



Short Communication

Reductive dehydration of butanone to butane over Pt/ γ -Al₂O₃ and HZSM-5

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ABSTRACT

We show that butanone can be reacted to form n-butane in an isothermal reactor containing a 1 wt.% Pt/ γ -Al₂O₃ and an HZSM-5 catalyst (total mass of 12–400 mg, Si/Al = 11.5) below 160 °C with up to 99% selectivity and 67% yield. The catalyst loading (12–400 mg) and temperature (100–250 °C) were varied to obtain primary products whose selectivities decreased with conversion and secondary/tertiary products whose selectivities increased with conversion. As conversion increased, the selectivities of butanol and butene decreased, showing the formation of butane from butanone through a series reaction pathway: butanone → 2-butanol → butene → butane. Butane selectivity increased as the temperature was increased from 100 to 200 °C when compared at similar conversions due to higher dehydration rates over the zeolite. Processing ketones at low temperatures over bifunctional catalysts may be an efficient means of obtaining high yields of stable paraffins from reactive oxygenates.

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1. Introduction

Significant interest has been generated in synthesizing and processing bio-oil for use as fuels or chemicals in a biofuel-driven economy. However, bio-oil contains a mix of oxygenated species such as aldehydes, ketones, esters, and other functional groups whose acidic and corrosive properties render them unsuitable for use as stable energy-carriers [1,2]. Ketones [3–5] and aldehydes [6,7], in particular, contain electrophilic carbonyl groups that are prone to nucleophilic attack from other molecules, leading to condensation reactions that increase the size of the product. Uncontrolled condensation reactions result in coke formation, leading to catalyst deactivation [3]. For example, conversion of acetone decreased over HZSM-5 at 400 °C from 55 to 20% after 300 min on stream when forming coke precursors such as olefins and aromatics [3]. Therefore, a method is needed to deoxygenate ketones or convert them to more stable functional groups that do not deactivate as quickly such as alcohols [3].

The first step in one possible deoxygenation route is the reduction of a ketone group to an alcohol. Hydrogenation of carbonyl groups to alcohol groups in an enriched H₂ atmosphere has been studied over Ru [8], Ag [9], and Pt [10] catalysts; however, a common challenge in hydrogenolysis is selectively cleaving C–O bonds over C–C bonds [11]. Meanwhile, dehydration of alcohols to olefins over zeolites such as HZSM-5 has been shown to produce high yields of olefins with minimal C–C bond scission [12–14]. For example, Sun et al. achieved a 75% yield of butene from 1-butanol over HZSM-5 at 225 °C and a 92% yield

over HFER at 300 °C [14]. One possible strategy that may afford more control over C–O bond scission involves incorporation of dehydration into the deoxygenation process by means of a bifunctional catalyst.

Alotaibi et al. observed a 22% yield of 2-methylpentane from methyl isobutyl ketone over 0.5 wt.% Pt/SiO₂ at 200 °C and predicted a bifunctional series reaction pathway that converts methyl isobutyl ketone to 4-methyl-2-pentanol and eventually to 2-methylpentane [10]. However, the pathway was proposed on the basis of a catalyst survey and experiments at one zeolite loading. We provide a more focused study across multiple space velocities and H⁺/Pt ratios to help confirm and elucidate the bifunctional mechanism for butanone.

2. Materials and methods

2.1. Catalyst synthesis

NH₄-ZSM-5 from Zeolyst (CBV 2314; Si/Al = 11.5) was calcined in 200 ml min^{−1} dry air (20–21% O₂, <10 ppm H₂O, Minneapolis Oxygen) and heated at a rate of 1.5 °C min^{−1} to 500 °C and held for 2 h. A 1 wt.% Pt on γ -Al₂O₃ sample was made from a Pt precursor (H₂PtCl₆, 8 wt.% in H₂O from Sigma Aldrich) dissolved in a slurry of γ -Al₂O₃ powder (99.97%; Alfa Aesar) and dried at 80 °C overnight. The powder was mechanically mixed with the calcined zeolite to obtain a zeolite to platinum molar ratio (H⁺/Pt) of 20. The mixed powder was heated in dry air at 1.5 °C min^{−1} to 500 °C and held for 2 h. The catalyst was then treated in 5% H₂ in Ar (200 ml min^{−1}) at 400 °C for 2 h and cooled. The sample was then pressed into disks at 2000 psi and crushed into pellets which were sieved to select for 599–710 μ m particles (24–30 mesh). The H⁺/Pt ratio was altered by varying the Si/Al ratio at constant zeolite loading. The Si/Al ratio was changed by using CBV 2314

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(Si/Al = 11.5), CBV 3024E (Si/Al = 15), CBV 5524G (Si/Al = 25), and CBV 8014 (Si/Al = 40) zeolite samples.

2.2. Reactor configuration and analysis

A 10 mm ID quartz tube was fabricated and connected to a vaporizer consisting of a 1/4" stainless steel tube heated to 200 °C with heating tape as shown in Fig. 1. The vaporizer inlet was sealed to a stainless steel nebulizer consisting of concentric 1/8" and 1/16" tubes. Butanone was fed through the nebulizer at 0.042 ml min⁻¹ and N₂ and H₂ were fed through the nebulizer each at 0.70 standard liters per minute (slpm) for a H₂ to butanone molar ratio of 60.

Composition analysis was conducted with an online HP 7890A gas chromatograph (GC) equipped with a thermal conductivity detector and flame ionization detector in series. The GC contained a HP PLOT/Q column (30 × 0.32 × 20). N₂ was used as an internal standard. Peak identification was verified with a HP 5890 Series II gas chromatograph containing a HP-1 column (50 × 0.32 × 1.05) connected in series with a HP MSD 5970 mass selective detector. Carbon balance closed to within 15%.

2.3. Experimental procedure

The catalyst was pretreated at 500 °C for 20 min in dry air at 0.3 ml min⁻¹ and 20 min in H₂ at 0.70 slpm. A constant N₂ flow rate was maintained at 0.70 slpm during pretreatment and throughout the course of the experiments. After pretreatment, the reactor was cooled to the desired temperature while maintaining constant flow rates. Three injections were analyzed at a time-on-stream of 7, 22, and 37 min. The catalyst temperature was varied from 100 to 250 °C. The catalyst was regenerated under the pretreatment conditions between each temperature. Space velocity was changed by varying the total catalyst loading from 12 to 400 mg at a constant reactant flow rate. Data at all loadings are plotted without consideration of bypass, which occurred at loadings below 30 mg, because the conversion did not exceed 10%. The WHSV was varied from 27 to 850 h⁻¹ or a residence time of 3–33 ms calculated on a gas hourly basis. Besides the bifunctional catalyst, monofunctional catalysts consisting of solely HZSM-5 or Pt/γ-Al₂O₃ were synthesized using the methods described above.

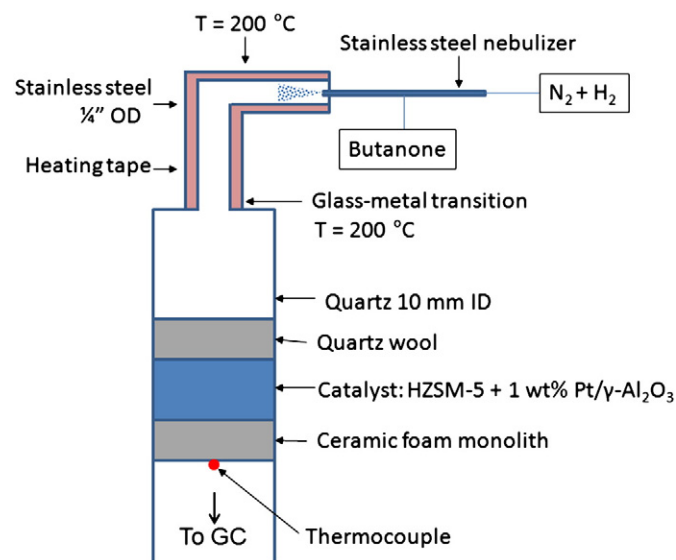


Fig. 1. Reactor schematic.

3. Results and discussion

3.1. Reactivity of butanone over HZSM-5

Butanone was initially unreactive over HZSM-5 without Pt/γ-Al₂O₃ at temperatures of up to 250 °C with conversions less than 1%. Similarly, Chang et al. reacted acetone over HZSM-5 and reported a conversion of 3.9% at 250 °C and a LHSV of 8.0 h⁻¹ [15]. While acetone and butanone have been shown to be reactive over HZSM-5 to form C₂₋₅₊ products at temperatures exceeding 370 °C through aldol condensation and cracking [16], the temperatures in our reactor may be too low for this to occur. The extent of bimolecular reactions is a function of partial pressure, which relates to surface coverage and temperature [4,17]. Higher temperatures are needed at lower surface coverages to initiate an aldol condensation reaction. Aldol condensations of acetone are typically done in the vapor phase from 250 to 400 °C [3]. The partial pressure of butanone used in our experimental conditions (0.83 kPa) may have been too low to achieve the minimum surface coverage needed to initiate significant bimolecular reactions such as aldol condensations, explaining the low observed reactivity.

3.2. Evidence for series reaction over Pt/γ-Al₂O₃ and HZSM-5

While butanone was inactive over HZSM-5 alone, the addition of Pt/γ-Al₂O₃ to the zeolite led to yields of butane up to 67% with less than 2% selectivity to butene and 2-butanol. The catalyst loading was varied at each temperature to change space velocity and conversion. Only trace amounts of ethylene and propylene were observed, indicating that cracking reactions were negligible. Less than 1% selectivity to products larger than C₄ was observed, possibly because the partial pressure of butanone was low enough to limit bimolecular reactions. When product selectivities were plotted as a function of conversion, as shown in Fig. 2, butane selectivity decreased as conversion decreased while butene increased. Butanol selectivity decreased from 15% to 10% at 100 °C as conversion increased from 2 to 60%. Increasing selectivity of butanol and butene at low conversions suggests that these species are intermediates in a series reaction that ultimately converts butanone to butane. In a series reaction that can be explained with Fig. 2, we propose that butanone was reduced over a Pt site to form 2-butanol. The butanol likely diffused to a zeolite acid site and subsequently dehydrated to an olefin. The olefin likely diffused back to a Pt site where the C=C bond was hydrogenated to form a paraffin compound. No butanol was observed at temperatures greater than 160 °C, possibly because it was consumed rapidly by the dehydration reaction. When compared across different temperatures at similar conversions, butane selectivity increased with temperature while butanol selectivity decreased, likely because zeolite-catalyzed dehydration rates increased with temperature [14], limiting the concentration of butanol. Deactivation was also observed as shown by a decrease in butanone conversion by 5% at 100 °C and 20% at 160 °C at the same time-on-stream. It is possible that coke formation may occur more readily at 160 °C causing greater changes in conversion than at 100 °C. Selectivities did not change with time-on-stream by more than 5% at any loading.

3.3. Reactivity of butanone over Pt/γ-Al₂O₃

When butanone was reacted over Pt/γ-Al₂O₃, the butane selectivity increased with temperature while butanol selectivity decreased, as shown in Fig. 3. As the temperature was increased, dehydration catalyzed by Lewis acid sites on γ-Al₂O₃ became important. γ-Al₂O₃ containing Lewis acid sites has been shown to be an active dehydration catalyst for isobutanol from 160 to 300 °C [18]. Lewis acid-catalyzed dehydration likely explains the decrease in butanol selectivity and subsequent increase in butane selectivity. When Pt/γ-Al₂O₃ was combined with HZSM-5, both Brønsted and Lewis acid sites likely carried out dehydration.

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