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Dehydration of butanol to butene over solid acid catalysts in high water environments

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ABSTRACT

The effects were studied of high water concentrations on the kinetics of alcohol dehydration, as encountered in aqueous-phase processing of biomass-derived oxygenated hydrocarbons. These studies were carried out for dehydration of an aqueous solution of 10 wt% 2-butanol at 513 K, and at a total pressure of 52 bar to maintain the water in the liquid state. Under these high pressures of water, silica-alumina, niobium phosphate and niobic acid are found to be stable and active for the dehydration of butanol. These three catalysts showed an increase in rate after contact with liquid water, caused by an increase in the concentration of Brønsted acid sites. Zeolite catalysts (Beta, USY, H-ZSM-5) and zirconia based catalysts (WO_x/ZrO_2, MoO_x/ZrO_2, and MgO/ZrO_2) were ineffective due to deactivation or low catalytic activity. The flow rate of inert gas at constant aqueous flow rate had a significant effect on the rate of butene production, due to vaporization of butanol and water. At low flow rates of gas, increasing the gas flow rate causes the preferential vaporization of butanol, leading to a decrease in the butanol pressure in the reactor and a corresponding decrease in the rate of dehydration. Above a critical gas flow rate, the liquid feed becomes completely vaporized in the reactor, and increasing the gas flow rate further leads to a decrease in the pressure of water and a corresponding increase in the rate of dehydration. In the vapor–liquid equilibrium regime, kinetic models predict that most of the catalyst is covered with multiple layers of water, and dehydration takes place by reaction of hydrated–adsorbed butanol with a hydrated surface site. In the vapor-only regime, kinetic models suggest that the fraction of vacant active sites increases with increasing gas flow rate, and dehydration takes place by reaction of adsorbed butanol with a vacant surface site.

1. Introduction

Renewable sources for fuels and chemicals must be developed as reserves of non-renewable petroleum feed stocks diminish, and biomass resources are promising alternatives to meet these demands. Considerable research has focused on sugars obtained from biomass, such as fructose and glucose, and their derivatives such as sorbitol [1–5]. Carbohydrates contain high extents of oxygenated functional groups that must be selectively removed or modified to create desired products. These oxygenated groups lead to high solubilities of carbohydrates in water, requiring aqueous-phase processing of these compounds to fuels and chemicals.

A particularly useful reaction sequence for aqueous-phase processing is dehydration followed by hydrogenation, in which oxygenated hydrocarbons, such as sorbitol, are first dehydrated over solid acid sites followed by hydrogenation to form alkyl species. Sequential operation of aqueous-phase dehydration/hydrogenation (APDH) leads to the formation of straight-chain alkanes, such as butane, pentane and hexane [3]. Olefinic species are not typically observed during APDH processing at temperatures near 520 K and pressures near 50 bar over catalysts consisting of Pt (e.g., 4 wt%) supported on acidic supports, such as silica-alumina or niobium phosphate [3,4], suggesting that dehydration is the rate limiting step. In the present paper, we report results of reaction kinetics studies of dehydration reactions over various solid acids catalysts in the presence of liquid water as well as water vapor. Sec-butanol was chosen as the reactant for studies of aqueous-phase dehydration, because it readily undergoes intramolecular dehydration to form butene products. To ensure that dehydration was, in fact, the rate limiting step in APDH processing, 2-butanol was converted to butane over the same Pt/silica-alumina catalyst used in our previous work [3], and 2-butanol was also converted to butenes over the silica-alumina support under the identical reaction conditions. The rates of production of butane and butenes were the same on these two catalysts, indicating that dehydration was indeed the rate limiting step.

Butanol dehydration to butenes has been studied by various authors under conditions involving water. For example, it has been

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reported that water vapor can either increase or inhibit 2-butanol dehydration over zirconia-supported tungsten and silicon based solid acids [6]. A decrease in the activity of WO_3/ZrO_2 in the presence of water was investigated by others [7]. However, the performance of solid acid catalysts has not been studied systematically for a wide range of water concentrations, especially high water concentrations and in the presence of liquid water.

2. Experimental

2.1. Catalysts

Silica-alumina, MCC 25 (SiAl), was obtained from Grace Davidson with a Si/Al ratio of 4. Beta-zeolite with a Si/Al ratio of 25 and USY-zeolite with a Si/Al ratio of 5 [8] were obtained from Engelhard and calcined at 773 K before use. H-ZSM-5 catalyst with a Si/Al ratio of 14 was obtained from Engelhard. Tungstated-zirconia, XZO1251/01 16% WO_3, was obtained from MEI Chemicals. MoO_x/ZrO_2, with 20.3% MoO_3, was prepared in a similar manner as reported in the literature [9], by incipient wetness impregnation of $(NH_4)_6Mo_7O_{24}{\cdot}H_2O$ (Aldrich) on ZrO_2 XZO 880/01 purchased from MEI Chemicals. The impregnated solids were dried overnight in air and then treated in a flowing gas mixture of 20% O_2 in He at 723 K. MgO/ZrO_2 was prepared as detailed elsewhere [10,11]. Niobic acid, HY-340 (Nb_2O_5), was obtained from CBMM in Brazil. Niobium phosphate ($NbOPO_4$) was prepared in a similar manner to previous reports [12]. Briefly, 4 g of $NbCl_5$ was reacted 1:2 with phosphoric acid. After thorough mixing, the resulting paste was diluted in 70 mL water and stirred for 40 min. The pH was then adjusted to 4.9 and the mixture was stirred for an additional 30 min. The $NbOPO_4$ was then filtered and washed until the silver nitrate test showed no additional Cl^- ions. The catalyst was dried overnight in air and then treated in a flowing gas mixture of 20% O_2 in He at 723 K.

For characterization purposes, SiAl, Nb_2O_5 and $NbOPO_4$ were additionally modified to study the effect of liquid water on acidity. In this treatment, approximately 0.5 g of catalyst was placed in a glass beaker with 50 mL of water. The beaker was placed in a sealed Parr reactor and heated to the reaction temperature of 513 K for 3 h. The reactor was cooled, the water was decanted, and the catalyst was then placed in an oven overnight to dry at 393 K.

2.2. Reactor setup

Catalysts were mixed with crushed silica and packed with quartz wool end-plugs in tubular quarter-inch stainless steel reactors. Except where noted otherwise, a ten weight percent solution of 2-butanol (Aldrich) in deionized water was fed with an HPLC pump in an up-flow direction over the catalyst bed. The effluent was collected in a gas–liquid separator. Inert gas (He or H_2 from Linde) was flowed through the catalyst bed by means of a mass flow controller, and this flow was used to control the water concentration within the reactor. In addition, inert gas was flowed though the separator to direct gaseous species to a gas chromatograph for on-line analysis. The pressure of the system was held constant at 52 atm by a back pressure regulator. The reactor was held at a constant temperature of 513 K as measured by a thermocouple attached to the exterior of the reactor and surrounded by aluminum blocks within an oven. The effluent gas was analyzed by an online GC, Varian GC-MS (Saturn 3) using an FID detector and a GS-Q capillary column (J&W Scientific). The liquid effluent was collected and analyzed by a Shimadzu GC2010 equipped with an FID detector and a DB 5 ms column (J&W Scientific). Total carbon material balances on individual points typically closed within 5%.

In a typical experimental run, the reactor was heated to the reaction temperature while inert gas was flowed over the catalyst. After reaching the reaction temperature, the inert gas was flowed for an additional hour before introducing the butanol/water mixture. After changing conditions, the system was allowed a minimum of 5 h to reach steady state before sampling the phases.

2.3. Catalyst characterization

The surface areas of all catalysts were determined from BET isotherms of N_2 adsorption at 77 K. The concentration of acid sites per gram of each catalyst was quantified by temperature programmed desorption of ammonia. Catalyst samples (~100 mg) were loaded into a glass flow through cell, ammonia was adsorbed onto the catalyst for 1.5 h at room temperature, physically adsorbed ammonia was then desorbed at 423 K, and TPD experiments commenced using a temperature ramp of 10 K/min. The desorbed ammonia was quantified on-line using a mass spectrometer.

The distribution of Brønsted and Lewis acid sites was determined from infrared measurements of adsorbed pyridine. Approximately 10 mg of catalyst was placed in a 1.2 cm dye and pressed into a pellet, which was then placed in a treatment/sampling cell where it was heated to 473 K under flowing dry N_2 (Linde) for 2 h. A reference spectrum of the catalyst was then taken. Pyridine was introduced into the cell for 30 min at room temperature, followed by heating at 473 K overnight under flowing dry N_2. The areas of the pyridine peaks at 1455 and 1545 cm^{-1} (Lewis and Brønsted sites, respectively) were then determined by subtracting the spectra of the sample before and after this exposure to pyridine.

2.4. Methods

The activity of each catalyst was tested under the same reaction conditions, consisting of a flow equal to 0.1 mL/min of feed solution (10 wt% butanol in water) and a gas flow of 200–215 cm^3(STP)/min. After this initial screening, the three zirconia-based catalysts, MgO/ZrO_2, WO_x/ZrO_2, and MoO_x/ZrO_2 were eliminated from further investigation, because the rates of butene production for these three catalysts were 1.3, 2.6 and 5.3 μmol/g/min, respectively; these values are an order of magnitude lower than the activities of the other catalysts. Beta-zeolite was also removed from further consideration, because although it initially demonstrated a high rate of butene production (1600 μmol/g/min), it showed a continual decrease in activity under the reaction conditions of this study, as shown in Fig. 1.

The rates of dehydration of the remaining five catalysts are shown in column 1 of Table 1. H-ZSM-5 and USY showed the highest rates of 2403 and 962 μmol/g/min, respectively. SiAl, Nb_2O_5

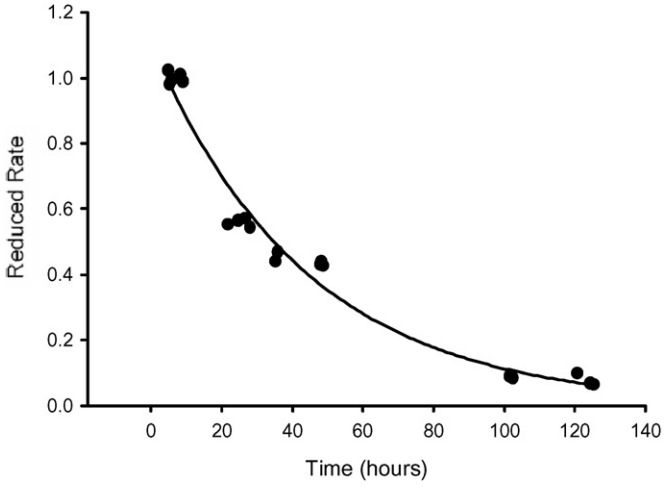

Fig. 1. Normalized rate versus time on stream in high water environment for Beta-zeolite.