Butadiene production from bioethanol and acetaldehyde over tantalum oxide-supported ordered mesoporous silica catalysts

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ABSTRACT

A series of ordered mesoporous silica (OMS) supported tantalum oxide samples (Ta/OMS) were tested as catalysts for the production of 1,3-butadiene (BD) from ethanol and acetaldehyde. To study the influence of the type of mesostructure, the pore size, and the particle morphology on the performance of the catalyst, Ta/OMS catalysts were prepared using two different mesostructured silica supports (2-D hexagonal SBA-15 and 3-D cubic KIT-6) and five different 2-D hexagonal OMS supports (SBA-15 series and MMS) with varied mesopore diameters in the range of 2.5–10.9 nm. The obtained Ta/OMS catalysts were characterized by a nitrogen physisorption analysis and X-ray diffraction, as well as by scanning electron micrography. The catalytic results showed that the pore size and crystal size of OMS samples are more important than mesopore structure such as pore dimension and pore shape to optimize the catalytic performance of Ta/OMS catalysts for BD production from ethanol and acetaldehyde.

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1. Introduction

1,3-Butadiene (BD) is an important chemical intermediate material in the petroleum chemical industry. BD is generally used as a starting material for commercially important synthetic rubbers and polymers such as styrene–butadiene rubber, polybutadiene, styrene–butadiene latex, acrylonitrile–butadiene–styrene polymer and nitrile rubber [1]. Recently, BD has received more attention due to the rapid economic growth of developing countries such as China and India.

Nowadays, the dominant technology for the production of BD is the naphtha cracking process, where BD is obtained as a co-product. However, the increasing rate of BD demand may lead to a serious shortage in BD production by current naphtha cracking processes. Moreover, in order to cope with the depletion of petroleum reserves, high oil prices and environmental issues including global warming, it is crucial to develop alternative technologies for BD production from renewable, non-petroleum resources such as bioethanol. Bioethanol is one of the most abundant sustainable raw materials of "bio-carbon" sources today [1,2]. Therefore, in the near future, BD production using bioethanol will be the most promising, sustainable and renewable technology among various on-purpose BD production technologies.

The catalytic conversion of ethanol into BD (ETB) is an old industrially proven process which was used from the 1920s to the early 1960s. This process was completely scrapped with increasing oil production after the development of large oilfields. However, the ETB process is becoming more attractive recently as a potential alternative route due to the high oil prices and wide supply of bioethanol. ETB processes are divided into a one-step process developed by Sergey Lebedev using a variety of mixed metal oxide catalysts [1–9] and a two-step process which is also known as Ostromyslensky's process and which was commercialized by Carbide and Carbon Chemicals Corporation in the USA using tantalum oxide silica as a second-step catalyst [10–15]. The two-step process includes partial ethanol dehydrogenation to acetaldehyde as the first step, followed by the transformation of the mixture of ethanol and acetaldehyde into BD as the second step. Both processes have short catalyst regeneration cycles, which are 12 h for one-step process and 120 h for two-step process [10–15], due to rapid catalyst deactivation by coking. This short regeneration cycle should be upgraded by developing catalysts tolerable to coke because it is main cause lowering the efficiency of both ETB processes. Few catalyst studies [16,17] of the two-step ETB process has been reported after several papers [10–15] published in the 1940s. In the previous literatures, several metal oxides including tantalum oxide had been screened simply for a comparison of their activity levels and

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BD selectivity characteristics. Especially, in tantala–silica catalyst system, no study for the influence of the type and properties of silica, which plays a role in support as well as catalyst in two-step ETB reaction, has reported although the type and physicochemical properties of the silica is very important factor for the optimization of the catalyst durability as well as the activity and selectivity in BD production.

The mechanism of the ethanol or ethanol/acetaldehyde to BD is very complicated and is still debating [1,2]. However, several literatures [1,2,9] had reported the following five principal steps: (1) acetaldehyde formation from ethanol; (2) aldol condensation of acetaldehyde to acetaldol; (3) dehydration of acetaldol to crotonaldehyde; (4) Meerwein–Ponndorf–Verley reaction between crotonaldehyde and ethanol to obtain crotyl alcohol and acetaldehyde; and (5) dehydration of crotyl alcohol to BD. Based upon the reaction mechanism, the ETB catalysts should have not only the redox ability but also the proper acidic and basic properties. Thus, the roles of supports as well as active metal oxides are very important.

In this study, a variety of ordered mesoporous silica (OMS) samples were synthesized and examined as a potential new support for a tantalum oxide base catalyst to be used in the two-step process. Moreover, the effect of the physical structure and properties of OMS on the performance of the two-step ETB reaction was examined and optimized by comparing OMS supports with different pore structures, pore sizes and crystal sizes. In this case, we used SBA-15 series, KIT-6 and MMS. This is the first study to apply various OMSs as a support and examine the effect of the pore size, pore structure and morphology of the OMSs on an ETB reaction.

2. Experimental

2.1. Synthesis of ordered mesoporous silica (OMS) supports

The ordered mesoporous silica support SBA-15 with a 2-D hexagonal structure was prepared by the procedure reported by Choi et al. [18]. 33.6 g of triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Aldrich) was fully dissolved in 18.3 g of 0.3 M HCl aqueous solution at 35 °C. After the addition of 54.2 g of tetraethyl orthosilicate (TEOS, Aldrich) to the solution, the mixture was stirred for 1 day and the reaction mixture was hydrothermally treated in a Teflon-lined autoclave at 35–130 °C for 1 day. After the hydrothermal treatment, the resulting white solid product was filtrated and dried at 100 °C in air. Finally, an organic template-free SBA-15 mesoporous silica support was obtained by a calcination process at 550 °C, and the SBA-15 OMS supports were designated as SBA-15-T, where T represents the hydrothermal treatment temperature of the SBA-15 OMS support.

Ordered mesoporous silica KIT-6 material with a 3-D cubic $Ia–3d$ structure was prepared following the process reported by Kim [19]. Briefly, 16.9 g of Pluronic P123 and 18.6 g of n-butanol (Aldrich) were dissolved in an aqueous HCl solution (33.2 g of HCl in 610.1 g of water). After complete dissolution, 43.6 g of TEOS was added to the mixture solution at 35 °C. After magnetic stirring for 1 day at 35 °C, the mixture was aged at 100 °C for 1 day in an oven as a hydrothermal treatment. After the hydrothermal treatment, the solid product was recovered by filtration and dried. The final KIT-6 support was obtained by calcination at 550 °C.

MCM-41-type ordered mesoporous silica MMS support was synthesized using a fluorosilicon compound as a silica source according to a procedure described earlier [20]. A hydrofluosilicic acid solution (H_2SiF_6) was prepared by gradually dissolving 10 g of fumed silica in 32.5 g of 24 wt% HF (Merck) and 25 ml of water. The H_2SiF_6 solution was added to 30.6 g of cetyltrimethyl ammonium bromide (CTMABr, Aldrich) in 600 g of distilled water and stirred at

60 °C for 1 h. A white gel was formed upon the addition of 150 g of 28 wt% NH_4OH solution, and this was vigorous stirred at the same temperature for 1 h. The mixture was moved to an oven and aged at 70 °C for 16 h. After filtration, the solid was washed with water and dried at 100 °C. The dried sample was calcined at 600 °C for 4 h to remove the surfactant.

2.2. Preparation of catalysts

All of the ordered mesoporous silica-supported 2 wt% tantalum oxide (Ta_2O_5) catalysts were prepared by an impregnation method using ethanol as a solvent. 1 g of OMS support was added to 100 ml of ethanol which contained 0.32 g of tantalum pentachloride (TaCl$_5$, Aldrich). After stirring for 2 h, the ethanol was removed by a rotary evaporator and the samples were dried at 120 °C for 10 h. The OMS-supported Ta_2O_5 samples (Ta/OMS) were obtained by calcination at 500 °C for 5 h. For comparison, two different commercial silica gels, Grade 62 and Silica gel 60, were obtained by Aldrich and Merck, respectively, and two different Ta_2O_5-supported commercial silica gels were obtained by the same impregnation method. These are denoted as Ta/Aldrich and Ta/Merck, respectively.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiplex instrument using Cu-Kα radiation (λ = 0.15406 nm) operated at 40 kV and 40 mA (1.6 kW). Nitrogen adsorption isotherms were measured at −196 °C on a Micromeritics Tristar 3000 volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed at 300 °C in a degassing station. The Brunauer–Emmett–Teller (BET) equation was used to calculate the apparent surface area from the adsorption data obtained at P/P_0 between 0.05 and 0.2. The total volume of micro- and mesopores was calculated from the amount of nitrogen adsorbed at P/P_0 = 0.95, assuming that adsorption on the external surface was negligible compared to adsorption in the pores. The pore size distributions (PSDs) were calculated by analyzing the adsorption branch of the N_2 sorption isotherm using the Barret–Joyner–Halenda (BJH) method. The external surface (S_{ext}) area was estimated from the nitrogen adsorption data using the α_s-plot method [21,22] in the α_s range of 1.7–2.7 (exceptionally, 2.2–6.6 for Aldrich and Ta/Aldrich samples). The reference adsorption isotherm reported elsewhere [23] used in these calculations.

Scanning electron micrograph (SEM) images were obtained with a Philips XL-30S FEG scanning electron microscope operated at 10 kV. The samples were coated with gold before the SEM measurement. Transmission electron microscopy (TEM) images were taken from the thin edges of the particles supported on a porous carbon grid, using a Philips Tecnai G220 device operated at 200 kV. Scanning transmission electron microscopy (STEM)/energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were taken with a Tecnai G2 F30 instrument with an accelerating voltage of 300 kV. Coke depositions of catalyst were investigated by recording weight changes on a thermogravimetric analyzer (TA Instruments TGA Q500). Runs under air were carried out with a heating rate of 10.0 °C/min from 100 °C to 700 °C after preheating at 100 °C for 1 h to remove water, reactants and products adsorbed weakly. CHN elemental analysis was carried out by using a Fisons EA 1108 instrument for the determination of the amount of carbon on the catalyst after the reaction.

2.4. Catalytic test

The production of 1,3-butadiene (BD) from ethanol and acetaldehyde was performed in a fixed bed reactor system with a 3/8 in. stainless steel (SUS) tube reactor, as shown in Fig. 1. The