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Biooxygenates Cross-coupling for Fuel Components Production

Polina A. Zharova*[a], Andrey V. Chistyakov[a], Ivan S. Levin[a], Mark V. Tsodikov[a] , Sergey A. Nikolaev[b]

[a] Topchiev Institute of Petrochemical Synthesis, R AS, Leninskii pr. 29, Moscow 119991, Russia
[b] Moscow State University, Leninskie Gory 1, Moscow 119991, Russia
zharova@ips.ac.ru

C-C bond formation is a pivotal method to construct complex molecules from some simple substrates, with the electrophilic alkylation of a given starting material being one of the most useful procedures. The straightforward routes to the creation of a variety of alcohols having intricate structures through alkylation of simple alcohols remain very unusual. Previously we found that during heterogeneously catalyzed conversion of ethanol with iso-propanol 2-pentanol formed with the yield equal to 35 wt.%. The general co-products were 1-butanol, 1-hexanol and 1-octanol that are valuable chemicals itself. Here we propose a heterogeneously catalytic route to convert such fermentation products as ethanol, acetone, 2-propanol and 1-butanol obtained from a variety of renewable carbohydrate sources into precursors for petrol, diesel and jet fuels. One of the work features is the use of heterometallic precursors, containing different pairs of metals closer to a distance less than the sum of their covalent radii, for supported catalysts creation.Introduction

1. Introduction

Natural biological routes to produce alcohols (ethanol and n-butanol) from carbohydrates have been known for more than 100 years, and these compounds have been produced in fermentations at high titres (100 and 15 g l21, respectively) and at yields near their theoretical maxima. These low-molecular-mass compounds are primarily suitable as additives or in certain situations (for example, E100 flex fuel vehicles) as alternatives to petrol. Advances in metabolic engineering have enabled the biological production of several higher-molecular mass jet and diesel fuel compounds from carbohydrates, but until now these processes have suffered from low titres and yields (Steen et al., 2010, Wang et al., 2011, Peralta-Yahya et al., 2011).
The use of biomass as raw material for the synthesis of fuels and chemicals is nowadays a major challenge because of the scarcity of fossil fuels and global climate change concerns. Although from a thermodynamic point of view, the use of biomass for satisfying the needs of fuels and chemicals is reliable (Tichit et al., 2003); many technological limitations burden this possibility. Only a very minor fraction of this biomass (triglycerides, sugars, and starches) can be selectively transformed into fuels (biodiesel) or chemicals (mainly ethanol), whereas most of the biomass components (cellulose, lignin) are not easy to transform into valuable organic molecules. Cost of the treatments of the whole biomass (such as pyrolysis or acid/enzymatic hydrolysis) leads to the formation of low-rank organic molecules of low molecular weight and high oxygen/carbon ratio. In this way, bioethanol is obtained in the fermentation of sugars and starches; chemicals such as acetone, acetic acid, phenols, furfural and another light oxygenates are released during the fast pyrolysis of biomass feedstock (Pandey, 2009), and a large number of oxidized derivatives of the sugars (such as furfural, hydroxymethylfurfural, glucuronic acid) are formed during the acid hydrolysis of wooden feedstocks (Kunkes et al., 2008). The transformation of molecules of low molecular weight into larger molecules must involve the formation of new carbon-carbon bonds (Ordóñez et al., 2011). C-C bonds formation is a pivotal method to construct complex molecules from some simple substrates, with the electrophilic alkylation of a given starting material being one of the most useful procedures (Schreiber, 2000). Alcohols are one of the most basic and important organic materials owing to their wide variety of uses in industrial and laboratory chemistry.

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The classic β-alkylation of secondary alcohol leading to higher alcohol usually requires tedious processes producing a lot of waste: oxidation, alkylation, and reduction, which cause some disadvantages in the atom economic (Sheldon, 2000) and environmental (Jenck et al., 2004) points of view. Thus any new strategy for the catalytic direct β-alkylation of secondary alcohols to create higher alcohols would be highly desirable, all the more so if it is an environmentally benign route with high atom efficiency (Yang et al., 2012).

The scope of the present work is to study the effect of Cu and Pd supported on γ-Al_2O_3 on selectivity and catalytic activity in bioalcohols cross-coupling reaction. Previously, we found that during heterogeneously catalyzed conversion of ethanol with isopropanol 2-pentanol formed with the yield equal to 35 wt.% (Zharova et al., 2016). The general co-products were 1-butanol, 1-hexanol, and 1-octanol that are valuable chemicals itself. Here we propose a heterogeneously catalytic route to convert such fermentation products as ethanol, acetone, 2-propanol, and 1-butanol obtained from a variety of renewable carbohydrate sources into precursors for petrol, diesel and jet fuels. One of the work features is the use of heterometallic precursors, containing different pairs of metals closer to a distance less than the sum of their covalent radii, for supported catalysts creation.

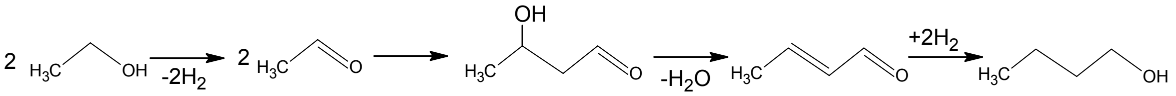
2. Materials and Methods

As a catalyst we used 0.1wt.%Pd-0.12wt.%Cu/γ-Al_2O_3 system. Analytical grade ethanol, isopropanol, and 1-butanol were used without further purification. Catalytic experiments were carried out in a 45 mL high-pressure Parr autoclave equipped with magnetic stirring. The reactor was loaded with the catalyst (typically 4.5 g). The catalyst testing procedure was as follows: the reactor with catalyst was loaded with equal volumes of ethanol (25 ml) or ethanol and isopropanol (typically 13 ml of each alcohol) or with 25 ml of mixture containing 60 vol.% 1-butanol, 30 vol.% acetone and 10 vol.% ethanol, closed and flushed with inert gas (Ar). The reactor was heated up to 275°C with a heating rate of 20°C/min. The reaction was carried out for 5 h. Then, the reactor was cooled down and analysis of the reaction mixture was performed.

Qualitative and quantitative analysis of the C_1–C_5 hydrocarbon gases was performed by gas chromatography (GC) with a Kristall-4000M chromatograph (carrier gas: He, column: HP-PLOT/Al_2O_3, 50 m × 0.32 mm; flame ionization detector). GC analyses of CO, CO_2, and H_2 were performed with a Kristall-4000 chromatograph (carrier gas: Ar, column: SKT, 1.5 m × 4 mm; thermal conductivity detector). The qualitative composition of the liquid organic products was carried out by gas-liquid chromatography coupled to mass spectrometry (GLC-MS) using an MSD 6973 - and an Autowt.-150 spectrometer - (EI = 70 eV, columns: HP-5MS, 50 m × 0.32 mm and CPSil-5, 25 m × 0.15 mm). The quantitative content of the organic compounds was determined by GLC using a Varian 3600 chromatograph (carrier gas: He, column: Chromtec SE-30, 25 m × 0.25 mm detector: flame ionization detector).

3. Results and Discussion

As it considered ethanol and acetone-butanol-ethanol (ABE) mixture might be a prospective bio-derived source for chemicals and fuels in future (Tiwari et al., 2015; Comwien et al.,2015). First, we tested the activity of Pd-Cu catalyst for self-condensation of ethanol to 1-butanol and higher molecule alcohols (Scheme 1). 1-butanol is known to be an effective additive to gasoline (Uyttebroek et al., 2015), so the efficiency of the catalyst was evaluated as the selectivity of 1-butanol formation and the conversion of ethanol.



Scheme 1. Ethanol self-condensation pathways.

The catalyst showed the highest yield of condensation product such as 1-butanol with the selectivity of 65.6 % at 56.3 % conversion of ethanol (Figure 1). An important aspect of any catalytic process is the lifetime of the catalyst that was investigated with a series of consecutive experiments. During the first 20 hours being on stream, the catalyst changes its activity and selectivity very markedly. After that, an insignificant (not more than 10%) decrease in the conversion of ethanol and an increase (no more than 10%) of the selectivity of the formation of 1-butanol is observed until 70 hours. The selectivity of the formation of 1-octanol and 1-hexanol remains constant. After 70 hours of operation of the catalyst, the reduction in the degree of conversion of ethanol becomes more pronounced, and the dynamics of increasing selectivity of 1-butanol formation slows down.

During the self-condensation reaction of ethanol, water forms. The results of the study of the effect of water content in ethanol on the selectivity of the reaction are shown in Figure 2. It is shown that when using absolute ethanol, its conversion is significantly increased, while the selectivity to 1-butanol remains practically constant. The selectivity of formation of 1-hexanol and 1-octanol decreases in proportion to the increase in water content. It is likely that a significant reduction in the degree of conversion of ethanol with increasing water concentration in the reaction zone is due to competitive chemisorption of water and ethanol at identical active sites. Perhaps the water molecules form tightly bound surface compounds with the catalyst, thereby blocking the active sites from the molecules of the alcohol.

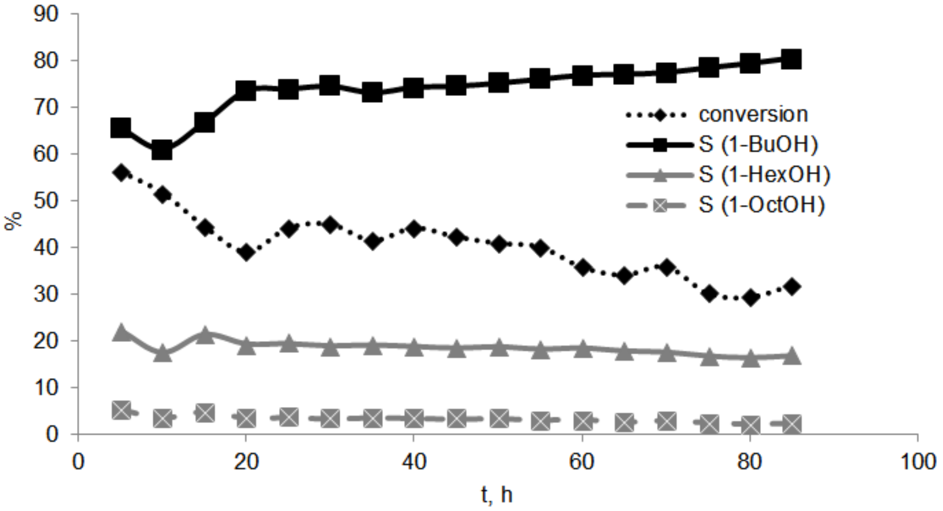


Figure 1: Dynamics of 1-butanol (S(1-BuOH)), 1-hexanol (S-(1HexOH)), 1-octanol (S(1-OctOH)) selectivity and ethanol conversion changes during stability experiments.

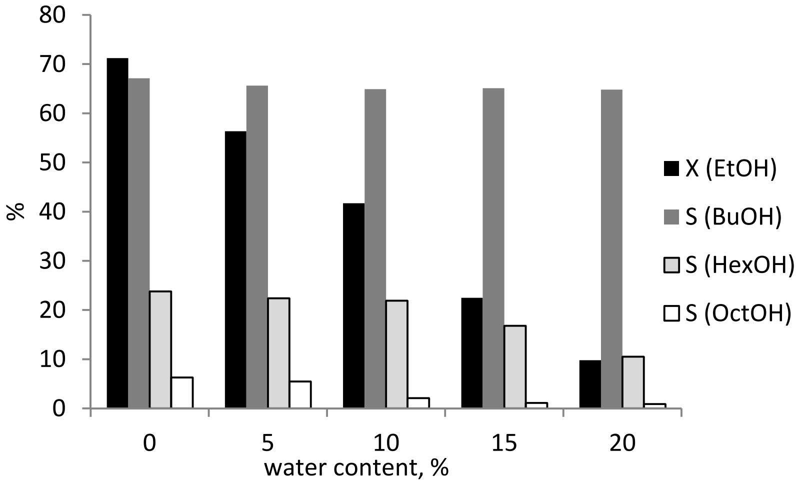


Figure 2: Water content effect on the self-condensation of ethanol reaction parameters.

To evaluate regularities of ABE mixture conversion first we tested ethanol and acetone mixture conversion and 1-butanol and acetone mixture conversion. Ethanol and 1-butanol do not react under the reaction conditions with each other. Products composition of 50 vol.% ethanol and 50 vol.% acetone mixture conversion are presented in Figure 3. Conversion of both reagents was approximately 50%. The first step of the reaction is dehydrogenation of ethanol to acetaldehyde followed by β-alkylation of acetone with acetaldehyde (Scheme 2). Products analysis indicates that acetone partially reduces to isopropanol. That is an undesirable process, that probably may be inhibited with catalyst composition tuning. The main products of alkylation of acetone with ethanol are 2-pentanon and 2-pentanol (Scheme 3, product A). The content of 4-

heptanol (Scheme 3, product C) is 4.5 times smaller than one of 2-pentanol and 2-pentanon. That phenomenon indicates that predominantly only one condensation step takes place.

The composition of the products of the co-conversion of 1-butanol and acetone is shown in Figure 4. It is seen from the figure that 4-heptanone dominates in the reaction products (Scheme 3, product B1), which indicates the high intensity of the stage of monoalkylation of acetone with 1-butanol. It should be noted that part of the acetone is converted to isopropanol, undergoing hydrogenation with hydrogen formed during the dehydrogenation of 1-butanol (Scheme 2). The yield of double alkylation products is lower than monoalkylated, but their content is approximately 20%. The main reaction products are ketones. The yield of alcohols is much lower. The high content of ketones in reaction products suggests that their composition is potentially promising for the preparation of C_{12}-C_{18} compounds, however, it is necessary to increase the condensing capacity of the catalyst.

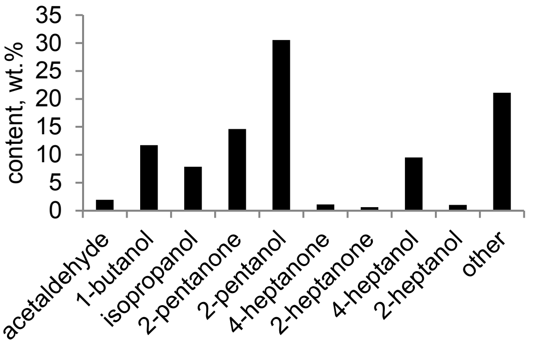


Figure 3: Products composition of 50 vol.% ethanol and 50 vol.% acetone mixture conversion

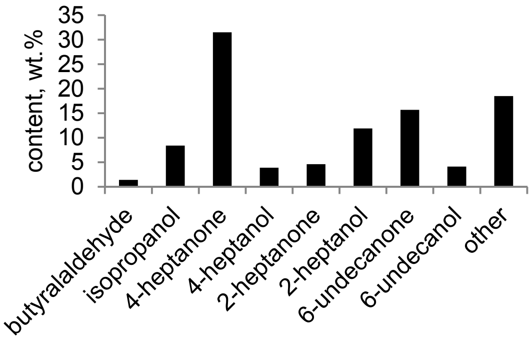
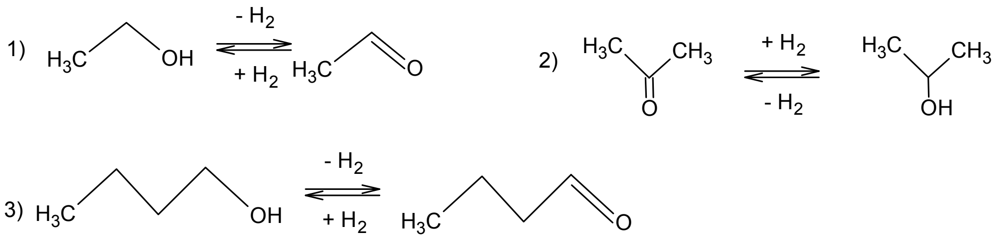


Figure 4: Products composition of 50 vol.% 1-butanol and 50 vol.% acetone mixture conversion

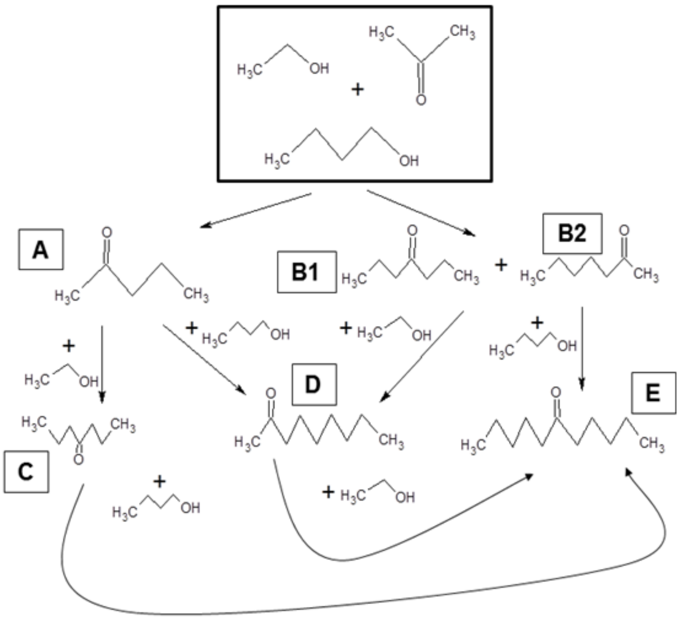


Scheme 2. The first step of the reaction dehydrogenation of alcohols 1) and 3). Undesirable reaction of acetone hydrogenation 3).

The composition of the products of the ABE mixture conversion is shown in Figure 5. In reaction products, ketones are observed up to three consecutive alkylation steps. Thus, the intensity of the condensation stage increases with increasing amount of initial reagents. We explored the mechanism of the reaction by following the reaction progress (Scheme 3). Monoalkylation of acetone with 1-butanol and ethanol produces 2-pentanone and 2-heptanone. These species underwent further reaction to form double-alkylated products. No aldehydes were observed during the reaction, suggesting that the aldehyde intermediates were present in very low concentrations and reacted rapidly with acetone and other ketones. Hence, the formation of Guerbet products was minimized, and acetone alkylation predominated.

The alcohols (1-butanol and ethanol) are dehydrogenated by the catalyst, generating the reactive aldehydes and hydrogen. At this stage, the aldehydes undergo either a self-aldol reaction to form the Guerbet product precursor or an aldol reaction with acetone. Under the conditions employed here, condensation with acetone seems to be favoured, because acetone is present at much higher concentrations than the transient aldehydes. Subsequent dehydration of the aldol product under the reaction conditions furnishes α, β-unsaturated ketones that undergo hydrogenation with the hydrogen generated in the first step. Completing the same cycle with monoalkylated products affords the expected double alkylation products. The relative ease of attack by the unsubstituted versus the substituted a-carbon of the monoalkylated products leads primarily to unbranched products. This combination of kinetic controls on the alkylation reaction, therefore, enables the conversion of a mixture of renewable metabolites into a well-defined range of ketone products.

Thus, the principal possibility of obtaining high-molecular alcohols and ketones from ABE mixture is shown. The products obtained can be additives to gasoline, or be hydroisomerized to produce branched alkanes, which are the main components of motor fuels.



Scheme 3. A general pathways of ABE fermentation mixture conversion.

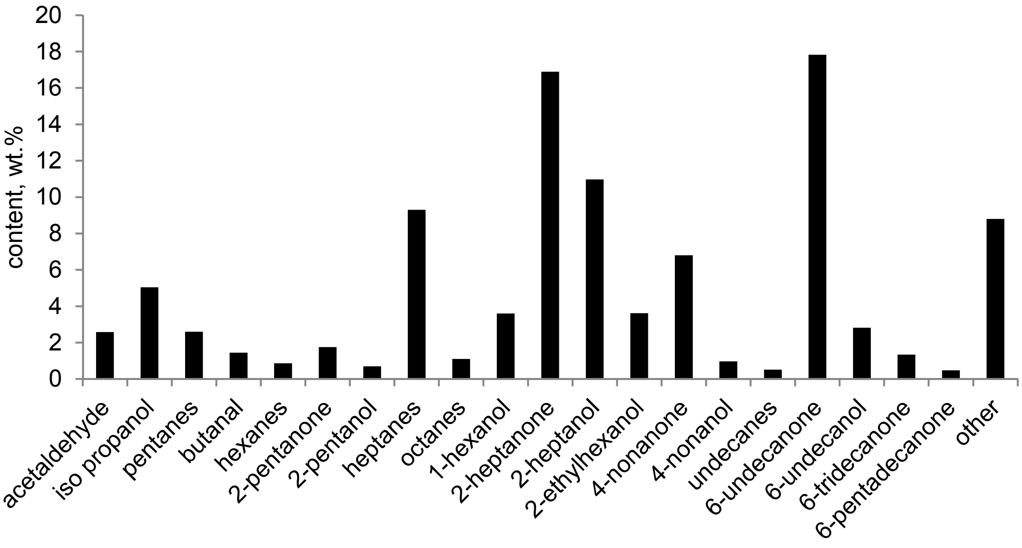


Figure 5: Products distribution of ABE mixture conversion.

4. Conclusions

The presented results demonstrate high potential of using heterogeneous Pd-Cu/γ-Al_2O_3 system for cross-condensation of bio-oxygenates. It should be noted that in the presence of metal complex catalysts in homogeneous catalysis, the selectivity of the formation of cross-condensation products is much higher, but heterogeneous systems allow to achieve significantly higher yields and, moreover, they are more environmentally friendly. The developed Pd-Cu/γ-Al_2O_3 catalyst allows one to convert ethanol with a selectivity of up to 80% into 1-butanol, that is an important industrial chemical and a promising component of gasoline.

Oxygenates containing up to 15 carbon atoms can be obtained on the basis of the ABE fermentation mixture, that after the hydroisomerization stage can be used as components of diesel fuel with a pour point of up to − 60°C. The main challenge for further research is to develop ways to eliminate the negative effects of water formed during the reaction, that apparently reduces the conversion of the raw materials. Obviously, the key to achieving this goal lies in the development of synthetic approaches to the directed tuning of the acidic-base properties of the catalyst surface, which our next work will be devoted to.

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