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Ethanol condensation to butanol at high temperatures over a basic heterogeneous catalyst: How relevant is acetaldehyde self-aldolization?



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ABSTRACT

The condensation of ethanol to butanol was investigated over a commercial hydroxyapatite catalyst in the 350–410 °C temperature range. An analysis of thermodynamic and kinetic data, including the measure of the concentration of water and dihydrogen formed during the reaction, unambiguously revealed that the pathway involving acetaldehyde self-aldol condensation is irrelevant at such high temperatures for the present catalyst. At least two reaction pathways are suggested to take place simultaneously. The main pathway would involve the condensation of two ethanol molecules with apparently no intermediate gaseous compounds (so-called "direct" route). A minor "indirect" route would involve the condensation of ethanol with acetaldehyde (formed from ethanol dehydrogenation) to form butenol, which is subsequently converted to butanol by hydrogen transfer from a sacrificial ethanol molecule. This minor route would be less selective, resulting in the formation of acetaldehyde and H₂ as by-products. The alcohol condensation mechanism(s) taking place over basic oxides at high temperatures would therefore be fundamentally different from that taking place over bi-functional solids (containing both metallic and basic sites) at lower temperatures. In a more general context, this work underlines the benefits of considering thermodynamic data when assessing the relevance of potential reaction pathways.

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1. Introduction

Ethanol, a renewable chemical, can be converted to higher molecular weight alcohols, so-called Guerbet alcohols [1,2], to be used, for instance, in the production of high-added value solvents and surfactants. The traditional (partly-homogeneous) synthesis of Guerbet alcohols is known to proceed via several consecutive steps [3,4]. Aldehyde formation by alcohol dehydrogenation and its self-aldolization is a well-accepted reaction pathway in the case of the reaction catalyzed by alkali metal hydroxides in the presence of a metallic catalyst.

In the case of the reaction starting from ethanol, the metal carries out the ethanol dehydrogenation to acetaldehyde, as well as the hydrogenation of reaction intermediates to butanol (Scheme 1). The homogeneous base is responsible for acetaldehyde self-aldolization to 3-hydroxybutyraldehyde, which is then dehydrated to crotonaldehyde. Crotonaldehyde hydrogenation eventually leads to butanol. It is clear that a purely heterogeneous process would present many advantages over the hybrid homogeneous-heterogeneous system aforementioned.

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The conversion of ethanol to butanol over purely heterogeneous catalysts has been reported in several publications and patents [2,5-15]. Basic oxide-supported metals and especially non-promoted (i.e. metal-free) basic oxides were shown to be active and selective, with hydroxyapatites presenting some of the highest selectivity to higher alcohols [6,7,13].

Several studies have addressed the nature of the reaction mechanism over purely heterogeneous basic solids. The relevance of the self-aldolization of acetaldehyde (second step in Scheme 1) has been widely discussed. A number of authors have proposed that acetaldehyde self-aldolization was a crucial reaction step [6–9]. In contrast, a direct reaction between two ethanol molecules was proposed on various basic solids such as a multicomponent oxide catalyst MgO—CuO—MnO [10], alkali-exchanged zeolites [11], MgO [12] and hydroxyapatites [13]. Iglesia and co-workers proposed that the conversion of ethanol to butanol could be achieved by two main reaction pathways, one direct and one via acetaldehyde self-aldolization [14]. These conclusions came from the facts that butanol was found to be both a primary and secondary reaction product.

In the present contribution, the concentration of the main reaction products, including for the first time water and dihydrogen, was monitored over a commercial hydroxyapatite (noted HAP). Surprisingly, our results will rigorously show that a mechanism



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Scheme 1. Ethanol condensation mechanism based on the self-aldolization of acetaldehyde.

based on acetaldehyde self-aldolization (as described in Scheme 1) has a negligible contribution to butanol formation, and that at least two other reaction pathways occurring simultaneously must be considered in our case.

2. Experimental

Ethanol (from Prolabo 99.5%, the main impurity being water) was fed using a saturator kept at 45 °C into a heat-traced stainless steel flow setup. The catalyst was placed in a quartz tube reactor and held between quartz wool plugs. The reactor was located in a tubular furnace. Ar was used as carrier gas. A combination of mass spectrometry, gas-chromatography and gas-phase FT-IR spectroscopy was used to determine the exact concentration of ethanol and the main products of interest (including H_2O and H_2) at the reactor exit.

The gas chromatograph (Bruker 450-GC) was fitted with Zebron ZB-BIOETHANOL column (30 m, 0.25 mm, film thickness: 1.00 μ m). A flam ionization detector (FID) was used and a precise quantification of all the detectable products was realized through the use of an internal standard (i.e. toluene) added to the analyzed stream before injection in the column. The concentration of most reaction products, including dihydrogen, could also be monitored by on-line mass spectrometry (Pfeiffer Omnistar 320). The contribution of large molecules to the fragment m/z = 2 was taken into account to determine the H₂ concentration, also using calibration curves. The concentration of some reaction products, in particular acetal-dehyde and water, was also monitored by on-line FT-IR gas analysis using a 27 cm-long single path gas cell fitted in a Nicolet 560 spectrometer. Calibration curves were drawn to relate IR band signal intensity to concentrations.

The hydroxyapatite $(82 \text{ m}^2 \text{ g}^{-1})$, supplied by Acros Organics (Batch A0312711), was activated under Ar at 480 °C for 1 h before introducing the ethanol/Ar feed at the reaction temperature. The



3. Results and discussion

3.1. Kinetic data

The activity of the HAP was measured over the 350–440 °C temperature range (Fig. 1). Butanol was always the main reaction product and acetaldehyde the main by-product. The conversion was always lower than 30% and the selectivity to C_{6+} products was negligible. The present HAP presented a lower selectivity to butanol (ca. 50%) than that of the HAP samples reported by Ueda and co-workers [7], possibly due to differences in the reaction conditions and/or sample composition and texture. It must be stressed that the point of the present contribution was not to improve on the highest reported selectivity to butanol, but to study a reference sample that displayed acceptable activity/selectivity patterns with respect to those measured on the many basic oxides that have been used for ethanol condensation [6–14].

The evolution of the concentration of butanol and acetaldehyde was followed as a function of the contact time (more precisely, the catalyst weight to ethanol molar flow ratio) at 400 °C (Fig. 2). The yield of acetaldehyde was initially proportional to the contact time before leveling off. This suggests that acetaldehyde was a primary reaction product, which led to secondary reaction products at higher conversions.

The yield of butanol was represented by a curve with a complex shape. The initial slope was different from zero, suggesting that the butanol was formed as a primary reaction product at low contact times. The production of butanol then increased more rapidly before showing again a monotonous increase. This indicates that some of the butanol was then also formed as a secondary reaction product. The sudden increase in butanol corresponded to the point at which acetaldehyde was leveling off, suggesting that part of the acetaldehyde was converted to butanol. The slope and offset of the lines representing butanol concentration in the limiting cases of low and high contact times (Fig. 2) suggest that most of the butanol was always formed via the direct "primary" reaction pathway.

Similar butanol concentration versus contact time curves had been observed by Iglesia and co-workers in the case of ethanol conversion over Mg—Al mixed oxides [14], which had also led these authors to propose that butanol was formed through more than one reaction pathway.

The facts that (i) the slope of the two lines relating to the formation of butenol at low and high W/F appears to be identical and (ii) the butanol formation shows an offset above a certain W/F are worth noting. A possible explanation of these observations is that



Fig. 1. Yields of the main C-containing reaction products during ethanol reaction over the hydroxyapatite as a function of temperature. Butenol refers to 2-buten-1-ol and 3-buten-1-ol. Feed: Ethanol = 15.2% in; WHSV = $14 h^{-1}$.



Fig. 2. Butanol and acetaldehyde partial pressure at the reactor exit at 400 °C for various W/F values. Ethanol concentration = 7.6%.

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