Article

Journal of
Nanoscience and Nanotechnology
Vol. 17, 4322–4325, 2017
www.aspbs.com/jnn

Catalytic Conversion of Bioethanol and Acetaldehyde to Butadiene Over a Tantalum Oxide-Supported Spherical Mesoporous Silica Catalyst in a Circulating Fluidized Bed

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Spherical silicas with mesopore (6 nm) supported tantalum oxide samples (Ta/SMS) were prepared with the impregnation method using different Ta loading amounts for the production of 1,3-butadiene (BD) from ethanol and acetaldehyde (ethanol to BD, ETB). To obtain the optimum Ta loading amount, the Ta/SMS catalysts were first tested in a fixed-bed reactor. The characteristics of the Ta/SMS catalyst was analyzed by scanning electron microscopy, inductively coupled plasma atomic emission spectrometry, and N_2 physisorption analysis. Before testing the catalyst in a hot-bed circulating fluidized bed (CFB) reactor, the mechanical strength and hydrodynamic properties of the Ta/SMS catalyst were examined by using the attrition test and a cold-bed CFB reactor, respectively. The catalytic results in the hot-bed CFB reactor revealed that the Ta/SMS catalyst had a different catalytic performance for production BD, which could be attribution to the feed concentration and circulation rate of catalyst. The hot-bed CFB test for ETB with the Ta/SMS catalyst was stably operated for 140 h, and an average conversion of 56.7% and BD selectivity of 70.5% were obtained.

Keywords: Butadiene, Spherical Mesoporous Silica, Circulating Fluidized Bed, Ta Oxide.

1. INTRODUCTION

1,3-butadiene (BD) is a base chemical, which is used in producing synthetic rubbers and polymers.[1] Among these applications, production of automotive tires is the main use of BD, and the global market for automotive tires is predicted to consistently increase based on the expansion of the automotive market, especially in China and India.[2] This long-term increase in the BD demand rate has attracted many researchers to the manufacturing of BD. Tire manufacturing companies have great interest in BD production from bio-based feed stocks to solve issues related to the global environment and rubber tree crops. Presently, BD is the most difficult component to procure in the supply chain of synthetic polymers and rubbers because BD is produce as a byproduct of ethylene production by steam cracking.[3] However, an increase in the natural gas supply from shale-gas would lead to an increase in the production of ethylene from ethane by ethane cracking, which would result in the long-term decrease in BD production. Therefore, the catalytic conversion of ethanol (EtOH) to BD (ETB) would be a promising and environmentally friendly technology for on-purpose BD-production because ethanol is the most plentiful bio-based feed stock.[1,4,5]

The ETB process is mainly divided into two processes: the Lebedev's (one-step) and Ostromyslensky's (two-step) process.[1,3,4] The two-step process consists of EtOH dehydrogenation to acetaldehyde (AA), and EtOH-AA condensation to BD, which uses a Ta/SiO_2 catalyst. However, ETB processes result in the rapid deactivation of catalysts by coking. To overcome rapid coke formation, ordered mesoporous silica supported tantalum oxide catalysts have been studied in ETB reactions in fixed-bed reactors.[5] To solve the coking problem in the process, circulating fluidized beds (CFBs) can used in ETB reactions for continuous regeneration of deactivated catalysts. From our previous report, the optimum spherical mesoporous silica (SMS) support for a CFB had both moderately large mesopores (~6 nm) with a particle size of 75–150 μm and good attrition resistance.[6] However, we only tested the catalytic activity of Ta/SMS catalysts in a fixed-bed reactor and examined its hydrodynamic properties in a cold-bed CFB test.[6] In this study, the optimum Ta amount in Ta/SMS was examined using a fixed-bed reactor. The optimum Ta/SMS

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 1533-4880/2017/17/4322/004 doi:10.1166/jnn.2017.13404

catalyst was used in a hot-bed CFB reactor, and ETB reactions were carried out under different operational conditions of the hot-bed CFB.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

Commercial SMS (CARiACT Q-6) was obtained from Fuji Silysia. Ta/SMS catalysts with different Ta loading amounts (1.8–3.5 wt%) were prepared with the impregnation method using EtOH as a solvent and $TaCl_5$ (Aldrich) as a Ta precursor. After EtOH removal with a rotary evaporator, the samples were dried at 120 °C and calcined at 500 °C.

2.2. Catalyst Characterization

N_2 isotherms were measured with a Tristar3000 (Micromeritics). The Ta amount of the catalyst was analyzed with inductively coupled plasma atomic emission spectrometry. Scanning electron microscope (SEM) images were obtained with a Philips XL-30S FEG SEM (10 kV). The attrition resistance of the SMS was determined with the ASTM D5757-11 method. Hydrodynamic properties such as the catalyst circulation rate were examined with a cold-bed CFB test.

2.3. Catalytic Performance Tests

The production of BD from EtOH and AA with Ta/Q-6 using different amounts of Ta was performed in a fixed-bed reactor (LHSV = 1.0 h^{-1}, 350 °C).[5,6] The hot-bed CFB test was done with a pilot-scale CFB plant (riser length: 4 m, riser inner diameter: 14.6 mm). A picture of the CFB plant used in the experiments is shown in Figure 1. The effluent gas products were measured with a gas chromatograph (6100GC, Young Lin Ins. Co.).

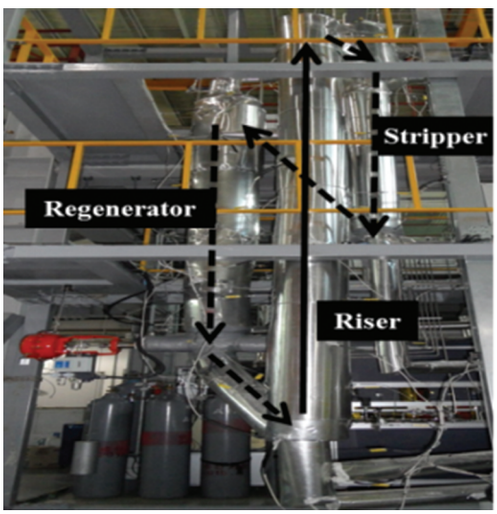

Figure 1. Hot-bed CFB pilot plant.

3. RESULTS AND DISCUSSION

In Figure 2, the SEM image of the Ta/SMS catalyst shows a spherical morphology with a particle size around 75–150 μm (avg. 113 μm). The narrow pore size distribution curve for the Ta/SMS clearly shows that the catalyst has relatively uniform mesopores. The structural properties such as avg. pore size, BET surface area, total pore volume, bulk density, and attrition resistance are 5.7 nm, 322 m^2/g, 0.58 cm^2/g, 0.57 g/ml, and 1%, respectively.

To investigate the effects of the loading amounts of Ta, the catalytic activities of Ta/SMS with different Ta loading amounts were examined in the ETB reaction in a fixed-bed reactor. Figure 3 shows the total conversion of EtOH and AA and the BD selectivity of the Ta/SMS with different Ta loading amounts. All the samples exhibited a gradual decrease in conversion and constant BD selectivity with the time-on-stream due to coke formation. Detailed catalytic activities at 20 h are presented in Table I. The total conversion increased with increasing Ta loading amounts up to 3.0 wt%; however, it decreased at the highest Ta loading amount (3.5 wt%), which might be connected to the dispersion of Ta oxide on the SMS surface.

Before the hot-bed CFB test, the hydrodynamic properties of the Ta/SMS sample were estimated in the cold-bed CFB (Fig. 4). In Table II, the minimum fluidization velocity (U_{mf}) of Ta/SMS is faster than that of the other catalysts

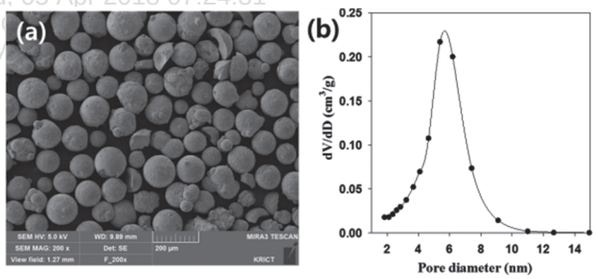

Figure 2. (a) SEM, and (b) pore size distribution of Ta/SMS.

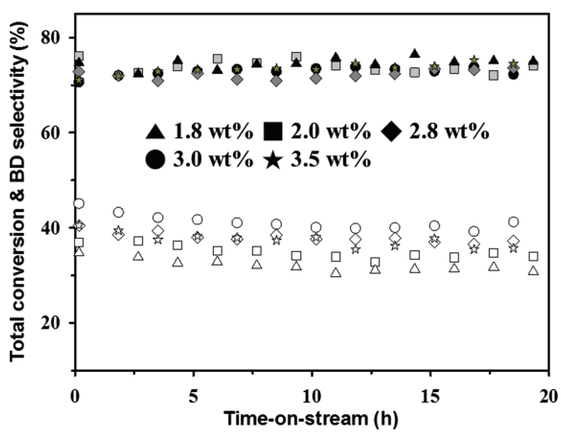

Figure 3. EtOH/AA total conversion (open symbol) and BD selectivity (solid symbol) of the Ta/SMS catalysts with different Ta loading amounts.

Table I. ETB results from Ta/SMS with different Ta loading amounts at 20 h.

Ta (wt%)	Total conv. (%)	Selectivity (C mol%)			
		BD	$C^{a}_{2=}$	DEE[b]	HV[c]
1.8	31.3	74.8	3.4	5.7	16.1
2.0	34.0	74.1	4.1	6.0	15.8
2.8	36.6	73.2	6.1	8.5	12.2
3.0	37.3	75.0	4.6	6.6	13.8
3.5	35.7	74.4	6.0	7.9	11.7

Notes: [a]$C_{2=}$, ethylene; [b]DEE, diethyl ether; [c]HV, heaviers.

Table II. Physical and fluidization properties of Ta/SMS and other CFB catalysts.

Catal.	Mean particle size (μm)	Apparent density (kg/m^3)	U_{mf} (cm/s)	U_{mb} (cm/s)	ΔP_{Umb} (Pa)	Bed expansion (Lf-Lm/Lm)	U_t (m/s)
Ta/SMS	113	2225	1.45	1.53	1215	0.15	0.53
FCC	53	1921	0.26	0.64	1006	0.15	0.18
	90		0.66	1.01	1026	0.14	0.47
	141		1.11	1.27	1055	0.12	0.86
SAPO-34	60	1497	0.19	0.48	991	0.17	0.18

because it has a relatively high particle density. Similar tendencies were observed in the minimum bubbling velocity (U_{mb}) and pressure drop (ΔP). Based on the fluidization properties of Ta/SMS, to circulate Ta/SMS, the minimum gas velocity should be larger than 0.53 m/s, and the contact time would be shorter than 7.5 s. The optimum ETB catalyst, 3.0 wt% Ta/SMS, was loaded into the hot-bed CFB. To evaluate the reaction conditions, we performed a hot-bed CFB test with different feed concentrations and catalyst circulation rates (CCRs) for the Ta/SMS catalyst at 350 °C. In Figure 5, the conversion decreased with an increase in the feed concentration and C_4 olefin (BD, $C_{4=}$) selectivity slightly increased (Table III). A lower feed concentration indicates a lower weight hourly space velocity (WHSV), which would increase the conversion. In addition, a high feed concentration may facilitate the formation of C_4 olefins due to the increased possibility of EtOH-AA condensation. An increase in the CCR led to a decrease in

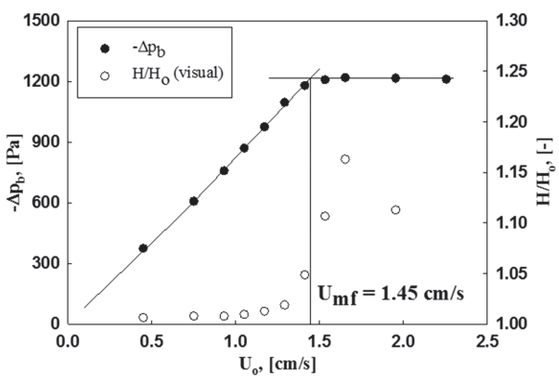

Figure 4. Pressure drop of Ta/SMS with superficial gas velocity (U_o).

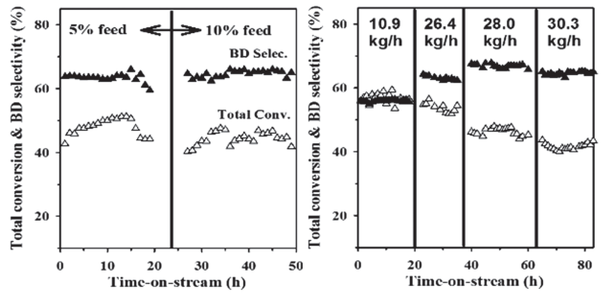

Figure 5. Catalytic results in the hot-bed CFB with different feed concentrations (left), and CCRs (right).

Table III. ETB results for different operating conditions in a hot-bed CFB.

Feed Conc. (%)	Circulation rate (kg/h)	Total conv. (%)	Selectivity (C mol%)				
			BD	$C_{2=}$	$C_{3=}$	$C_{4=}$	DEE
5	26.4	50.4	63.8	26.6	3.9	0.9	4.8
10		45.4	64.9	22.4	4.0	2.2	0.8
10	10.9	57.1	55.8	25.9	3.7	4.8	8.6
	26.4	53.7	62.9	17.5	3.1	3.3	9.6
	28.0	46.9	66.9	15.5	3.2	1.5	9.2
	30.3	42.8	64.7	17.5	3.5	1.0	7.7

the conversion at the same feed concentration. The conversion is relative to the residence time of the catalyst in the riser of the hot-bed CFB. As the CCR increases, the residence time decreases, which subsequently lowers the conversion. From these results, the optimum operating condition for the ETB reaction with the highest BD selectivity in a CFB is a feed concentration of 10% and a CCR of 28.0 kg/h.

Finally, to verify the availability of the Ta/SMS catalyst in the ETB reaction using a hot-bed CFB reactor, a longevity test was done using the optimum operating conditions for 160 h (Fig. 6). After an initial reaction stabilization time (<20 h), the conversion and BD selectivity only showed slightly fluctuations, and the CFB reactor stably operated for 20–160 h without catalyst deactivation.

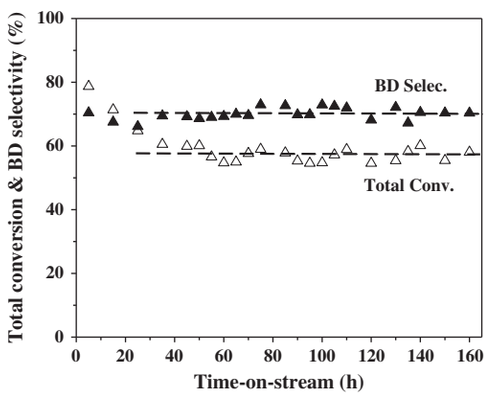

Figure 6. ETB hot-bed CFB results with the Ta/SMS catalyst for 160 h.

The avg. conversion and BD selectivity were 56.7% and 70.5%, respectively. After the longevity test, the spent and regenerated Ta/SMS catalysts were obtained from the CFB reactor. The morphology and particle size of the catalyst from the reactor was the same as those from fresh catalyst in the SEM analysis (data not shown). In addition, TGA analysis of the spent catalyst showed 0% coke. These results indicate that Ta/SMS regenerated well without particle breakdown during CFB operations.

4. CONCLUSION

The SMS supported Ta oxide was prepared as a catalyst for application in the ETB reaction in a hot-bed CFB. The optimum Ta amount in the catalyst was evaluated using a fixed-bed reactor, and the 3.0 wt% Ta/SMS catalyst had the highest catalytic activity for the ETB reaction. This optimum catalyst was loaded into a hot-bed CFB reactor and examined under different operating conditions. The optimum operating conditions were a feed of 10% and a CCR of 28.0 kg/h. Stable performance for the ETB reaction was achieved in the hot-bed CFB test using the optimum operating conditions. We observed an average conversion of 56.7% and BD selectivity of 70.5% for 140 h.

Acknowledgments: This work was supported by funding from the R&D Convergence Program of MSIP (Ministry of Science, ICT and Future Planning) and NST (National Research Council of Science and Technology) of the Republic of Korea (CRC-14-1-KRICT), and the R&D Convergence Program of MSIP and ISTK (Korea Research Council for Industrial Science and Technology) of the Republic of Korea (CMP-3-6-KIER).

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Received: 30 December 2015. Accepted: 2 May 2016.