrogenation of ethane to ethylene in a continuous process at atmospheric pressure. An ethane conversion of 55.2% with ethylene selectivity of 92.1% can be achieved without any severe deactivation up to 80 h over the catalyst.

2. Experimental section

2.1. Materials synthesis

A typical preparation of ultrathin TiO_2 nanorods are as follows: 5 ml titanium isopropoxide were taken in 75 ml ethanol, and 0.2 g octadecyldimethyl (3-trimethoxy silylpropyl) ammonium chloride was added drop wise under vigorous stirring [43,44]. The pH of the mixed solution was adjusted to 7–10 by the addition of 1(M) NaOH solution. Finally, the mixing gel was heated at 80 °C for 1–2 h. The resultant mixture was transferred to a Teflon-lined stainless steel autoclave at 180 °C for 24 h. The white precipitate (TiO_2) was collected by filtration, washed thoroughly with distilled water, ethanol and dried at 100 °C overnight. Finally, the dried TiO_2 material was subjected to calcination at 700 °C with a temperature ramp of 1.5 °C/min in air for 4 h. After successful calcination 0.9–1.1 g, TiO_2 nanorod was obtained per batch.

Supported Mo catalyst was prepared by the following method; 0.2108 g (1.04 mmol) $MoCl_3$ was mixed with 30 ml ethanol under continuous stirring. 1.04 mmol PVP-40 (Polyvinylpyrrolidone-40) were added dropwise, and the solution was kept at 60 °C for 30 min. Then, 2 g prepared TiO_2 was suspended with 20 ml ethanol with continuous stirring for 1 h and mixed with the Mo-PVP mixture very slowly and stirred for another 2 h at 60° C. The mixture was dried overnight at 80 °C and calcined at 700 °C for 4 h in the air. The prepared catalysts were denoted as (Mo wt%)Mo/TiO_2. For comparison purpose, we also prepared Mo catalyst using commercial TiO_2 (~21 nm particle size) nano-powder and the catalyst were denoted as 5%Mo-TiO_2^{NP}. The catalyst was also prepared by physical mixing with commercial TiO_2 and commercial MoO_3 (5% wt. respect to TiO_2) and denoted as 5%Mo-TiO_2^{PM}. The catalyst prepared by co-precipitation method by taking titanium isopropoxide, and $MoCl_3$ is denoted as 5%Mo-TiO_2^{CP}. The catalyst prepared by conventional impregnation method by taking $MoCl_3$ using prepared TiO_2 nanorods and denoted as 5%Mo-TiO_2^{Imp}.

2.2. Oxidative dehydrogenation of ethane

The oxidative dehydrogenation of ethane to ethylene was carried out in a fixed-bed down flow quartz reactor at atmospheric pressure. Typically 200 mg palletized granular catalyst (followed by sieved, 0.180 mm) diluted with 5% porcelain beads was placed in between two quartz wool plugged in the center of the 6 mm quartz reactor. ODH of ethane was carried out in the temperature range between 350 to 650 °C. The gas hourly space velocity (GHSV) was varied between 10000 ml g^{-1} h^{-1} to 30000 ml g^{-1} h^{-1} with a molar ratio of C_2H_6:O_2: He of 1:1:8. The reaction products were analyzed using an online gas chromatography (Agilent 7890A) equipped with a flame ionization detector using Al_2O_3/KCl capillary column (for analyzing C_1-C_4 gases) and thermal conductivity detector using PoraPak-Q (for analyzing O_2 and CO_2) and molecular sieve (for analyzing H_2). The conversion and selectivity of the catalyst were calculated as:

$$Conversion\quad (mole\%) = \frac{Moles\ of\ ethane\ reacted\ (mole\%)}{Moles\ of\ ethane\ initially\ used\ (mole\%)}\ x\ 100$$

$$Selectivity\ (mole\%) = \frac{Moles\ of\ products\ (mole\%)}{Moles\ of\ ethane\ reacted\ (mole\%)}\ x\ 100$$

2.3. Materials characterization

The microstructures of the catalyst surfaces of the samples were observed using scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM-EDS) (FEI Quanta 200 F), field emission scanning electron microscopy (FE-SEM) (FEI Quanta 200 F), and transmission electron microscopy (TEM) (JEM-2010DM, JEOL). The crystal structure was confirmed by powder X-ray diffraction (XRD) (Bruker D8 Advance, Bruker Corp.) using Cu Kα (λ = 0.154 nm) as an incident beam. The BET surface area of the catalysts was examined by N_2 adsorption-desorption isotherms at −196 °C (Belsorbmax, BEL, Japan) using BET equation. Pore size distributions were determined using Barrett-Joyner-Halenda (BJH) model of cylindrical pore approximation. Raman spectrum of the sample was measured using a micro-Raman spectroscope (XploRA, HORIBA, Ltd.). The incident light used for the experiments was a 532 nm semiconductor laser. The chemical state of the samples was carried out by X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Scientific Corp.). The monochromatized X-ray Mg Kα radiation (1253.6 eV) was used. The core levels were calibrated by reference to the first component of the C ls core level peak (unfunctionalized hydrocarbons) set at 284.6 eV. Extended X-ray absorption fine structure spectroscopy (XAFS) measurements of Cu-K edge were carried out at the High Energy Accelerator Research Organization (KEK-IMMS-PF), Tsukuba, Japan. The EXAFS spectrum of the fresh catalyst was measured in the transition mode, whereas for the spent catalyst the EXAFS spectrum was measured in the fluorescence mode using a Lytle detector with Ar gas and spectra were taken at BL-7C and BL-9C at the Photon Factory, Tsukuba, Japan. The electron storage ring was operated at 2.5 GeV and 450 mA; synchrotron radiation from the storage ring was monochromatized by a Si(111) channel-cut crystal. Ionized chamber, which was used as detectors for incident X-ray (Io) and transmitted X-