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Effect of the SiO_2 support on the catalytic performance of $Ag/ZrO_2/SiO_2$ catalysts for the single-bed production of butadiene from ethanol

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ABSTRACT

A ternary $Ag/ZrO_2/SiO_2$ catalyst system was studied for single-step conversion of ethanol to butadiene by varying the catalyst composition (Ag, Ir, or Pt metal component, Ag/ZrO_2 loading, and choice of SiO_2 support) and operating conditions (space velocity and feed gas composition). Exceptional catalytic performance was achieved over a $1\%Ag/4\%ZrO_2/SiO_2$-SBA-16 catalyst leading to 99% conversion and 71% butadiene selectivity while operating under mild conditions (325 °C, 1 atm, and $0.23\,h^{-1}$). Several classes of silica—silica gels, fumed silicas, mesoporous silicas)—were evaluated as catalyst supports, and SBA-16 was found to be the most promising choice. The SiO_2 support was found to significantly influence both conversion and selectivity. A higher SiO_2 catalyst surface area facilitates increased Ag dispersion which leads to greater conversion due to the accelerated initial ethanol dehydrogenation reaction step. By independently varying Ag and ZrO_2 loading, Ag was found to be the main component that affects ethanol conversion. ZrO_2 loading and thus Lewis acid sites concentration was found to have little impact on the ethanol conversion. Butadiene selectivity depends on the concentration of Lewis acid site, which in turn differs depending on the choice of SiO_2 support material. We observed a direct relationship between butadiene selectivity and concentration of Lewis acid sites. Butadiene selectivity decreases as the concentration of Lewis acid sites increases, which corresponds to an increase in ethanol dehydration to ethylene and diethyl ether. Additionally, adding H_2 to the feed had little effect on conversion while improving catalytic stability; however, selectivity to butadiene decreased. Finally, catalyst regenerability was successfully demonstrated for several cycles.

1. Introduction

With an annual production of 11 million tons/year, butadiene is the most important conjugated diene, being the basis of a wide variety of synthetic rubbers, elastomers, and polymer resins upon polymerization by itself or in conjunction with other polymerizable monomers [1]. Currently, butadiene is primarily obtained as a byproduct of the ethylene production by steam cracking. The amount of butadiene produced from a steam cracker depends on the composition of the cracking feedstock used [2]. Heavier feedstocks such as naphtha produce more butadiene than lighter feedstocks such as ethane [2]. For example, an ethane steam cracker typically produces ~2 lb of butadiene per 100 lb of ethylene, while a naphtha steam cracker produces ~16 lb of butadiene per 100 lb of ethylene [3]. Currently, ethane is produced inexpensively from shale gas, which has become the preferred feedstock for steam cracking units in North America. Hence, butadiene coproduction has been in decline over the past decade. In addition to the shift in lighter feedstocks, crude oil price swings have historically led to corresponding price fluctuations in the cost of butadiene which is not ideal for end users. Thus, alternative technologies for producing butadiene are highly desired [4].

Ethanol-to-butadiene (ETB) represents an attractive alternative technology. Ethanol is commercially produced from renewable biomass or waste sources. In addition, the ethanol “blend wall” coupled with advancements in production efficiency and feedstock diversification will potentially lead to excess ethanol at competitive prices available for production of a wide range of fuels and commodity chemicals [5]. Furthermore, in recent publications, Patel et al. described an early-stage assessment method [6,7]. They compared the bioethanol-based pathway for butadiene production with the naphtha-based route and suggested that the bioethanol pathway could be a promising alternative to the naphtha-based process [6,7].

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Research on butadiene production was initiated in the early 20th century and numerous articles have since been published. One-step and two-step processes were developed in the former Soviet Union and the United States, respectively, for ethanol conversion to butadiene. A one-step catalytic process developed for ethanol conversion to butadiene was commercialized for some time to produce synthetic rubber but was abandoned later due to low-cost oil making more convenient the production of butadiene from petrochemical sources [8]. In principle, the one-step process offers greater simplicity and lower operating costs as compared to two-step processes. However, achieving high yields to butadiene at industrially relevant process conditions has been challenging. A large number of catalytic systems (e.g., doped Al_2O_3, promoted MgO-SiO_2, sepiolites, ZrO_2-Fe_2O_3, and zeolite-based catalysts) that are capable of converting ethanol to butadiene in one processing step have been reported [9–14]. These catalytic systems have been well summarized in recent reviews [1,4,8]. A number of studies have reported achieving 70 to 80% selectivity to butadiene. However, these results are usually obtained at low single-pass conversion (e.g., $< 45\%$) or low catalyst space velocities (e.g., $< 0.20\,h^{-1}$). For the single-step process to be commercially realized higher single pass conversions coupled with high selectivity ($\geq 70\%$) are likely required. Recently, several catalytic materials have distinguished themselves from others for their high catalytic performance. Using a $Cu_{1.0}Hf_{3.0}Zn_{0.5}/SiO_2$ catalyst operating at 360 °C, weight hourly space volume (WHSV) = $0.21 g_{EtOH}\ g_{cat}^{-1}\ h^{-1}$ and atmospheric pressure, 72% butadiene selectivity at 99% conversion was obtained [15]. Under similar conditions (350 °C, WHSV = $0.3 g_{EtOH}\ g_{cat}^{-1}\ h^{-1}$, P = 1 atmosphere), 75% butadiene selectivity of was obtained at 100% conversion for a 2% Zn/8%Y/beta catalyst. Ag/ZrO_2 catalysts supported on SiO_2 and Zeolite Beta also have shown very promising performance levels [14,16]. A $1\%Ag/10\%ZrO_2/SiO_2$ catalyst has been reported with catalytic performance achieving 74% butadiene selectivity and 88% conversion at 320 °C, WHSV = $0.04 g_{EtOH}\ g_{cat}^{-1}\ h^{-1}$, and atmospheric pressure [17]. Under similar conditions and at low conversion a $1\%Ag/1\%ZrO_2BEA$ was found to be four times more active than a $1\%Ag/1\%ZrO_2/SiO_2$. However, commercialization of zeolite-based catalysts can be challenging because of the nature of chemicals used in the synthesis (e.g., hydrofluoric acid) and the waste produced (e.g. hydrochloric acid). In addition, pore confinement also can lead to increased catalyst deactivation by pore blocking and coking.

In this study, we have focused our understanding and further development of $Ag/ZrO_2/SiO_2$ catalysts for the ETB reaction. Although very encouraging results were obtained for the previously reported $1\%Ag/10\%ZrO_2/SiO_2$ catalyst [17], increasing catalytic activity while maintaining high selectivity to butadiene, thus enabling faster throughput, is highly desirable for commercial application. Therefore, we have further investigated the $AgZrO_2/SiO_2$ catalyst system with the goal of better understanding its structure-function relationship and improving yield to butadiene through improved catalyst design. We have studied the role that each individual component, Ag, ZrO_2, and SiO_2, has on the reaction mechanism. A supported Ag catalyst was compared to supported precious metal (i.e., Ir and Pt) catalysts. We comparatively evaluated several classes of silica supports studied how the nature of the SiO_2 support affects catalytic performance. We also evaluated catalyst lifetime and regenerability.

2. Experimental

2.1. Catalysts Synthesis

A series of $xAg/yZrO_2/SiO_2$ catalysts were synthesized by incipient wetness impregnation of SiO_2 with silver nitrate powder and zirconyl nitrate solution dissolved in deionized water. A total of 11 different SiO_2 materials were used as supports: 636, 645, 646, 923 (Davisil), silica gel large pores (alfa Aeser), silica gels KSKG-GOST 3956-76 and KSMG-GOST 3956-76 (JSC Karpov), mesoporous silicas SBA-15 and SBA-16 (ACS Materials), fumed silica Aerosil 380 (Degussa) and L90 (Cab-O-Sil). After impregnation, the catalysts were dried at 110 °C for 8 h and calcined at 500 °C for 4 h. The Ag loading “x” was varied from 1 to 8 wt.% and the ZrO_2 loading “y” was varied from 1 to 10 wt.%. A bare SiO_2 was synthesized by impregnation of SiO_2 (Davisil 646) with deionized water and calcined under similar conditions as the other catalysts. A $4ZrO_2/SiO_2$ was prepared similarly to the $xAg/yZrO_2/SiO_2$ catalysts without addition of silver nitrate by impregnation of a silica gel 646 (Davisil). A $4Ag/SiO_2$ was prepared similarly to the $xAg/yZrO_2/SiO_2$ catalysts without addition of zirconyl nitrate solution by impregnation of a silica gel 646 (Davisil). A $1Ir/4ZrO_2/SiO_2$ catalyst, a $2Ir/4ZrO_2/SiO_2$ catalyst, and a $1Pt/4ZrO_2/SiO_2$ catalyst were prepared by incipient wetness impregnation of SiO_2 (Davisil 646) with zirconyl nitrate solution and Ir acetate solution (14 wt.%) or Pt nitrate solution (12 wt.%) dissolved in deionized water. The catalysts were dried at 110 °C for 8 h and calcined at 500 °C for 4 h. The supported Ir catalysts contain 1 wt.% and 2 wt.% of metal, while the supported Pt catalyst contains 1 wt.% metal. These three catalysts contain 4 wt.% ZrO_2.

In the test, SiO_2 from Davisil was labeled SiO_2-x where x stands for the Davisil number. The large-pore silica gel (alfa Aeser) was labeled SiO_2-AA. Silica gels KSKG-GOST 3956-76 and KSMG-GOST 3956-76, the mesoporous silica materials SBA-15 and SBA-16 (ACS Materials), and fumed silica Aerosil 380 (Degussa) and EL90 (Cab-O-Sil) were labeled SiO_2-KSKG, SiO_2-KSMG, SiO_2-SBA15, SiO_2-SBA16, SiO_2-A380 and SiO_2-EL90, respectively.

2.2. Catalyst characterization

2.2.1. BET

We used an automatic adsorptiometer (Micromeritics ASAP 2000) to measure nitrogen adsorption at 77 K. Samples were pretreated at 150 °C for 12 h under vacuum. Surface areas were determined from adsorption values for five relative pressures (P/P_0) ranging from 0.05 to 0.2 using the Brunauer-Emmett-Teller (BET) surface method. The pore volumes were determined from the total amount of N_2 adsorbed between $P/P_0 = 0.05$ and $P/P_0 = 0.98$.

2.2.2. Pyridine adsorption/ desorption followed by infrared spectroscopy

We used a Nicolet FT-IR spectrometer IS50 equipped with a mercury cadmium telluride detector (resolution: $4\ cm^{-1}$, 128 scans) to record IR spectra. All spectra presented in this manuscript were normalized for 100 mg of the catalyst. Samples were pressed into pellets (ca. 20 mg for a 2-cm^2 pellet), and a pellet was placed inside the transmission IR cell. Samples were pretreated at 400 °C under N_2 for 2 h and then under 10% H_2/N_2 at 325 °C for 1 h before final cooling to 50 °C. After pretreatment, pyridine was introduced at 50 °C ($P_{equilibrium} = 133$ Pa), and the spectra were recorded following desorption from 50 to 350 °C. The number of Lewis acid sites titrated by pyridine was calculated using an integrated molar absorption coefficient value of $\varepsilon = 2.22\ cm.\mu mol^{-1}$ for ν_{19b} vibration of coordinated pyridine at ca. 1450 cm^{-1} [18].

2.2.3. X-ray powder diffraction

X-ray diffraction (XRD) spectra were recorded using a Philips X'pert MPD (Model PW3040/00) diffractometer with copper anode ($K\alpha1 = 0.15405$ nm) and a scanning rate of 0.007° per second between $2\theta = 10°$ to $70°$. We used Jade 5 (Materials Data Inc., Livermore, CA) and the Powder Diffraction File database (International Center for Diffraction Data, Newtown Square, PA) to analyze diffraction patterns. The catalyst was reduced at 325 °C for 1 h under $5\%H_2/N_2$ prior to XRD analysis.

2.2.4. Scanning transmission electron microscopy

Transmission electron microscopy (TEM) measurements were conducted with an FEI Titan 80–300 operated at 300 kV. All images were digitally recorded using a charge-coupled device (CCD) camera and were analyzed using Gatan Digital Micrograph. TEM images were