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Promoted catalytic performances of highly dispersed V-doped SBA-16 catalysts for oxidative dehydrogenation of ethane to ethylene

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ABSTRACT

V-doped SBA-16 catalysts (V-SBA-16) with 3D nanocage mesopores have been successfully synthesized by a modified one-pot method under weak acid condition. The obtained materials were characterized by means of small angle XRD, N_2 adsorption–desorption, TEM, UV–Vis and UV-Raman spectroscopy. These characterization results indicated that well-order mesoporous structures were maintained even at higher vanadium loadings and high concentration of VO_x species were incorporated into the framework of SBA-16 support. The catalytic performances of V-SBA-16, V/SBA-16 and V/SiO_2 catalysts were comparatively investigated for the oxidative dehydrogenation of ethane to ethylene. The highest selectivity to ethylene of 63.3% and ethylene yield of 25.6% were obtained over 1.0V-SBA-16 catalyst. The superior catalytic performance of V-SBA-16 catalysts could be attributed to the presence of isolated framework VO_x species, the unique structure of SBA-16 support and weak acidity. Moreover, V/SiO_2 catalyst exhibited relatively poor catalytic activity duo to the formation of V_2O_5 nanoparticles on the surface of SiO_2 support and the low dispersion of VO_x species. These results indicated that the catalytic performances of the studied catalysts were strongly dependent on the vanadium loading, the nature and neighboring environment of VO_x species and the structure of support.

1. Introduction

With the rapid development of economy, the global demands for ethylene which is an important chemical raw material are increasing rapidly [1]. At present, ethylene is mainly produced via steam cracking of long chain hydrocarbon, fluid-catalytic cracking of gas oils [2]. Unfortunately, these processes are very energy intensive. The catalytic oxidative dehydrogenation of ethane to ethylene (ODHE) with molecular oxygen as oxidant is of great potential to be an alternative process for producing ethylene in the future, in which neither high-energy input nor regeneration of the catalysts is necessary. Moreover, ethane from natural gas sources or shale gas is cheaper than long chain hydrocarbon or oil, and the process of ODHE could be operated at relatively low reaction temperature in the range of 250–650 °C.

The selectivity to ethylene is limited due to the unselective combustion pathways, therefore, the research and development of efficient catalysts are key issues for ODH of ethane. Over the past few decades, numerous research works focusing on different catalytic systems for ODH of ethane have been done [3–8]. The majority of these catalysts studied in literature were transition metal oxides because of their excellent redox ability and acid–base properties to activate oxygen and ethane [9], particularly vanadium oxides (VO_x) as the essential component. However, bulk V_2O_5 sample is inactive for ODH of ethane to ethylene. In fact, the catalytic performances were improved by the proper deposition of VO_x species on the surface of various support, such as Al_2O_3 [3,4], Nb_2O_5 [5] and MCM-41 [10]. Martin et al. [4] prepared a series of V_2O_5/Al_2O_3 catalysts by varying Al_2O_3 supports for ODH of ethane, and the best catalytic performance was obtained over γ-Al_2O_3 with high surface area (200–300 m^2/g) supported VO_x species. However, the selectivity of ethylene was less than 60%. Čapek et al. [8] reported a positive effect of the selectivity to ethylene due to the formation of isolated monomeric and oligomeric VO_x species over mesoporous support. A clear relationship between the kinds of vanadia species and the selectivity of ethylene was observed and oligomeric tetrahedrally coordinated VO_x species favored the improvement of selectivity to ethylene. These literature results and considerations indicated that the

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dispersion and nature of formed VO_x species could be affected by the special structures and characters of support material, the vanadia loading and the specific alkane feed, thus affected the catalytic performances of V-based catalysts. In a sense, the effect of different supports on the dispersed surface VO_x species is very important. However, there are few literature reports concerning the mesoporous materials as carrier to support or incorporate vanadium oxide for ODHE due to the partial cleavage of Si–O–V bonds under reaction conditions, which is also able to reduce the stability of catalysts. Because of the large surface area, well-defined channel systems, uniform pore size and good thermal stability, mesoporous materials-supported metal oxide catalysts have been reported to exhibit superior catalytic performances for various catalytic reactions, such as benzene hydroxylation [11], oxidative dehydrogenation of propane to propylene [12] and selective oxidation of ethylbenzene [13].

The supported vanadia catalysts with weak support–O–V bonds and V_2O_5 microcrystallites by traditional impregnation method, even at low vanadium loadings showed the low catalytic activity [14]. In order to solve these problems, we have adopted the active metal to incorporate into the framework of mesoporous materials for ODHE to control the dispersion of VO_x active sites, change the neighboring environment of vanadia species and increase the content of highly dispersed VO_x species with tetrahedrally coordinated. Mesoporous SBA-16 material with unique 3D cubic channel structure has been applied to the heterogeneous catalysis and these catalysts showed superior catalytic performance [15–17]. In our recent work, we explored the catalytic performances of Mo-SBA-16 catalysts for ODHE [17], and found that the framework-incorporated Mo-SBA-16 catalysts presented a good catalytic performance at high temperature ($>$ 600 °C). However, the yield of ethylene was low below 550 °C (less than 12%). Consequently, there is an attempt for improving the yield of ethylene at relatively low temperatures. Up to now, vanadium-based catalysts are proved to be effective for ODHE. Although V-doped SBA-16 (V-SBA-16) has been synthesized under strong acid condition in the literature [13,18], the range of V:Si molar ratio was relatively narrow and the materials were not applied for ODHE. In this work, the synthesis method of V-SBA-16 has been improved in order to increase the content of vanadium in the framework of SBA-16. Moreover, we focus on studying the effect of support and dispersion of VO_x species on the catalytic performance for ODHE in range of 500 °C to 600 °C. Here, 3D cubic V-SBA-16 materials with nanocage mesopores were prepared by utilizing the modified literature method under weak acid condition and the catalytic performances of V-SBA-16, V/SBA-16 and V/SiO_2 were comparatively investigated.

2. Experimental

2.1. Synthesis of catalyst

V-doped SBA-16 catalysts (V-SBA-16) were synthesized by a modified literature method [13,18]. Pluronic F127 (2 g) and 37.5 wt% HCl (4.2 g) were added into 95 g deionized water at 38 °C. After fully dissolved, 6.0 g BuOH (1-butanol) was added until well mixed. After stirring for 2 h, 10 mL TEOS (tetraethyl orthosilicate) and the required amount of NH_4VO_3 (ammonium metavanadate) were added simultaneously. The homogeneous mixture was kept under stirring for 24 h at 38 °C and then transferred into Teflon-lined autoclave for crystallization another 24 h at 100 °C. After cooling to room temperature, the pH value of the obtained mixture was adjusted up to 5.0–6.0 by adding $NH_3{\cdot}H_2O$ dropwise and sequentially stirred at 38 °C for 24 h. And the final product was filtered, washed again and again, dried at 80 °C overnight and calcined under air atmosphere at 550 °C for 6 h.

The siliceous SBA-16 support was prepared by the same procedure except for the addition of NH_4VO_3. SBA-16-supported vanadium (V/SBA-16) and SiO_2 (V/SiO_2) (silica Cabot Aerosil as support, BET area 200 m^2/g) catalysts were prepared by the ultrasound assisted incipient wetness impregnation. The support materials (SBA-16 and SiO_2) were added to the equal volume of NH_4VO_3 solution. The mixture were stirred at room temperature for 30 min and ultrasonically treated for 30 min. Then the impregnated catalysts were dried under a vacuum oven at 50 °C for 24 h. Finally, the catalysts were calcined at 550 °C under air atmosphere for 6 h. The prepared V-based catalysts were denoted as xV-SBA-16, yV/SBA-16 and zV/SiO_2, in which x, y and z represented the nominal vanadium molar percentage (x: 0.1∼8.0; y: 0.05∼5.0; z: 0.5).

2.2. Characterization of catalyst

Small-angle X-ray diffraction (SAXRD) patterns were analyzed using a powder X-ray diffractometer (Bruker D8 Advance) using Cu $K\alpha$ ($\lambda = 0.15{,}406$ nm, 40 kV and 40 mA) in the range of 0.5°–5°. The practical vanadium loadings were analyzed utilizing inductively coupled plasma atomic mass spectrometry (ICP) allied analytical system on Perkin–Elmer Optima 7300 optical emission spectroscopy spectrometer. N_2 adsorption–desorption isotherms were recorded using a Micromeritics TriStar II 3020 porosimetry analyzer. All samples were dehydrated at 350 °C for 3 h. The specific surface area was calculated by the BET (Brunauer–Emmett–Teller) method and the pore-size distribution was determined by the BJH (Barrett–Joyner–Halenda) method using the desorption branch of the isotherm. TEM (transmission electron microscopy) images were obtained using a JEOL JEM-2100 electron microscope equipped with LaB_6 filament equipment as the source of electrons operating at 200 kV. The diffuse reflectance ultraviolet-visible (UV–Vis) spectra between 200 and 800 nm were recorded on a Hitachi U-4100 equipped with an integration sphere and $BaSO_4$ was used as a reference. UV- Raman spectra of dehydrated samples were obtained by a Renishaw inVia Reflex Raman spectrometer with UV laser excitations (244 nm). The laser power at the samples was kept at 1 mW. The dehydration was operated by heating the catalysts in situ cell of 10% O_2/He mixed flow (60 mL/min) from 20 to 550 °C and the spectra acquisition composed of eight accumulations of 100 s. NH_3-TPD measurements were carried out on a self-made apparatus. Firstly, 0.2 g sample was pre-heated from 25 °C to 600 °C for 2 h. Then, it was cooled to room temperature in N_2 flow. Secondly, NH_3 was adsorbed at 25 °C for 30 min, and the sample followed a purge with N_2 flow for 30 min. Finally, the sample was heated to 600 °C at a rate of 10 °C/min, and the NH_3 desorption signal was monitored by TCD.

2.3. Catalytic activity measurements

The catalytic activities of ODHE were tested in a fixed bed quartz reactor (i.d. 12 mm) with an electric furnace and the reaction temperature ranged from 500 to 600 °C. And the feed composition was 25.5 vol% C_2H_6:8.5 vol% O_2:64 vol% N_2 with a total flow of 22 mL/min. In a typical process, 0.3 g catalyst with the granularity of 40–60 mesh which was diluted with 1.0 g silica sand with same size was filled in the center of reactor tube and was pre-activated at 550 °C for 30 min in O_2 atmosphere. Then the temperature was reduced to 500 °C and the whole system was purged with nitrogen for 10 min and the gas flow was switched from O_2 to the reactants mixture. After the initiation of reaction, the temperature was raised gradually from 500 to 600 °C (25 °C per step) and was held constant for 60 min at each reaction step. The reactants and products were analyzed by on-line gas chromatographs (SP3420, Beijing, China) equipped with two flame ionization detectors (FID) and two methane converters operating at 380 °C