Ethanol-to-Butadiene: A Highly Active ZnTa/SiO_2 Mesoporous Catalyst

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Abstract: We synthesized a catalyst based on zinc and tantalum oxides supported on mesoporous silica, with very high performances in the conversion of ethanol to *1,3*-butadiene. The catalyst is capable of a stable selectivity towards the desired product over 65%. Preliminary characterization suggests that the mesoporous morphology and the right balance of acid and basic properties contribute to this remarkable activity.

Keywords: ethanol-to-butadiene, mesoporous catalyst, Lebedev process

1. Introduction

1,3-butadiene (BD) is an unsaturated hydrocarbon essential to the manufacturing of various polymers such as synthetic rubber[1]. Currently, it is generally obtained as a by-product of petroleum refining, an economically and environmentally unsustainable production method. Interest is growing for an on-purpose and eco-friendly technology capable of generating *1,3*-butadiene. One such technology is the Lebedev process: a catalytic conversion to *1,3*-butadiene of ethanol, which can itself be derived from biomass. Academic interest has spurred in the recent years, but activity remains too low to guarantee the industrial viability of such a process[2].

Herein, we report a mesoporous silica-supported tantalum and zinc oxide catalyst with exceptional butadiene productivity – Sels *et al.* have identified productivity ($g_{BD}.g_{cat}^{-1}.h^{-1}$) as a key parameter to evaluate activity[3]. The performances of this catalyst are ostensibly attributable to its mesoporous morphology and high dispersion[4].

2. Experimental

Amorphous mesoporous silica with metal oxides (Ta(V) and Zn(II)) were prepared *via* the sol-gel technique in a one-pot synthesis; the metallic ions were introduced during gelification after dissolving them in ethanol; amine chelating agents were used to keep the ions dispersed; hydrothermal treatment in a Teflon-lined stainless-steel autoclave and calcination followed.

Morphological properties of the synthesized materials were characterized by N_2 physisorption at −196 °C, on a Micromeritics Tristar II instrument. Powder X-ray diffraction (XRD) patterns at low and high angles were recorded on a Bruker AXS D5005 diffractometer using a CuKα radiation (λ = 1.54184 Å) as an X-ray source.

The catalytic activity tests were carried out with a Multi-R® device from Teamcat Solutions SAS[5]. Multi-R® is a high-throughput equipment for heterogeneous catalysts screening: a gaseous feed is split into four micro-fixed bed reactors, tuned to receive an equal inlet flow in terms of gas composition and flow rate; reactor outputs are analyzed by an on-line GC-FID. The reaction was performed at 400 °C and 1 atm. Gas flow and catalyst mass were adjusted to provide a weighted hourly space velocity (WHSV) of 5.3 h^{-1}.

3. Results and discussion

N_2 physisorption results indicates that the synthesis method affords mesoporous materials with a large surface area, always above 500 m^2/g; the pore size distribution was fairly uniform and could be tuned by adjusting the synthesis parameters. Table 1 illustrates the morphological properties of the catalyst presented here (TaZn/M-SiO_2). Powder XRD diffractograms revealed no sign of large oxide particles, suggesting that the oxidic phases are well dispersed on the support.

Catalyst	Specific surface (m^2/g)	Average pore size (nm)	Pore volume cm^3/g
TaZn/M-SiO_2	**600**	**10.4**	**1.9**

Table 1. Morphological properties of the most active TaZn/M-SiO_2 catalyst measured by N_2 physisorption at −196 °C

The catalytic activity at 400 °C of various mesoporous catalysts with different amounts of Ta and Zn was assessed until a highly active material was obtained (TaZn/M-SiO_2). Ethanol conversion, selectivity towards major products and BD productivity after a time-on-stream (TOS) of 3 hours are summarized in Table 2; major products were ethylene ($C_{2=}$), acetaldehyde (AcH) and BD; other products such as propylene, butenes and butanol were detected in trace amounts (<1%).

Catalyst	**Ethanol conversion, %**	**Selectivity relative to products, %**			**BD yield, %**	**BD prod., $g_{BD}.g_{cat}^{-1}.h^{-1}$**
		BD	**AcH**	**$C_{2=}$**		
TaZn/M-SiO_2	**94.5**	**72.9**	**13.1**	**12.2**	**68.9**	**2.14**

Table 2. EtOH-to-BD over the most active TaZn-containing mesoporous SiO_2 (T: 400 °C, P: 1 atm, WHSV: 5.3 $g_{EtOH}.g_{cat}^{-1}.h^{-1}$)

Catalytic activity was monitored for 20 hours so as to evaluate the stability of the catalytic activity. While the overall conversion of ethanol suffered from some degree of deactivation (around 10 points), selectivity remained remarkably stable, in the range of 68 to 73%; only 5 points were lost for the period of 20 hours. Selectivity towards ethylene, the main undesired side product, was substantially constant at ~ 10%.

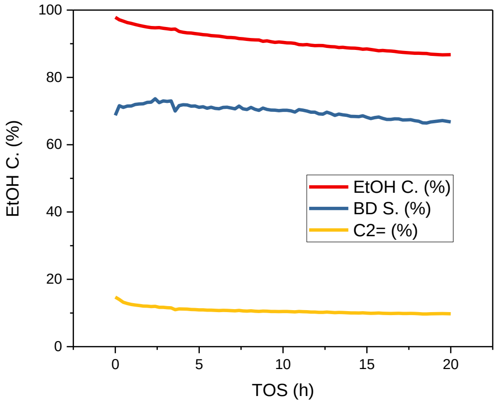

Figure 1. Ethanol conversion, BD and $C_{2=}$ selectivity using TaZn/M-SiO_2 (T = 400 °C, P = 1 atm, WHSV= 5.3 $g_{EtOH}.g_{cat}^{-1}.h^{-1}$)

The reason for remarkable activity of the catalyst in not fully understood yet. However, some evidences suggest that mesopores combined with highly dispersed metal oxide phase enable an increase in the performances of supported catalysts for the ethanol-to-butadiene reaction[4,6]. The synthesis method employed here generates both the mesoporosity and dispersion required in a one-pot process - it does away with the post-synthesis often employed in making catalysts for this reaction[4,7,8]. Further characterization is ongoing to elucidate the source of high activity.

4. Conclusions

We report a highly active, highly stable Ta and Zn oxide catalyst for the conversion of ethanol to butadiene. When compared with productivity found in the literature, this catalyst outperforms all others but one[2,8] by a fair margin, which warrants further investigation. Additional characterization is ongoing to fully understand the performances of this catalytic system, and to enable rationalized back-optimization.

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