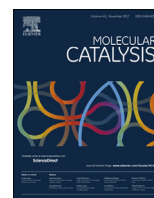




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## Tuning solid catalysts to control regioselectivity in cross aldol condensations with unsymmetrical ketones for biomass conversion

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## ABSTRACT

Several families of catalysts characterized by different types of acid and base sites were developed to steer regioselectivity in the aldol condensation of unsymmetrical ketones. The catalysts were propyl sulfonic acid (PrSO<sub>3</sub>H) functionalized SBA-15 with various acid loadings and with or without hydrophobization by octyl groups (Oc); isomorphously substituted BEA zeotypes; and sulfated zirconias with various sulfate loadings. Benzaldehyde and 2-butanone served as test reactants at a temperature of 140 °C. Sulfonic acid-functionalized catalysts preferentially formed branched condensation product and metal-substituted BEA zeotypes selectively formed linear condensation product. Maximum condensation product yields were 65% branched at 98% conversion with the highest site density Oc/PrSO<sub>3</sub>H/SBA-15 and 76% linear at 94% conversion with Sn-BEA. Sulfated zirconia catalysts were less selective. Product distributions analyzed at different conversions revealed how kinetics and equilibria of addition and dehydration govern regioselectivity. Further observations were: 1. Increasing the acid site density significantly increased the turnover frequency for PrSO<sub>3</sub>H/SBA-15, suggesting a cooperative effect between adjacent acid sites. 2. Brønsted acid sites catalyzed an undesired side reaction, the cleavage of the branched addition product to β-methyl styrene and acetic acid. This reaction was suppressed by hydrophobizing the surface through octyl co-functionalization. 3. Deactivation upon re-use was generally slight, and Sn-BEA could be fully regenerated by calcination.

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### 1. Introduction

Biomass is a promising renewable, carbon-neutral resource for the sustainable production of chemicals and transportation fuels [1]. Techno-economic analyses performed on the potential technologies for biomass conversion show that pyrolysis is the most cost-efficient route for obtaining transportation fuels [2]. In contrast to the constituents of petroleum, the major components of biomass (cellulose, hemicellulose, and lignin) have high oxygen content. Therefore, bio-oil produced by pyrolysis is comprised of oxygenated molecules with alcohol, carbonyl, and carboxylic functionalities. Typical pyrolysis oils contain ≈40% aldehydes and ketones [3,4]. This composition makes an ideal feedstock for upgrading via aldol condensation, which can be accomplished by either acid or base catalysis.

Aldol condensation has drawn keen interest for the valorization of short oxygenates in biomass-derived pyrolysis oil to produce

molecules with longer carbon chains and lower oxygen content, thereby improving energy density. A variety of inorganic solid catalysts have been tested for aldol condensation of biomass-derived feedstocks, including metal oxides [5], hydrotalcite [6,7], metal-substituted zeotypes [8], zeolites [9], and metal-organic frameworks [10,11], with efforts focused on catalyst activity and stability. Inorganic-organic hybrid materials constitute another group of catalysts for aldol condensations; which include silicas functionalized with amine groups [12–17] and periodic mesoporous organosilicas (PMOs) synthesized via direct condensation of bridged organobissilanes of the form (R'O)<sub>3</sub>Si-R-Si(OR')<sub>3</sub> in the presence of a surfactant [18–23]. With these catalysts, efforts have been directed towards optimizing the: length of the tether for the functional group [14,16], the organic bridging group (R) of the PMOs for tuning hydrophobicity [18], the site density [12] and the arrangement [12,17] for cooperative effects between silanol groups and amines, or between acidic and basic functional groups.

Investigations focusing on mechanistic detail in surface-catalyzed aldol condensations are scarce and provide only partial answers about the aldol reaction steps (*i.e.*, addition and dehydration). One report proposed acid-base pairs in zeotypes as

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active sites for the addition step [8]. Another report left open whether increased strength of Lewis acid sites or the presence of Brønsted acid sites in zeolites promoted the dehydration step [9]. Such investigations are limited to the simple reaction networks observed when symmetrical ketones react with aldehydes without  $\alpha$ -hydrogens. For more complex scenarios, an understanding of the regioselectivity and a demarcation of the two reaction steps are lacking.

Regioselectivity in the addition of unsymmetrical ket-2-ones is useful in preferentially obtaining branched or straight carbon chains. In the majority of the reports on aldol condensation, the nucleophile was acetone which only gives straight chain products that could become renewable additives for diesel [24]. Regioselective control in aldol condensation of unsymmetrical ketones opens up unprecedented routes for obtaining branched alkanes, which are more suitable as gasoline additives.

Regioselective control is also critical in the large-scale production of flavors and fragrances [25,26]. For instance, the branched aldol condensation product of campholenic aldehyde and 2-butanone is a valuable intermediate in the manufacture of sandalwood fragrances [6], and is desired over its linear isomer which is an impurity in this process. The current industrial aldolizations use homogeneous catalysts such as caustic soda [25,26] with the well-known disadvantages of corrosion, waste generation and expensive catalyst separation and re-use. Hence, there is a need to develop selective solid catalysts for processes required in the conversion of biomass to fuels and chemicals, and potentially also for other processes.

Another area of limited knowledge is the association of activity with particular sites on the solid catalyst. Many oxidic materials possess both Brønsted and Lewis, acidic and basic sites. Regioselectivity can be used as a diagnostic tool to identify the contributing sites on the surface of a solid catalyst. For instance, in the case of 2-butanone, reaction at the methylene group should indicate acid catalysis and reaction at the methyl group should indicate base catalysis [27].

Regioselective control has been successfully demonstrated in homogeneous catalysis using organocatalysts. (S)-Prolinamide [28] and C<sub>2</sub>-symmetric bisprolinamide [29] were shown to preferentially form linear products, whereas L-proline [30] and N,N-dialkylated di-aminocyclohexanes [31] formed branched aldol products. Soluble organocatalysts are typically used in stoichiometric amounts [32], which make them unsuitable for large-scale processing, and they also pose problems with catalyst separation and recycling. Supported organocatalysts were also explored to evaluate their applicability in the industry [33,34]. This approach was only partially successful, and some immobilized organocatalysts were less effective (i.e., giving lower yields or lower stereoselectivity) than their non-supported counterparts or they lost activity upon recycling, with leaching being one of the identified causes [33].

Very few reports focus on controlling regioselectivity with soluble or solid inorganic catalysts. Zhao et al. [35] investigated the aldol condensation of furfural with levulinic acid using NaOH solution and reported higher selectivity for the linear products. No addition products were identified in this report. Liang et al. [36] tested several solid metal oxides for the same reaction and observed linear products with MgO and branched products with ZnO. In this investigation, the combined selectivity to addition and condensation products was used to characterize the regioselective preference of the catalyst. Interestingly, in a number of reports on the homogeneously catalyzed reaction of butanone and benzaldehyde, termination at the intermediate aldol stage sometimes resulted in branched products, whereas continuation to the  $\alpha,\beta$ -unsaturated ketone stage resulted in linear products [37–40]. Hence, demarca-

tion of the addition and condensation steps is essential to ascertain the course of the reaction.

The goal of this work was to identify the factors that govern regioselectivity and to generate the knowledge for rational development of solid catalysts. To ensure broad validity of design principles, several families of catalysts with different characteristic acid and base sites were evaluated, namely sulfonic acid functionalized SBA-15 with or without hydrophobization [41], amine functionalized SBA-15, isomorphously metal-substituted zeolites (Lewis acid-base pairs) [42], and sulfated zirconias (complex amphoteric surface with both Brønsted and Lewis sites) [43]. Hydrophobicity was expected to play a role in dispelling the reaction product water. The aldol condensation of a non-enolizable aromatic aldehyde, benzaldehyde, and an unsymmetrical ketone, 2-butanone, served as a test reaction to minimize the number of aldol products and to elucidate the association of activity with sites on the solid catalysts. Moreover, observation and quantification of the intermediate aldols allowed delineation of addition and condensation steps. It is demonstrated that both aldol reaction steps (addition and dehydration) and regioselectivity of the cross-aldol condensation involving unsymmetrical ketones can be controlled by tuning the nature, density, and environment of the active site.

## 2. Experimental section

### 2.1. Synthesis and functionalization of SBA-15

#### 2.1.1. Synthesis of SBA-15

SBA-15 was synthesized according to the method reported by Zhao et al. [44]. Ten grams of Pluronic P123 triblock copolymer were dissolved in 250 ml of 2 M HCl solution and 75 ml of DI water by stirring at 35 °C. After addition of 23 ml of TEOS, the mixture was stirred continuously for 20 h at 35 °C. The resulting gel was aged at 80 °C for 24 h. Later, the solid product was filtered, washed with DI water and calcined in static air at 550 °C for 5 h.

#### 2.1.2. Propylamine (PrNH<sub>2</sub>) functionalization of SBA-15

One milliliter of aminopropyltrimethoxy silane (APTMS, Sigma) was added to a suspension of 1 g SBA-15 and 30 ml of toluene (Fisher 99%). The suspension was then refluxed at 125 °C under stirring for 24 h, after which the resulting functionalized solid was filtered, washed three times with methanol (Fisher) and dried at 80 °C overnight.

#### 2.1.3. Propyl sulfonic acid (PrSO<sub>3</sub>H) and octyl co-functionalization of SBA-15

The synthesis procedure was adapted from Ref. [41]. SBA-15 and 3-mercaptopropyl trimethoxysilane (MPTMS, Sigma) were combined in an appropriate ratio (MPTMS/SBA-15 between 0.01 and 1) in 30 ml of toluene to vary the thiol coverage. The suspension was refluxed for 24 h; then the thiol-functionalized solid was retrieved by filtration, washed with methanol and dried at 80 °C. One portion of the thiol-functionalized sample was oxidized with H<sub>2</sub>O<sub>2</sub> at room temperature for 24 h (30 ml of 33 wt% H<sub>2</sub>O<sub>2</sub> per gram of material) to prepare sulfonic acid-functionalized SBA-15, and the other portion was used for co-grafting with *n*-octyl groups. The samples are denoted as x-PrSO<sub>3</sub>H/SBA-15 where x corresponds to the wt% sulfur measured by CHNS analysis.

To introduce octyl groups, thiol-grafted samples ( $\approx 1$  g) were refluxed in a solution of 1 ml of octyltriethoxysilane in 30 ml of toluene for 24 h. Washing, drying and oxidation of the thiol groups to sulfonic acid were performed as described above. Sulfur and carbon contents of the final octyl co-derivatised samples were remeasured by CHNS analysis. This series is denoted as Oc/x-PrSO<sub>3</sub>H/SBA-15 where x corresponds to the weight% of S measured by CHNS analysis in the parent sample.

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