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FULL LENGTH ARTICLE

Selective nano alumina supported vanadium oxide catalysts for oxidative dehydrogenation of ethylbenzene to styrene using CO_2 as soft oxidant

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Abstract Nano alumina-supported V_2O_5 catalysts with different loadings have been tested for the dehydrogenation of ethylbenzene with CO_2 as an oxidant. High surface area nano-alumina was prepared and used as support for V_2O_5 as the catalyst. The catalysts were synthesized by impregnation techniques followed by calcinations and microwave treatment, denoted as V_2O_5/γ-Al_2O_3-C and V_2O_5/γ-Al_2O_3-MW, respectively. The V_2O_5 loading was varied on nano-alumina from 5 to 30 wt%. The support and catalysts were characterized by X-ray diffraction (XRD), Barett–Joyner–Halenda (BJH) pore-size distribution, N_2-adsorption isotherms, Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and temperature programed desorption (TPD-NH_3). The characterization results indicated that V_2O_5 is highly dispersed on alumina up to 30%-V_2O_5/γ-Al_2O_3-MW prepared by MW method. The TPD studies indicated that there are significant differences in acid amount and strength for V_2O_5/γ-Al_2O_3-C and V_2O_5/γ-Al_2O_3-MW-catalysts. The catalytic activity of the prepared catalysts was evaluated in the temperature range 450–600 °C in relation to the physicochemical properties and surface acidity. The results revealed that optimum catalytic activity and selectivity (~100%) toward styrene production were obtained using 10% V_2O_5/γ-Al_2O_3-MW catalyst treated with microwave.

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1. Introduction

The dehydrogenation of alkylbenzenes is a commercial process used for the production of alkenylbenzenes monomers such as divinylbenzene and styrene. The catalytic dehydrogenation of ethylbenzene to produce styrene, as a representative process, is performed in industry over promoted iron oxide catalyst in the presence of a large quantity of steam, at high tempera-

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ture of 600–700 °C [1–4]. Since the process is equilibrium –limited and energy intensive, there is a great interest, recently, for the development of an alternative methodology. Thus, the use of CO_2, as a soft oxidant, in the selective catalytic oxydehydrogenation of ethylbenzene has been widely investigated [5–8]. The process should be energy saving and environmentally friendly in respect of utilization of CO_2 which is one of the greenhouse gases causing global warning, and the energy required is much lower [8]. In addition, CO_2 can decrease the partial pressure of reactants more effectively than steam and it has highest heat capacity among various typical gases (9, 10). Further, in the presence of CO_2, coupling between reverse water gas shift ($CO_2 + H_2 \leftrightarrow CO + H_2O$) and dehydrogenation reaction becomes more favorable [4,10–12].

Several catalysts exhibited high catalytic activity for the dehydrogenation of ethyl benzene in presence of CO_2 [6–9,13–16]. Among these catalysts, vanadia supported on alumina (VO_x/Al_2O_3) catalysts, were more stable and exhibited better performance for oxidehydrogenation of ethyl benzene with CO_2 [8,13–17].

On the other hand, it is well known that the physical and chemical properties of support have an important effect on catalytic activity [18,19]. Thus, high specific surface area helps the active component of catalysts to disperse well and is extremely beneficial in improving catalytic activity. In this respect, nano alumina particles with the features of large specific surface and high reactive activity are used as carriers for petroleum cracking catalysts [20]. The crystal phase, specific surface area, pore distribution and other physical–chemical properties of nano-alumina particles specific to the needs of catalytic reactions can be obtained by changing the preparation conditions of nano-alumina particles [21].

Herein, we report the preparation of nano alumina by two methods, conventional and microwave method. The prepared nano-alumina was used as support for V_2O_5 catalysts. The performance of prepared catalysts is discussed from different faces.

2. Materials and methods

2.1. Material preparation

Aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$, 95%; Merck), sodium carbonate (Na_2CO_3, 98%; Merck) and deionized water were used as starting chemicals. $Al(NO_3)_3{\cdot}9H_2O$ (25 g, 0.066 M) solution and Na_2CO_3 (10.38 g, 0.125 M) solution were dissolved in 600 mL of deionized water, separately. Then Na_2CO_3 and $Al(NO_3)_3{\cdot}9H_2O$ solutions (from two separate burettes) were added drop by drop into a 2-L capacity round-bottom flask containing 60 mL of ethylene glycol dissolved in 400 mL of deionized water under stirring to precipitate Al^{3+} cations as hydroxides form. The pH of the solution was adjusted in the range of 7.5–9 using HNO_3 and/or NaOH (Merck, GR). The precipitate was aged at 70 °C for 3 h, filtered off and washed several times with water/ethanol (70/30; wt/wt) until solution free Na and NO_3 ions are obtained. The white precipitate was dried at 100 °C overnight and calcined in a programmable furnace at 550 °C with heating rate of 2 °C min^{-1} for 5 h in air to produce γ-Al_2O_3 powder [22].

A series of 5–30%VO_x@Al_2O_3 catalysts were prepared from solutions of ammonium metavanadate (NH_4VO_3; Merck, >99%) and oxalic acid (Alfa Products, UK). Thus, the obtained mixture was divided into two equal parts [5,6,27]:

Part I, required amount of NH_4VO_3 that gives 5–30% of V_2O_5 was dissolved in adequate amount of water in the presence of oxalic acid (NH_4VO_3/oxalic acid = 75.1 wt%). The solution was added to γ-Al_2O_3 powder with solution impregnation method. After 2 h the catalyst was heated to 80 °C under stirring to vaporize the excess water and then dried at 110 °C for 5 h. Finally, the mixture product was calcined in air at 600 °C with ramping rate of 2 °C/min for 5 h and the prepared catalysts are denoted as C1, C2, C3 & C4 for 5, 10, 20 & 30% V_2O_5/γ-Al_2O_3 respectively.

Part II, the previous solution of NH_4VO_3-oxalic acid mixture was precipitated on γ-Al_2O_3 with a ratio of 5–30% at ambient temperature under stirring for 2 h. Then the mixture was subjected to microwave energy radiation (300 W; 10 s on and 20 s off for 10 min) to obtain vanadium oxide supported on γ-Al_2O_3. After self-cooling of mixture, the catalyst was filtered off, dried at 50, 80, and 110 °C for 5, 5 and 2 h, respectively, and the prepared catalysts are denoted as MW1, MW2, MW3 & MW4 for 5, 10, 20 & 30% V_2O_5/γ-Al_2O_3 respectively.

2.2. Characterization methods

X-ray diffractograms were obtained on a XPERT X-ray diffractometer, operating with CuKα radiation (λ = 0.1542 nm) and X-ray radiation (X-ray generator current and voltage set at 40 mA and 45 kV). The diffractograms were recorded in the 2θ range of 4–80° with a 2θ step size of 0.01° and a step time of 10 s.

Fourier transform infrared spectroscopy (FTIR) measurements were performed using Nicolet IS-10 FTIR over the wave number 4000–400 cm^{-1}.

Nitrogen adsorption and desorption isotherms were measured at −196 °C on a NOVA 3200 system (USA). The samples were out gassed for 3 h at 300 °C under vacuum in the degas port of the adsorption analyzer. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) model. The pore size distributions were obtained from the desorption branch of the nitrogen isotherms by the Barrett–Joyner–Halenda (BJH) method.

Thermal stability was carried out in TA Instruments SDTQ 600 simultaneous TGA-DSC thermogravimetric analyzer. The analyses were conducted for a total sample mass of 10.0 ± 0.2 mg. The samples were heated under nitrogen flow (100 ml min^{-1}) from 50 to 750 °C, at 20 °C min^{-1}.

Transmission electron microscopy (TEM) images were recorded on a JEOL 2011 microscope (Japan) operated at 200 kV. Before TEM characterization, the samples were dispersed in ethanol. The suspensions of the samples were dropped on a holey carbon coated copper grid.

Scanning electron microscopy (SEM) pictures were determined on a JEOL JSM-6700F field emission scanning electron microscope.

Temperature programed desorption of ammonia (NH_3-TPD) was measured on a CHEMBET 3000 chemical absorber (Quantachrom). Before measurements, the samples were firstly activated at 500 °C for 1 h under helium atmosphere. After the temperature cooled down to 100 °C, the samples were swept by ammonia for 1.5 h, then the gas was switched into helium to remove the physically adsorbed ammonia molecules, until the baseline was flat. After this,