

62(1), pp. 91-96, 2018

<https://doi.org/10.3311/PPch.10390>

Creative Commons Attribution 

György Onyestyák^{1*}

RESEARCH ARTICLE

Received 10 December 2016; accepted after 21 February 2017

Abstract

Bioethanol valorization to butanol by continuous heterogeneous catalytic self-alkylation provides an option for the fuel industry. Dimerization of ethanol (E) was studied over activated carbon supported metal loaded and metal-free alkaline catalysts using a flow-through tube microreactor, applying $WHSV_E$ of 0.20-2.0 $g_E/h g_{cat}$, 21 bar total pressure and 275-400°C reaction temperature. Activated carbon (AC) was impregnated with various alkaline salts as the catalysts of the aldol reaction. Different basicity of the investigated catalysts resulted in differing catalytic activities. Butanol was the product of highest yield. Longer chain primary aliphatic alcohols, having even number of carbon atoms were also obtained with yield decreasing significantly with increasing chain length.

Keywords

bioethanol valorization, butanol, Guerbet coupling reaction, carbon supported alkaline catalyst

1 Introduction

Applications of ethanol as a platform chemical have generated new interest because of new economic opportunities seen in bio-based feedstocks, particularly if it is derived from non-food crops and lignocellulosic materials (second-generation biomass). Although ethanol is being explored as a renewable alternative to gasoline, it poses several disadvantages. Ethanol has lower energy density than gasoline, readily adsorbs water and can be corrosive to engines made by current technologies. Alternatively, butanol offers a more viable option, as it has properties similar to that of gasoline. Consequently, upgrading of ethanol into an advanced biofuel, such as butanol, offers a more efficient alternative fuel from biomass sources. Traditionally, bio-butanol is produced with the fermentative ABE (Acetone-Butanol-Ethanol) process using *Clostridium* species. However, the chemical conversion route from bioethanol is more preferable, because the reaction proceeds more quickly and less steps are required to get the product [1].

The direct catalytic α -alkylation of carbonyl compounds by alcohols through hydrogen borrowing route is known as Guerbet alkylation. The heavier alcohol obtained by alcohol coupling reaction is called "Guerbet alcohol". A great variety of organic chemicals can be synthesized with this method [2]. It is green chemical process because water is the sole by-product. Remarkable achievement of the field is the successful replacement of homogeneous catalyst systems by active heterogeneous catalysts allowing the development of waste-free and environmentally benign processes [3]. Appropriate selection of reaction condition and well-thought development of the catalytic system are of great importance as both the proportion and strength of each different site need to be properly tuned in order to maximize the yield and the selectivity of the target alcohol [4]. Despite the debate with respect to base or acid pair active sites, generally it has been accepted that basic sites are essential to the formation of butanol. Up to now, catalysts such as modified zeolites, metal oxides and modified hydroxyapatites, among others, have been widely used [5]. Because a wide variety of catalyst compositions, reaction conditions and reactor configurations used to study the reaction it is quite complicate

¹ Institute of Materials and Environmental Chemistry,
Research Centre for Natural Sciences,
Hungarian Academy of Sciences,
1117 Budapest, Magyar Tudósok krt. 2, Hungary

* Corresponding author, e-mail: onyestyak.gyorgy@tk.mta.hu

a direct comparison of various catalysts. The most active metal oxide and phosphate catalysts apparently have significant densities of weak acid and medium to strong basic sites [6]. What is not known is the proximity of the acid and base sites.

Numerous investigations have shown over a variety of heterogeneous systems, including zeolites, MgO, MgAl mixed oxides and hydroxyapatites [7, 8]. Hydroxyapatites are particularly noteworthy because higher activity and selectivity to butanol [9, 10]. However, many of these systems suffer from poor conversion or selectivity. Carbon is inert and it can be suitable as catalyst support. Carbon nanofibers (CNF) having a relatively high surface area ($150 \text{ m}^2\text{g}^{-1}$) was already successfully applied for supporting alkaline earth metal oxide nanoparticles toward production of Guerbet alcohols from bio-based resources [11].

Recently, Anbarasan and co-workers proposed a novel chemical route to convert fermentation ABE product into hydrocarbons that can be used for fuel [12]. For the Guerbet cross-condensation of acetone and alcohols carbon supported palladium was found superior to the other metals (Ir, Ru, Rh, Pt, Ni) using in various forms with different bases in molar equivalent to alcohols. K_3PO_4 base additive seemed to be the most efficient. G. Xu and co-workers - mimicking ABE fermentation product - demonstrated direct α -alkylation of ketones with alcohols in water (instead of toluene [12]) over Pd/C catalytic system in autoclave. In the reaction mixture equivalents of different bases (K_3PO_4 , LiOH, NaOH or KOH) to the amount of acetone were used [13]. Q. Xu and co-workers conceive that transition-metal-catalysed α -alkylation of ketones with alcohols still have drawbacks, consequently they prefer the "catalyst-free" dehydrative α -alkylation. Henceforward, high amount of bases (NaOH or KOH) are still applied in the studied alkylation reactions [14]. The cited literature shows as yet only investigations in small batch reactor systems [12-14] which have several disadvantages and those tests give information with limited details. Broad spectrums of catalysts were already tested, but the acting catalysts were not at all characterized. References [12, 13] did not give specification about the used "5% palladium on carbon" catalysts. In our former studies, a commercial pelletized activated carbon (AC) ($1150 \text{ m}^2\text{g}^{-1}$) as inert support was applied [15-17]. The AC was impregnated with CsOH, KOH or K_3PO_4 solutions using incipient wetness method and finally loaded with 5 m % palladium. In alkylation of acetone with ethanol the overall yield, selectivity to longer ketones and alcohols and constant activity on such palladium catalyst were found outstanding. It is a pronounced important observation, that self- and cross-condensation steps are equally characteristic to the consecutive alkylation. Thus, butanol can be formed inevitable from ethanol self-addition, which can take part in cross-condensation reaction with acetone [15-17].

The present work was motivated by the finding that significant self-coupling of ethanol to butanol occurs in the ethanol-acetone mixture over activated carbon loaded with alkaline

salts and palladium. Investigation of ethanol condensation alone over such catalyst varieties can be exciting. This study reflects also the importance of the support.

2 Materials and methods

In our former [15-17] and the present works a commercial pelletized activated carbon (AC) (cylinders with 0.8 mm diameter and 2-4 mm length, Norit ROX 0.8 EXTRA, specific area: $1150 \text{ m}^2\text{g}^{-1}$) as inert support was applied. The AC first was dried at 110°C , then impregnated with various alkaline compounds (lithium hydroxyde (LiOH), sodium hydroxyde (NaOH), potassium hydroxyde (KOH), cesium hydroxyde (CsOH), potassium phosphate K_3PO_4 , calcium acetate $\text{Ca}(\text{Ac})_2$, magnesium acetate $\text{Mg}(\text{Ac})_2$ and zinc acetate $\text{Zn}(\text{Ac})_2$) solutions using incipient wetness method and dried again at 110°C . For 1 g support 0.1 g or 0.3 g base were added resulting in plus 10 or 30 m% loadings. Finally, 10 or 30 m% nickel is also loaded using nickel acetate, $\text{Ni}(\text{Ac})_2$. From these precursors were formed the active catalysts under calcination in H_2 prior to the experiment in situ in the high-pressure catalytic reactor at 400°C . The same designation was used for the catalyst precursor and the corresponding catalyst, containing the symbol of the base and the metal, and the name of the support, such as, e.g. 10KOH/AC, 30KOH/AC, 30KOH10Ni/AC, 30KOH30Ni/AC, etc.

The catalyst precursor was loaded into a high-pressure, fixed bed, flow-through reactor and reduced in a flow of $100 \text{ cm}^3\text{min}^{-1}$ pure hydrogen *in situ* in the reactor at 400°C and 21 bar for 1h. The self-condensation reaction of ethanol (E) (Molar Chemical, Hungary) was studied in hydrogen flow at 21 bar total pressure and at in the $275\text{-}400^\circ\text{C}$ temperature range. The reactor effluent was cooled down to room temperature, the liquid and gaseous products were separated. The liquid was analyzed using gas chromatograph (Shimadzu 2010) equipped with a Restek Rt-U-BOND capillary column, and a flame ionization detector. The gas was analyzed by on-line gas chromatograph (HP 5890) equipped with Carboxen 1006 PLOT capillary column and thermal conductivity cell. The product distributions are represented as stacked area graphs (unusual but more expressive plotting) where the distance between two neighboring curves represents the yield of a given product in mole percent.

XRD patterns of the catalysts were recorded at elevated temperatures in hydrogen flow using a high-temperature XRD cell a Philips PW 1810 diffractometer. The mean crystallite size of the metal particles was calculated by the Scherrer equation. Adsorption isotherms of nitrogen were determined at -196°C using Quantochrome Autosorb 1C sorptometer.

The reducibility of the samples was examined by temperature-programmed H_2 -reduction (H_2 -TPR) using a flow-through quartz microreactor. About 30 mg catalyst was pretreated in a flow of 30 mlmin^{-1} nitrogen at 350°C for 1h. The pretreated sample was then cooled to room temperature in the same N_2 flow before was contacted with a $30 \text{ cm}^3\text{min}^{-1}$ flow of

9.7% H_2/N_2 mixture. The reactor temperature was ramped up at a rate of $10^\circ\text{C min}^{-1}$ to 400°C and maintained for 1h at latter temperature. The effluent gas was passed through a liquid nitrogen trap and a thermal conductivity detector (TCD). Data were recorded and processed by computer. Calculation of the corresponding hydrogen consumptions based on the peak areas was carried out by using the calibration value determined with the H_2 -TPR of CuO reference material.

3 Results and Discussion

Hydrotalcite-supported palladium or nickel catalysts can be used equally well for acetone alkylation with ethanol to longer ketones and alcohols in the presence of flowing hydrogen [18]. Accordingly, nickel catalyst can replace more expensive palladium (see the characteristic distribution of main products in Fig1B at 300°C). The layered structure of the HT is destroyed at 200°C . Mixed oxide $MgO\cdot Al_2O_3$, referred here to as AHT was obtained. That has higher surface area than hydrotalcite. Guerbet coupling of ethanol and acetone ($E/A=2$) was also tested over metal-free AHT catalyst. In absence of the metallic component the formation rate of longer ketones was much lower. The selectivity was very poor. Cyclic products, mainly cyclohexanol derivatives were obtained with higher yields than the aliphatic ketones. Conversion of acetone was much more significant than that of ethanol, suggesting that acetone self-condensation was preferred [18].

During Guerbet alkylation self- and cross-condensation steps run parallel. Thus, butanol can be inevitable formed from ethanol. Butanol can take part in further cross-condensation reaction with ketones. Cross-condensation of butanol with acetone results in reaction products such as 2-heptanone, 4-nonanone, 6-undecanone [18]. No serious selectivity problems were found when self-coupling of pure ethanol to butanol was studied over the metal-free AHT catalyst [18]. Only diethyl ether with low yield was formed as side product because of presence of Al_2O_3 component in AHT. Metal-loaded AHT catalyst was tested also with pure ethanol shown Fig. 1A. Data demonstrate that the nickel as metal component in such catalyst is quite disadvantageous because butanol hardly formed and the main product was methane. Although the activated carbon supported alkaline compounds and nickel catalyst ($30KOH10Ni/AC$) shows lower activity in cross-coupling reaction (compare Fig. 1B and D). However, it seems to be advantageous in self-coupling of pure ethanol (see Fig. 1C). Several variations of such catalytic systems are investigated in this work.

Activated carbon support is inert in the studied reaction and its pelletized forms are well applicable in fixed bed flow-through systems. In Fig. 2 isotherms of nitrogen adsorption related to carbon content characterize the porosity of the support and the prepared catalysts. Shape of these isotherms reflects highly microporous materials with high specific surface area ($>1000\text{ m}^2/\text{g}$) which is characteristic for activated carbons

containing less slit-like pores than 1 nm between carbon sheets. Presence of hysteresis loop indicates mesopores (mean pore diameter (BJH) is approx. 4 nm) of low diffusional resistance probably created in the course of pellet formation process.

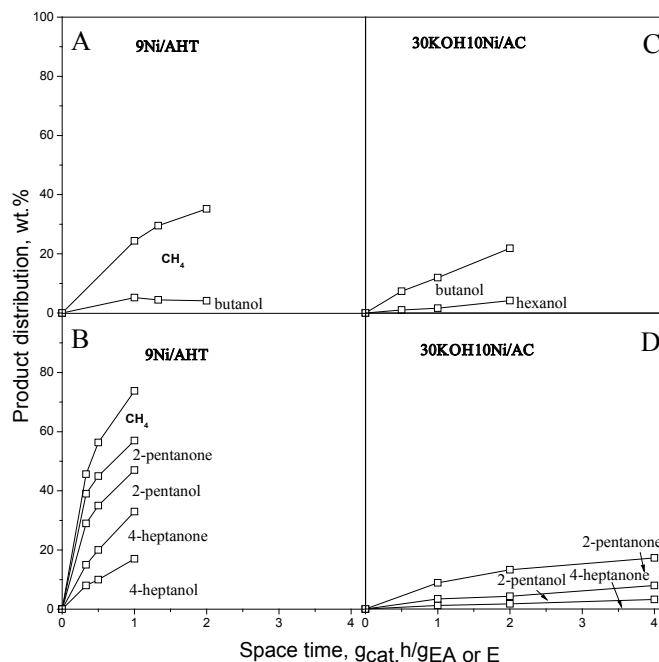


Fig. 1 Stacked area graphs representing product distribution of pure ethanol (A and C) and ethanol-acetone (2:1) mixture (B and D) Guerbet coupling as a function of space time at 300°C and 21 bar over the AHT (A and B) and AC (C and D) supported and nickel promoted catalysts.

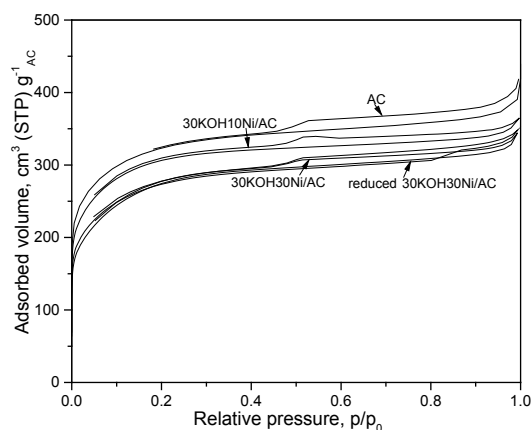


Fig. 2 Adsorption isotherms of nitrogen obtained at -196°C on the parent AC, $30KOH10Ni/AC$, $30KOH30Ni/AC$ and reduced $30KOH30Ni/AC$ samples. Only these samples are shown because all impregnated samples give quite similar isotherms (related to the AC content).

In the cited batch reactor experiments [12-14] high amount of bases, some equivalents in the ratio of one of the reactants were used in the reaction mixtures. Such high base/reactant ratio can be also given in our experiments over fixed catalyst beds. Presence of impregnated bases on AC only slightly decrease the adsorbed amount of nitrogen related to AC content. Admission of metal also results in slight decrease (see Fig. 2) which means that larger alkali and nickel metal crystallites can

form in the mesopores than at the entrance of narrower micropores. Contrary to micropores the mesoporous volumes, area of hysteresis loops, are decreased significantly. Since active components, the alkaline material and the metal are located in the larger pores among carbon crystallites, consequently the catalytic reactions take place in the spacious mesopores.

A H_2 -TPR curve is a fingerprint of the evolution of active metallic phase (nickel) following the reduction in H_2 flow as shown in Fig. 3. Reduction seems to be almost completed up to 400°C heating up the sample with 10 °C/min rate. To tell the truth this technique can give only qualitative information about reducibility because of its dynamic nature.

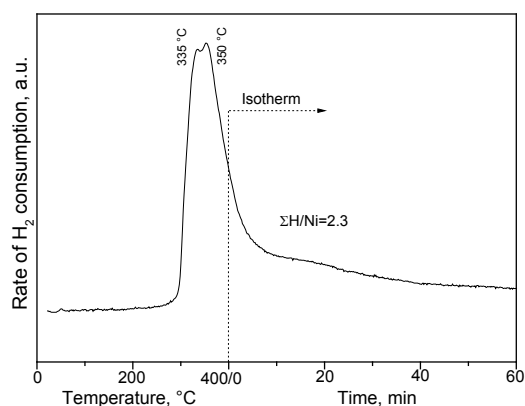


Fig. 3 H_2 -TPR of the 30KOH30Ni/AC catalyst precursor.

Observations obtained with HT-XRD technique are more important (see HT-XRD patterns in Fig. 4) parallel to dynamic measurement as H_2 -TPR. Nickel content of the catalyst seems to be nearly fully reduced already below 300°C heated up the samples with 50°C steps. The average size of Ni^0 particles obtained at 400°C and estimated by the Scherrer equation was found 9 and 17 nm for the catalysts containing 10 and 30 wt.% metal, respectively.

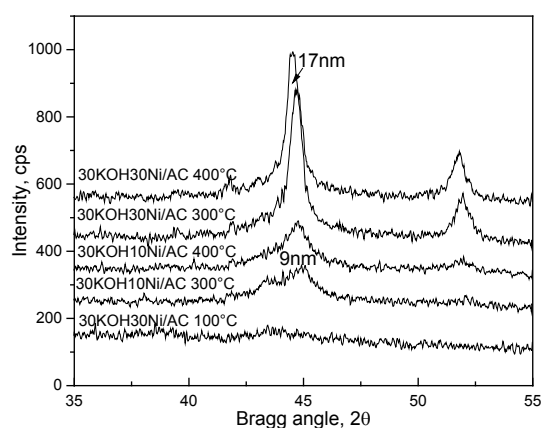


Fig. 4 HT-XRD patterns of the 30KOH10Ni/AC and 30KOH30Ni/AC catalyst precursors recorded in H_2 flow. The materials were kept at the indicated temperature for half hour before recording a diffractogram.

In chromatograms of the liquid products shown in ref. [19] the characteristic components of ethanol self-coupling represent the results obtained also over all catalysts of this study. Guerbet alcohols, having even number of carbon atoms appear (hexanol, octanol, decanol). The alcohol yield decreased parallel with increasing chain length. Traces of aldehydes in the product mixture prove that mechanism is based on the aldol reaction of aldehyde intermediates.

In Fig. 5 catalytic behaviour of metal-free and metal-loaded (Ni and Pd) KOH/AC catalyst can be compared in ethanol self-coupling reaction under equal reaction conditions. Only yields of the main product Guerbet alcohols, butanol, hexanol, octanol and the gaseous products are shown in the stacked area plots. The influence of increasing KOH loading on the activated carbon support is clearly demonstrated with Fig. 5A and B. Without metallic function over the alkaline catalysts gaseous products (CO and CH_4), cracked derivatives of ethanol cannot be observed. The yields of Guerbet alcohols (mainly butanol) and the reaction rates (initial slopes of the conversion curves) significantly increase with increasing KOH loading. Tripled the KOH concentration approx. doubled initial reaction rate can be attained. The presence of palladium in 30KOH5Pd/AC catalyst generated higher dehydrogenation/ hydrogenation activity enhancing the rate of Guerbet coupling to approx. double (see Fig. 5B and D). However, this metallic component can initiate hydrogenolysis of ethanol as indicated by the appearance gaseous products, carbon monoxide and methane in an amount that is higher at higher temperatures [19]. Such side reaction is uncharacteristic for nickel containing catalysts (e.g. see Fig. 5C). This is the other advantage of use of the cheaper nickel in the Guerbet catalysts enhancing hydrogen borrowing activity. The influence of nickel loaded in the KOH/AC catalyst is significant (compare Fig. 5B and C).

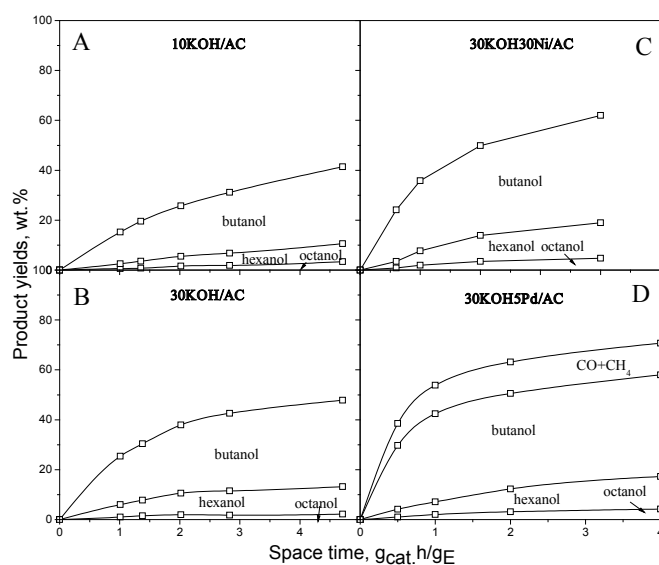


Fig. 5 Stacked area graphs representing main products of ethanol Guerbet coupling as a function of space time at 350 °C and 21 bar over the metal-free catalysts containing 10 (A) or 30 wt.% KOH (B) and the 30KOH10Ni/AC (C) and 30KOH5Pd/AC (D) samples.

However, it is simpler and cheaper to use KOH with higher loading, however this possibility is limited to aim the enlargement of the catalytically active surface. Consequently, modifying of alkaline catalysts with metals seems to be practical.

The lower activity of metal-free Guerbet catalysts can be additionally compensated by increasing the reaction temperature up to 375 °C, because side reactions, gaseous products appear only at 400 °C. Beyond the increase of the alkaline content, promotion with a metal component or enhanced reaction temperature, the catalytic activity can be changed using different alkaline materials to ensure appropriate basicity for aldol condensation. Fig. 6 permits of the comparison catalytic properties of eight different alkaline materials supported on activated carbon. The great advantage of these transition metal free alkaline catalysts that, these enable to attain high selectivity to form longer alcohols with high stability. Activities were found practically constant during 2-3 days being studied the selected catalyst sample. Strong alkaline compounds are the alkali metal hydroxides. In line with this fact these alkalis gave the most active catalysts supported on AC (Fig. 6A-D). Their catalytic activity and selectivity seem to be hardly different at 350 °C. Interestingly the potassium containing K_3PO_4/AC catalyst sample showed nearly the same catalytic behaviour than alkalis applied in hydroxide form of alkali metals from the first column of the periodic table. Alkaline earth metals and zinc can form medium strong bases and such AC supported catalysts showed approx. the half of initial reaction rates obtained over alkaline metal hydroxide variants. The different activities are well reflected with Arrhenius plots represented in Fig. 7.

The lowest reaction rate of ethanol self-coupling was observed over medium strong base catalyst hardly depending on type of the studied bivalent element (so only MgO loaded sample is shown in Fig. 7). Slopes of Arrhenius plots seem to be hardly different suggesting practically equal activation energies on every catalyst. It is somewhat surprising in comparison of alkaline compounds (containing mono- or bivalent metals) of significantly different basicity. This suggests that reaction step controlled by basic sites is not a rate controlling step. But then in Fig. 7 the intercepts of vertical axis are very different. The issues such as number of active sites, access of reactants to active sites and type of active sites may play important roles. Essentially the number of catalytically active sites can be different if the concentration of loaded active components is different. However, so far the effect of active component dispersion on the support was not investigated in this work. Further efforts are required for detailed conclusions because Guerbet coupling is a complex reaction coming into existence from four consecutive reactions.

Alkalis from the first column of the periodic table having high basicity reflect much higher activity. Catalytic activities are strongly influenced by the loaded amount of these

materials but only slightly by sort of the applied alkali metals. Modifying these catalysts with admission of a dehydrogenating/hydrogenating metal component increased activities are observed. Contrary, using medium strong bases, e.g. MgO and modified with metal, e.g. Ni and supported on AC, the situation is quite different. Results observed over 10MgO10Ni/AC are very similar than it was shown in Fig. 1A using an originally alkaline support, activated hydrotalcite (AHT), a mixed oxide $MgO.Al_2O_3$. This finding suggests that a balance of two different function, dehydrogenation/ hydrogenation and aldol condensation is necessary for selective Guerbet coupling, additionally the strength and concentration of basic sites on the active surface of primary importance.

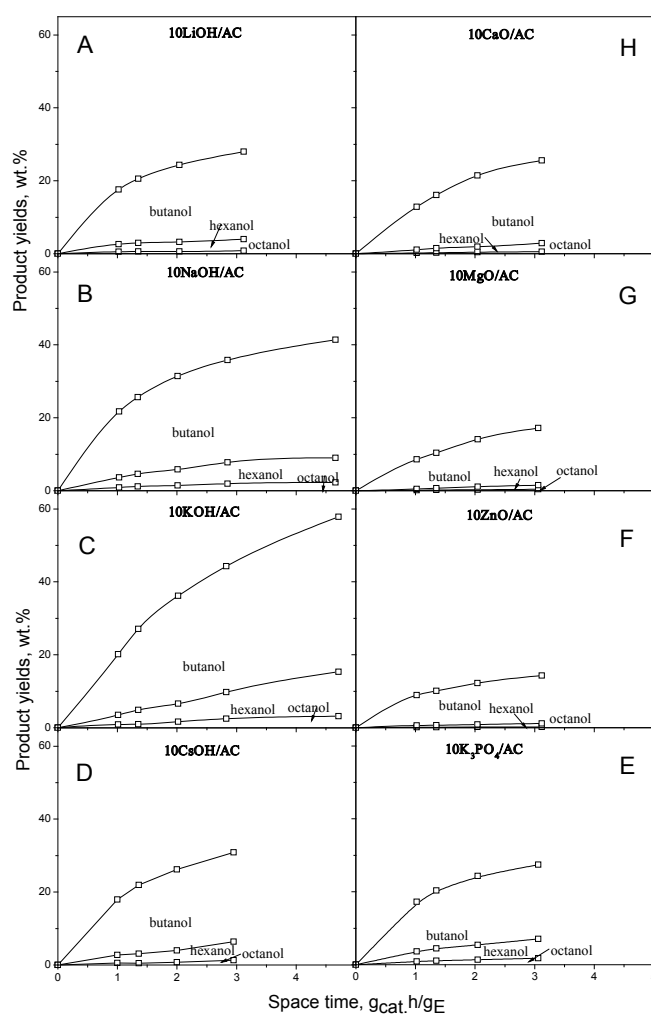


Fig. 6 Stacked area graphs representing main products of ethanol Guerbet coupling as a function of space time at 350 °C and 21 bar over the metal-free catalysts containing only various alkalis.

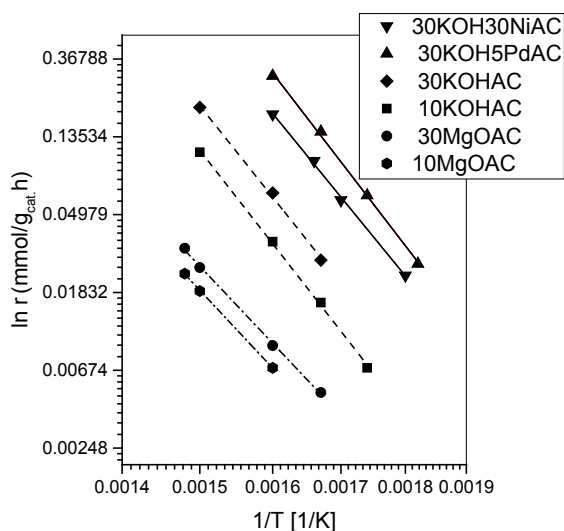


Fig. 7 Arrhenius plotting of initial reaction rates of longer alcohol formation represent different groups of Guerbet catalysts.

4 Conclusion

Guerbet self-alkylation of ethanol over activated carbon supported alkalis results in a mixture of butanol as main product and other higher alcohols. Relative to the ethanol the produced alcohol mixture can be already considered as an upgraded fuel additive. The higher alcohol components are value-added products that is not necessary recover from the mixture by proper separation technology if we use it as fuel. It was shown that the Guerbet alcohol coupling reaction can be carried out using continuous-flow, fixed bed, heterogeneous catalytic process. Nickel-containing and alkali metal salt modified activated carbon was shown to give high productivity and selectivity.

Acknowledgements

Just before my retirement, many thanks are due to my *alma mater*, Budapest Technical University for supporting my walk of life with a fundamental knowledge.

References

- [1] Ndaba, B., Chiyanzu, I., Marx, S. "n-Butanol derived from biochemical and chemical routes: A review." *Biotechnology Reports*. 8, pp. 1-9. 2015. <https://doi.org/10.1016/j.btre.2015.08.001>
- [2] Obora, Y. "Recent Advances in α -Alkylation Reactions using Alcohols with Hydrogen Borrowing Methodologies." *ACS Catalysis*. 4(11), pp. 3972-3981. 2014. <https://doi.org/10.1021/cs501269d>
- [3] Shimizu, K. "Heterogeneous catalysis for the direct synthesis of chemicals by borrowing hydrogen methodology." *Catalysis Science & Technology*. 5(3), pp. 1412-1427. 2015. <https://doi.org/10.1039/C4CY01170H>
- [4] Gabriels, D., Hernandez, W. Y., Sels, B., Van Der Voort, P., Verberckmoes, A. "Review of catalytic systems and thermodynamics for the Guerbet condensation reaction and challenges for biomass valorization." *Catalysis Science & Technology*. 5(8), pp. 3876-3902. 2015. <https://doi.org/10.1039/C5CY00359H>
- [5] Sun, J., Wang, Y. "Recent Advances in Catalytic Conversion of Ethanol to Chemicals." *ACS Catalysis*. 4(4), pp. 1078-1090. 2014. <https://doi.org/10.1021/cs401134d>
- [6] Kozlovski, J.T., Davis, R. J. "Heterogeneous Catalyst for the Guerbet Coupling of Alcohols." *ACS Catalysis*. 3(7), pp. 1588-1600. 2013. <https://doi.org/10.1021/cs400292f>
- [7] Galadima, A., Muraza, O. "Catalytic Upgrading of Bioethanol to Fuel Grade Bio-butanol: A Review." *Industrial & Engineering Chemistry Research*. 54(29), pp. 7181-7194. 2015. <https://doi.org/10.1021/acs.iecr.5b01443>
- [8] Early, J. H., Bourne, R. A., Watson, M. J., Poliakoff, M. "Continuous catalytic upgrading of ethanol to n-butanol and $>C_4$ products over Cu/CeO₂ catalysts in supercritical CO₂." *Green Chemistry*. 17(5), pp. 3018-3025. 2015. <https://doi.org/10.1039/C4GC00219A>
- [9] Hanspal, S., Young, Z. D., Shou, H., Davis, R. J. "Multiproduct Steady-State Isotopic Transient Kinetic Analysis of the Ethanol Coupling Reaction over Hydroxyapatite and Magnesia." *ACS Catalysis*. 5(3), pp. 1737-1746. 2015. <https://doi.org/10.1021/cs502023g>
- [10] Ho, C. R., Shylesh, S., Bell, A. T. "Mechanism and Kinetics of Ethanol Coupling to Butanol over Hydroxyapatite." *ACS Catalysis*. 6(2), pp. 939-948. 2016. <https://doi.org/10.1021/acscatal.5b02672>
- [11] Patel, A. D., Telalovic, S., Bitter, J. H., Worrell, E., Patel, M. K. "Analysis of sustainability metrics and application to the catalytic production of higher alcohols from ethanol." *Catalysis Today*. 239, pp. 56-79. 2015. <https://doi.org/10.1016/j.cattod.2014.03.070>
- [12] Anbarasan, P., Baer, Z. C., Sreekumar, S., Gross, E., Binder, J. B., Blanch, H. W., Clark, D. S., Toste, F. D. "Integration of chemical catalysis with extractive fermentation to produce fuels." *Nature*. 491, pp. 235-239. 2012. <https://doi.org/10.1038/nature11594>
- [13] Xu, G., Li, Q., Feng, J., Liu, Q., Zhang, Z., Wang, X., Zhang, X., Mu, X. "Direct α -Alkylation of Ketones with Alcohols in Water." *ChemSusChem—Chemistry & Sustainability, Energy & Materials*. 7(1), pp. 105-109. 2014. <https://doi.org/10.1002/cssc.201300815>
- [14] Xu, Q., Chen, J., Tian, H., Yuan, X., Li, S., Zhou, C., Liu, J. "Catalyst-free dehydrative α -alkylation of ketones with alcohols: green and selective autocatalyzed synthesis of alcohols and ketones." *Angewandte Chemie International Edition*. 53(1), pp. 225-229. 2014. <https://doi.org/10.1002/anie.201308642>
- [15] Novodárszki, Gy., Onyestyák, Gy., Farkas Wellisch, Á., Pilbáth, A. "Catalytic Alkylation of Acetone with Ethanol Over Pd/carbon Catalysts in Flow-through System Via Borrowing Hydrogen Route." *Acta Chimica Slovenica*. 63(2), pp. 251-257. 2016. <https://doi.org/10.17344/acsi.2015.1992>
- [16] Onyestyák, Gy., Novodárszki, Gy., Barthos, R., Klébert, Sz., Farkas Wellisch, Á., Pilbáth, A. "Acetone alkylation with ethanol over multifunctional catalysts by a borrowing hydrogen strategy." *RSC Advances*. 5(120), pp. 99502-99509. 2015. <https://doi.org/10.1039/C5RA17889D>
- [17] Onyestyák, Gy., Novodárszki, Gy., Farkas Wellisch, Á., Pilbáth, A. "Upgraded biofuel from alcohol-acetone feedstocks over a two-stage flow-through catalytic system." *Catalysis Science & Technology*. 6(12), pp. 4516-4524. 2016. URL: <https://doi.org/10.1039/C6CY00025H>
- [18] Novodárszki, Gy., Onyestyák, Gy., Barthos, R., Farkas Wellisch, Á., Thakur, A. J., Deka, D., Valyon, J. "Guerbet alkylation of acetone by ethanol and reduction of product alkylate to alkane over tandem nickel/Mg,Al-hydroxalcite and nickel molybdate/ γ -alumina catalyst systems." *Reaction Kinetics, Mechanisms and Catalysis*. 121(1), pp. 69-81. 2017. <https://doi.org/10.1007/s11144-016-1132-4>
- [19] Onyestyák, Gy., Novodárszki, Gy., Farkas Wellisch, Á., Thakur, A. J., Deka, D., Valyon, J. "Guerbet self-coupling for ethanol valorization over activated carbon supported catalysts." *Reaction Kinetics, Mechanism and Catalysis*. 121(1), pp. 31-41. 2017. <https://doi.org/10.1007/s11144-016-1125-3>