



Perspective

Towards a green bulk-scale biobutanol from bioethanol upgrading[☆]Qi Zhang^a, Jing Dong^{a,b}, Yongmei Liu^a, Yangdong Wang^{b,*}, Yong Cao^{a,*}^aShanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, China^bSINOPEC Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China

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ABSTRACT

Biobutanol is attracting increasingly interest as a source of renewable energy and biofuels because of its many advantages over bioethanol that include higher energy density, fuel efficiency, and reduced engine damages. Currently, there is a growing interest in producing biobutanol from bioethanol, in view of the tremendous potential benefits of this transformation for the bulk production of biobutanol in a target specific manner. This perspective paper describes recent progress for the ethanol to butanol process. The different catalysts, including homogeneous and heterogeneous catalytic systems, for ethanol to butanol are outlined and compared, and the key issues and requirements for future developments are highlighted. A major challenge for further development and application of ethanol to butanol process is to find an optimal balance between different catalytic functions and to suppress the formation of side products that has plagued most catalytic bioethanol upgrading systems.

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1. Introduction

One of the greatest challenges of the 21st century is to meet the growing demand of energy while mitigating emissions and their impact on the environment [1]. Production of biofuels, such as bioethanol, has been advocated as an option to meet these requirements in a sustainable manner. The direct use of ethanol as fuel or as blending component of gasoline offers advantages such as a higher octane number and reduced greenhouse gas emissions [2]. However, ethanol presents several drawbacks including the need for engine adaptations, with only 2/3 the energy of gasoline, and the propensity to absorb water which may cause severe damage to the engine [3]. These limitations have therefore prompted considerable interest in exploring new alternative bio-based strategies to fulfill the strict requirements for applications in transportation sector. Higher alcohols, such as 1-butanol (1-BuOH), have fuel properties that more closely resemble those of gasoline. For instance, 1-BuOH has an energy density closer to gasoline (90%), is noncorrosive and immiscible with water, thus can be blended with gasoline at higher concentrations (16%) than ethanol [4]. These improved

features lead to 1-BuOH being referred to an “advanced biofuel”, and having potential as a “drop-in” replacement for gasoline.

1-BuOH is an important chemical that is commercially manufactured by propylene hydroformylation (oxo process) with subsequent hydrogenation of the aldehydes formed, using metal catalysts such as Co, Rh or Ru [5]. In 2014, the global production of this alcohol was around 4.2 million tons [6]. The main use of 1-BuOH is for the manufacture of butyl acetate used as a solvent for monomers applied in surface coating. The acrylic ester of 1-BuOH has also become increasingly important since it is used as essential component of latex. With increasing interest in using 1-BuOH as an advanced biofuel, research has been directed to the development of processes based on alternative feedstocks for the production of 1-BuOH. While there has been considerable recent interest focused on revisiting the potential of the ABE (acetone, butanol, and ethanol) fermentation process, such bio-chemical systems typically furnish an intractable mixture of acetone, 1-BuOH, and ethanol [7,8]. Moreover, the high cost of fermentation substrate, serious inhibition by 1-BuOH and low 1-BuOH concentration in the product limit the productivity of 1-BuOH from fermentation route. Therefore, targeted and efficient synthesis of 1-BuOH from bio-feedstocks still remains a major challenge for the biorefinery industry.

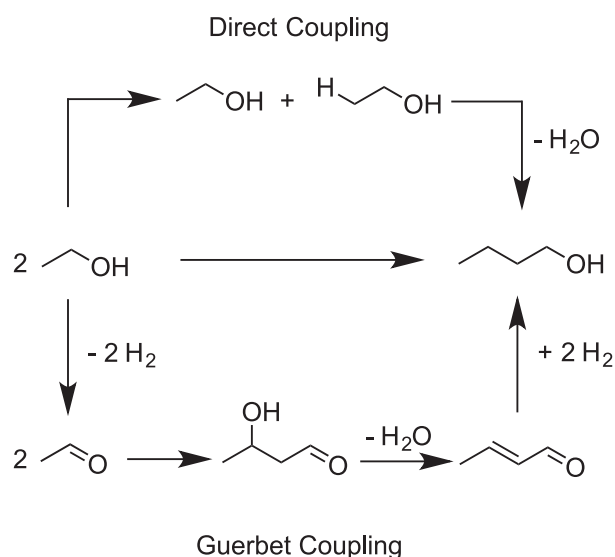
2. Catalytic upgrading bioethanol to biobutanol

Another widely discussed option with potentials to circumvent the negative issues associated with ABE fermentation is the up-

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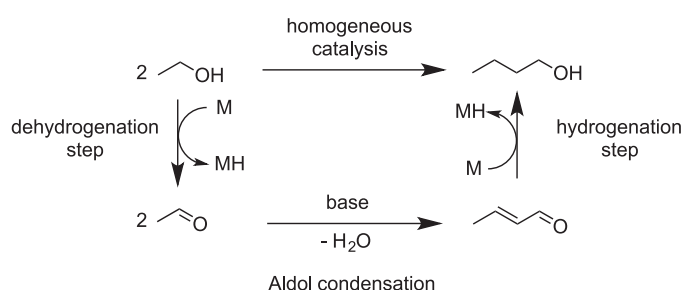


Scheme 1. Two proposed mechanisms for the one-step synthesis of 1-BuOH from ethanol [26].

grading of ethanol to butanol (ETB), which can allow 1-BuOH being produced at dramatically higher levels of selectivity and productivity [9,10]. The chemistry of ETB is believed to proceed via two distinct reaction pathways (i.e., the direct coupling and the Guerbet mechanism) [11]. The direct coupling, also known as the bimolecular mechanism, may proceed via a one-step concerted water elimination involving two ethanol molecules (upper routes in Scheme 1). In the more generally accepted Guerbet pathway (lower routes in Scheme 1), ethanol is initially dehydrogenated to produce acetaldehyde. Subsequent steps involve the intermediate formation of crotonaldehyde via aldol condensation of two molecules of acetaldehyde, followed by generating 1-BuOH as the final product. Although well-established and practiced commercially in some long-chain primary alcohols [12–14], the Guerbet process utilizing ethanol as a substrate has proven particularly difficult. The main reasons for such scenario lie in the thermodynamic challenges associated with the dehydrogenation of ethanol [15,16] and the formation of side-products due to the uncontrolled base-catalyzed aldol condensation of high reactive acetaldehyde [17].

As a result of the high activation barrier required for the rate-determining ethanol dehydrogenation step, most early research focused on targeted production of 1-BuOH from ethanol has been conducted in the vapor-phase at a temperature within the range from 300 to 400 °C over heterogeneous catalysts. Various basic materials, such as MgO [18], Mg/Al mixed oxides [19,20], hydroxyapatites (HAPs) [21–23] and basic zeolites [24] have been studied and the reaction behaviors have already been reviewed extensively [6,25,26]. However, clear drawbacks of these methods are the requirement of high temperature (>300 °C) and difficulty to achieve the desired selectivity toward 1-BuOH at high conversion levels. For instance, Ogo et al. [22] had shown that the Guerbet ethanol reaction can proceed over alkali-doped HAPs at 300 °C. The Sr-HAP exhibited highest 1-BuOH selectivity (81%) at ca. 7% conversion, but selectivity rapidly falls to 60% when the conversion of ethanol increases to 30%. The introduction of one or more dehydrogenating metals of Group VIII including platinum, palladium, nickel and copper allow the reaction to proceed at a lower temperature [27–29], but the issue of low 1-BuOH selectivity must be overcome prior to development of large-scale applications.

Research into alternative methods for the ETB process has been conducted to alleviate the need for high temperatures. A notable progress in this regard has been the introduction of homogeneous catalysis for liquid phase ethanol upgrading [30–34]. In gen-

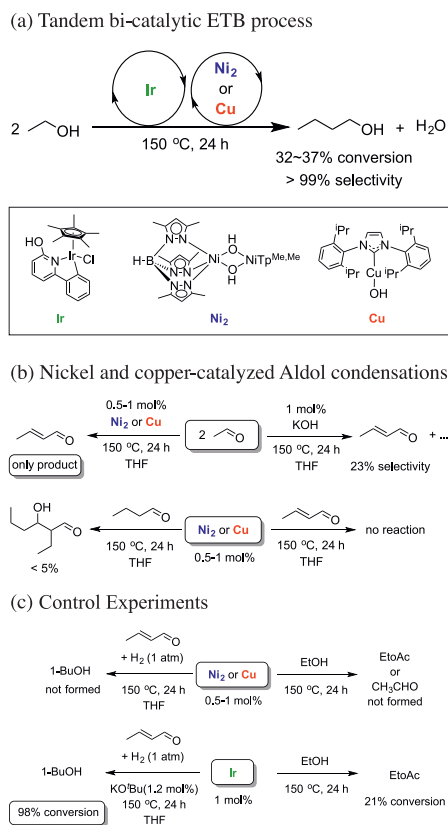


Scheme 2. Homogeneous catalytic strategy for Guerbet process of ethanol to 1-BuOH [30].

eral, homogeneous systems that catalyze the Guerbet process typically feature precious metal catalysts for the sequential hydrogenation/hydrogenation steps and an inorganic base to aid in the aldol-coupling step (Scheme 2). In 2013, Wass et al. [30] described a ruthenium-based homogeneous catalyst that can promote targeted production of 1-BuOH with selectivity as high as >94% at 22% ethanol conversion. The use of small bite angle biphosphine ligand, bis(diphenylphosphanyl) methane (dppm), is the key to achieve this high selectivity. However, an extra equivalent of ligand was needed to stabilize the catalytic system. Further interesting advances has been made by the same group via changing ligands to mixed donor phosphine-amine ligands (PA), thereby permit furnishing comparable selectivity of 1-BuOH (93%) at an even higher ethanol conversion (31%) [31]. In situ reaction monitoring highlights the critical role of a metalated phosphorus alkyl amine complex for achieving excellent selectivity in these catalytic systems.

One of the challenges that remain in the homogeneous catalyzed ETB process is the elimination of the need for a base additive, whilst retaining reasonable levels of selectivity/activity under mild conditions. A recent publication by Jones and co-workers has made a significant step towards this [32]. This has been accomplished by using a tandem bicatalytic system where the synergistic benefits of the two individual components results in a high performance. The two catalysts used, a bifunctional iridium catalyst coupled with bulky nickel or copper hydroxides, worked cooperatively by steering the key aldol condensation step, i.e., the coupling of acetaldehyde, to yield exclusively the C₄ intermediate crotonaldehyde. This was remarkable as traditional inorganic base additives such as NaOEt often lead to uncontrolled excessive condensation pathways, largely accounting for the decreased 1-BuOH selectivity. The authors noted that fine-tuned Ni₂ or Cu complexes can only catalyze the aldol condensation between two acetaldehyde molecules, which is the origin of the observed high selectivity (Scheme 3b and c). As a consequence, ethanol can be smoothly converted with an almost exclusive selectivity toward 1-BuOH at good conversions (up to 37% at 150 °C, Scheme 3a).

Studies conducted so far with homogeneous metal-based catalysts have focused on the improvement in 1-BuOH selectivity/yield. From both economic and engineering points of view, some other key parameters such as the turnover number (TON), turnover frequency (TOF) as well as the specific productivity in terms of the space-time yield should also be considered to evaluate the overall reaction efficacy. At this point, it should be noted that the extremely high selectivity (99%) for ETB conversion over the two-component Ir-based catalyst has been achieved at the expense of activity (TON = 185, TOF = 8 h⁻¹). A brief survey of the recent literature revealed that prior state-of-the-art catalysts can only afford a TON of 458 [30] (46% conversion; TOF = 19 h⁻¹) or 314 [31] (31% conversion; TOF = 79 h⁻¹). A further advancement toward higher levels of activity has recently been attained by Szymczak et al. [33] In this instance the use of an amide-derived N,N,N-Ru(II) complex exhibiting a TON of 530 with a TOF of 265 h⁻¹ was reported.



Scheme 3. Selective conversion of EtOH to 1-BuOH through a tandem bicatalytic system [32]. (a) Tandem bi-catalytic ETB process. (b) Nickel and copper-catalyzed Aldol condensations. (c) Control Experiments.

Considering the large scale application in the transportation sector, these values are still far from satisfactory. Therefore, more attention should be given to the development of new catalysts capable of delivering significantly higher TONs and TOF.

In view of the inherent limitation of homogeneous catalysis for achieving a sustainable and cost-competitive catalytic process, a

wave of recent research has also been directed to identify new heterogeneous catalytic systems that can facilitate ETB conversion under liquid phase conditions at a temperature usually under about 280 °C. It is worth noting that, beside the recognized advantages in terms of their stability, easy recovery, and reusability, heterogeneous catalysis can be readily adapted to flow reactor designs, permitting effective scale-up for the large scale 1-BuOH production. Despite these merits, only a handful of heterogeneous systems were found to be effective for the selective liquid-phase coupling of ethanol. Scattered examples include nickel loaded on alumina [35–37] ($\text{Ni}/\gamma\text{-Al}_2\text{O}_3$), aluminum oxide supported Cu catalyst [38] ($\text{Cu}/\text{Al}_2\text{O}_3$), Pd-Mg-Al mixed oxide [39] (Pd_5MgAlO), Cu-Mg-Al mixed oxide [40] (Cu_7MgAlO) and La_2O_3 modified $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts [41]. Unfortunately, most of these heterogeneous systems still suffered from harsh conditions (generally, $T > 250$ °C), low transformation efficiency and prohibitive levels of poor selectivity (Fig. 1). Therefore, from both green and synthetic points of view, the development of efficient and stable heterogeneous catalysts for the liquid-phase direct conversion of ethanol into 1-BuOH should be a future direction.

There are some other issues need to be addressed with regard to the development of new generation of heterogeneous catalysts capable of efficient and durable ETB transformation. One such challenge is creating potent catalysts that are both more active and more selective, leading to the higher rate of reaction and reducing the amount of unwanted byproducts. The formations of 1-BuOH involve multi-step reactions, and the selectivity of aldol condensation largely determines the final selectivity of 1-BuOH. Thus, multifunctional catalysts contain well-designed basic sites are typically required. Efficient acceptorless dehydrogenation of ethanol under lower temperature is another challenge for the overall Guerbet process. By optimizing the microenvironment of active component, such as composition, surface electronic properties, particle size and acidic/basic properties, more efficient heterogeneous catalysts with a delicate balance between activity, selectivity and stability might be developed. Finally, it must also be pointed out that, in contrast to the fact that bioethanol is usually produced in the form of an aqueous solution containing between 8 and 12 wt% ethanol [7,8], the selected examples as documented in this perspective paper have engaged in the use of pure ethanol as the feedstock

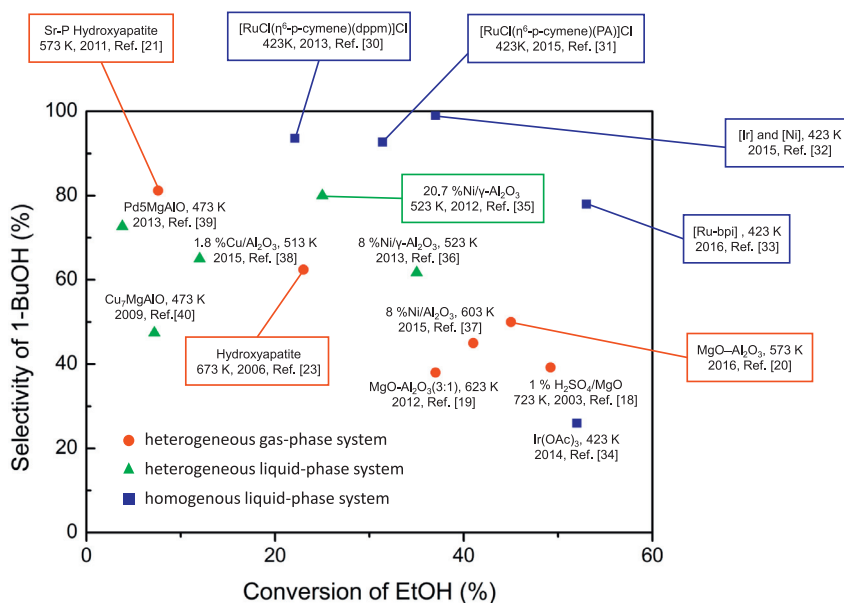


Fig. 1. Reported catalysts for EtOH to 1-BuOH transformation in 2003 or later.

[30–33,35]. Despite the anticipated advantages, attempts to use aqueous ethanol to produce 1-BuOH have met with limited success [31,33,35]. With these issues eventually being tackled, a practical protocol for efficient 1-BuOH production from bioethanol might be within reach. Clearly, this would reshape the biofuel production area and might be helpful for design new advanced catalytic systems, which are indispensable to establish new effective supply chains that can offer added value whilst providing environmental benefits.

3. Conclusions

In summary, catalytic upgrading bioethanol to 1-BuOH represents a highly attractive option holding promise to handle the engine and efficiency problems associated with the utilization of ethanol as fuel blends. However, for the opportunities that this process offers to be fully realized, many problems still remain to be solved, and the level of the overall efficiency in terms of efficient and durable 1-BuOH production needs to be substantially improved. Low temperature liquid phase ETB is still a less explored field, with notable recent advances in the area of homogeneous transition metal-catalyzed ethanol upgrading. In this connection, bifunctional iridium catalyst and Ru-bpi complex have proven very efficient in the targeted production of 1-BuOH with excellent selectivity (up to 99%) at moderate ethanol conversion levels. Despite the seemingly “high efficiency” of these systems, the limited turnover numbers and the lack of compatibility with continuous flow systems remains as a pressing issue toward the development of a viable, more sustainable chemical industry. Conceptually, these studies which provided proof of principle for highly selective ETB using transition metal complexes, will serve as a basis for the development of heterogeneous catalyses amenable to bulk scale processing.

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