

Scientific paper

Catalytic Alkylation of Acetone with Ethanol Over Pd/carbon Catalysts in Flow-through System Via Borrowing Hydrogen Route

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Abstract

Consecutive alkylation of acetone with ethanol as model reactants was studied in order to obtain biomass based fuels by continuous processing of acetone-butanol-ethanol (ABE) mixture. Butanol, which can inevitably form as Guerbet side product in a self-aldol reaction of ethanol was not applied in our study as an initial component, in order to follow the complexity of the reaction mechanism. A flow-through reactor was applied with inert He or reducing H₂ stream in the temperature range of 150–350 °C. Efficient catalysts containing Pd and base (K₃PO₄ or CsOH) crystallites were prepared applying commercial activated carbon (AC) support. The catalyst beds were pre-treated in H₂ flow at 350 °C. Mono- or dialkylated ketones were formed with high yields and these products could be reduced only to alcohols over palladium.

Keywords: Acetone; Alcohols; C-alkylation; Pd/C catalysts

1. Introduction

A major 21st century goal is the economical utilization of biomass resources for production of fuels and chemicals. The technologies on various biomass platforms involve combinations of mechanical, thermal, chemical, and biochemical processes including separation operations.^{1–3} Instead of the less advantageous thermochemical routes, favorable microbiological destruction process – e.g. Mix-Alco – can be applied⁴ to produce volatile fatty acids, mainly acetic acid.^{5–6} The overall chemical reaction without loss of biomass conducted by species of anaerobic bacteria, including members of the genus *Clostridium* may be represented as:



The selective deoxygenation of carboxylic acids to alcohols seems to be successfully solved recently using indium co-catalyst with nickel or platinum host metal.⁷

Nowadays the *Clostridium* species attracted again interest and are accepted for their ability to produce aceto-

ne, n-butanol and ethanol in a 2.3:3.7:1.0 molar ratio from sugars, carbohydrates, lignocelluloses, etc. for use as renewable alternative transportation fuels. Although co-production of acetone lowers the yield of alcohol biofuels, but the lower oxygen content of ABE mixture is advantageous compared to carboxylic acids.

A recent study was aimed to develop an improved *Clostridium acetobutylicum* strain with enhanced alcohol production capability, but complete conversion of acetone into isopropanol are further challenges.⁸ Catalytic dehydration of the ABE mixtures was studied in order to deoxygenate it, but the resulted products were mostly unsaturated hydrocarbons.⁹ The obtained mixture was similarly disadvantageous as the products of thermochemical method. Anbarasan and co-workers¹⁰ proposed a chemical route to convert fermentation ABE product into hydrocarbons that can be used for fuel. Nucleophilic α -carbons of acetone can form C–C bond with electrophilic alcohols produced in ABE fermentation, resulting in longer chain length hydrocarbons than the original fermentation products. Thus, the paired functionalities (nucleophilic α -carbons of the acetone and electrophilic α -carbon of the alco-

hols) enable to construct higher alkanes from two-carbon, three carbon and four-carbon precursors. The alkylation under suitable conditions (110 °C in toluene using stirred pressurized batch reactor) results in C₅–C₁₁ or longer-chain ketones,¹¹ which may be deoxygenated to paraffin, the components of fuel. Palladium on carbon was superior to the other metals (Ir, Ru, Rh, Pt, Ni) using in various forms with different bases in molar equivalent to alcohols. K₃PO₄ base additive seemed to be the most efficient. The applied metals are working based on hydrogen borrowing methodology.^{11–13} Further the applied bases type and amount is a determining factor in the process.

G. Xu and co-workers¹⁴ – mimicking ABE fermentation product – demonstrated direct α -alkylation of ketones with alcohols in water (instead of toluene¹⁰) over Pd/C catalytic system in autoclave. Equivalents of different bases (K₃PO₄, LiOH, NaOH or KOH) to the amount of ketone were also used. Q. Xu and co-workers¹⁵ conceive that transition-metal-catalyzed α -alkylation of ketones with alcohols still have drawbacks, consequently they prefer the “catalyst-free” dehydrative α -alkylation. However, high amount of bases (NaOH or KOH) are still applied in the studied alkylation reactions.

The literature shows as yet only studies in small reaction tubes which have several disadvantages and are applicable only as quick catalyst tests. Processing of ABE mixture – which can be one way of biomass utilization in high volume – needs a continuous procedure. For this purpose move from batch to flow-through system was aimed for a detailed study. The present study relates to the application of the carbon supported catalysts in fixed beds working in vapor phase α -alkylation using acetone and ethanol, as model reactants instead of ABE mixture. Butanol as reactant can form as Guerbet side product in a self-aldol reaction of ethanol, consequently it was not feed in the reactor in order to follow and understand the reaction mechanism.

2. Experimental

Cited references did not give detailed information about the usually used “5% palladium on carbon” catalysts. In this study, 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 m²/g) as inert support was applied. The AC first was dried at 110 °C, then impregnated with CsOH (Fluka AG) or K₃PO₄ (Aldrich) solutions using incipient wetness method and dried again at 110 °C. For 1 g support 0.2 g bases were added resulting in plus 20 m% loadings. Finally 5 m% palladium is also loaded using tetraamine-palladium(II)nitrate solution (STREM Chemicals).

Nitrogen physisorption measurements were carried out at –196 °C using Thermo Scientific Surfer static volumetric adsorption analyzer. Before the adsorption analysis samples were outgassed for 3 h at 200 °C.

The catalytic alkylation of acetone (A) (99.5 %, Reanal) with ethanol (E) (99.7 %, Reanal) mixed in 1:2 molar ratio was studied in a high-pressure fixed bed flow-through reactor¹⁶ at 21 bar total pressure in the temperature range of 150–350 °C using inert helium or reducing hydrogen streams. Weight of catalyst bed (1.2–4.6 g) and flow rate of liquid mixture (1.2–4.6 g_{AE}/h) were varied controlling WHSV values between 1–4. In general the catalysts were pretreated *in situ* in hydrogen flow in the reactor at 350 °C and 21 bar for 1 h in order to obtain active metallic surface. The reaction was allowed to run one hour at each condition to attain steady state. The effluent during the second hour was collected, depressurized and cooled to room temperature. The liquid product mixture at ambient conditions was analyzed by gas chromatograph using a GC-MS (Shimadzu QP2010 SE,) capable to identify products formed in low concentration, equipped with a ZB-WAX plus capillary column. The gaseous reactor effluent was analyzed for detection of CO₂, CO, CH₄ and light hydrocarbons using an on-line gas chromatograph (HP 5890) with thermal conductivity detector (TCD) on Carboxen 1006 PLOT capillary column.

The conversion of the two component reaction mixture cannot be well defined, due to the complex reaction network shown later. Both of the reactants are transformed to such a kind of by-products (isopropyl alcohol, acetaldehyde and butanol), which can take part further in the main alkylation reaction network. Thus, the main alkylated products (ketones and alcohols) with the actual yields given by the calculation method below are used for characterizing the activity and selectivity of the applied catalysts:

$$\text{yield (wt\%)} = \frac{\text{flow of a product}_{\text{out}} \text{ (g/h)}}{\text{flow of the reaction mixture}_{\text{in}} \text{ (g/h)}} \times 100$$

3. Results and Discussion

AC support is well applicable in fixed bed flow-through reactors being inert in the studied reaction system. In Fig. 1 isotherms of nitrogen adsorption related to carbon content characterize the porosity of the support and the prepared catalysts.

Shape of isotherms reflects highly microporous materials with high specific surface area (>1000 m²/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 created in the course of pellet formation process.

In the cited batch reactor experiments^{10,14–15} high amounts of bases, some equivalents related to one of the reactants were used in the reaction mixtures. Such high base/reactant ratio is also given in our experiments over fixed catalyst beds. Presence of impregnated bases on AC only hardly decrease the adsorbed amount of nitrogen re-

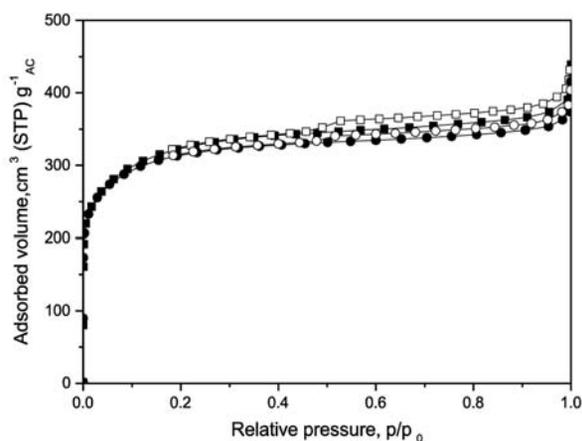


Figure 1. Adsorption isotherms of nitrogen obtained at $-196\text{ }^{\circ}\text{C}$ on the parent AC (■ – adsorption, □ – desorption) and the CsOH loaded (● – adsorption, ○ – desorption) samples. Only the parent and the CsOH loaded samples are shown in figure, because all impregnated samples give nearly the same isotherms.

lated to AC content (Fig. 1) which means that base and palladium metal can form in the mesopores larger crystals than the entrance of micropores. However, the mesoporous volumes, area of hysteresis loops significantly decreased. Active components are on the surface, including surface of larger pores, consequently the catalytic reaction take place in the mesopores, too.

Table 1 and 2 designed in identical structure demonstrate differences in formation of main products using inert (helium) or reactive (hydrogen) carrier gases, respectively. In helium the mono-alkylated- (2-pentanone, 2-heptanone) and the bi-alkylated-ketones (4-heptanone, 4-nonanone) are the main products formed with desired good selectivity. Without palladium loading only low catalyst activities were observed. The “catalyst-free” dehydrative α -alkylation¹⁵ cannot be suggested in flow-through system.

To picture the conversion of mixture (acetone + ethanol) in Table 1 and 2 sum of main products (with exception of isopropyl alcohol) are shown which values ap-

Table 1. Yields (wt%) of main products obtained in helium stream.

Catalyst Reac. temp. $^{\circ}\text{C}$	5Pd,20K ₃ PO ₄ /AC				5Pd,20CsOH/AC			
	200	250	300	350	200	250	300	350
isopropyl alc.	–	0.9	2.0	2.2	0.6	1.0	1.5	1.8
butanol	–	–	–	–	–	–	–	–
2-pentanone	0.7	18.3	24.9	34.7	12.6	19.4	24.1	29.6
2-pentanol	–	–	–	–	–	–	–	–
4-heptanone	0.8	4.6	14.3	21.6	2.9	7.5	13.8	20.0
2-heptanone	–	1.1	1.7	2.1	0.3	2.0	3.1	4.3
4-heptanol	–	–	–	–	–	–	–	–
4-nonanone	0.2	0.6	1.8	7.8	0.4	2.2	5.7	6.5
CO	–	0.8	4.1	9.0	–	0.9	3.7	7.0
CH ₄	–	1.7	5.1	7.9	–	0.5	2.2	5.5
CO ₂	–	–	4.1	5.3	–	–	1.1	4.4
Sum	1.7	27.1	56.0	88.4		32.5	53.7	77.3

(WHSV = $1\text{ g}_{\text{AE}}\text{ h}^{-1}\text{ g}_{\text{cat}}^{-1}$; $p = 21\text{ bar}$; A/E = 1:2 mol/mol) Other products with low yield: acetaldehyde; ethyl acetate; methyl isobutyl ketone; butanoic acid ethyl ester; 4-decanone; 4-undecanone; 6-undecanone; 4-heptanone, 3-ethyl, 2-methyl; 2-pentanone, 3-ethyl; 2-heptanone, 4-methyl; etc.

Table 2. Yields (wt%) of main products obtained in hydrogen stream.

Catalyst Reac. temp. $^{\circ}\text{C}$	5Pd,20K ₃ PO ₄ /AC				5Pd,20CsOH/AC			
	200	250	300	350	200	250	300	350
isopropyl alc.	23.6	19.9	15.0	9.1	22.5	18.4	12.4	5.8
butanol	0.3	1.0	3.1	1.2	–	1.3	4.2	–
2-pentanone	1.5	3.6	10.6	19.5	3.1	3.8	8.8	15.8
2-pentanol	7.5	11.3	9.4	5.5	13.5	17.1	4.2	3.1
4-heptanone	–	–	7.6	18.4	–	–	13.8	23.0
2-heptanone	–	–	0.5	2.0	–	–	0.5	1.0
4-heptanol	0.2	2.7	2.7	2.7	0.3	6.5	6.9	5.3
4-nonanone	–	–	1.1	3.6	–	1.1	2.2	5.2
CO	–	0.2	1.8	6.7	–	–	2.6	4.3
CH ₄	–	0.6	2.6	5.6	–	–	1.7	3.6
CO ₂	–	–	2.8	2.3	–	–	0.8	1.9
Sum	9.5	19.4	42.2	67.5	16.9	29.8	45.7	63.2

(WHSV = $1\text{ g}_{\text{AE}}\text{ h}^{-1}\text{ g}_{\text{cat}}^{-1}$; $p = 21\text{ bar}$; A/E = 1:2 mol/mol) Other products with low yield: heptane; nonane; etc.

proach the conversion of the fed mass flow. The significant production of 2-heptanone and 4-nonanone is interesting which testify that butanol can form as a Gourbet by-product, although it cannot be directly detected using helium. Consequently numerous variations of potential ketones can be detected in very different concentration alike as real ABE mixture has been studied.

Alcohols did not appear when applying helium – those were significantly formed only in hydrogen. Over Pd catalysts ketones can be reduced to alcohols; paraffin preferable for fuels are detected only under severe reaction conditions, at high temperature where numerous useless by-products are formed. The Pd/C catalyst proved to be efficient in the desired alkylation reactions however total deoxygenation could not be reached similarly to the results of P. Anbarasan and co-workers.¹⁰ To increase the hydrogenation reaction rate higher than atmospheric pressure was applied. In order to reach the total reduction of ketones or alcohols further development of a new efficient catalyst system is a must.

Any alkenes or unsaturated ketones could not be detected, thus the used carbon support proved to be inert. Without bases (K_3PO_4 or $CsOH$) over Pd/C much lower alkylation activity (approx. half of the conversion than it was measured on catalysts containing both active components) can be observed. Pd-free catalysts containing only bases (K_3PO_4 or $CsOH$) show only less than tenth of activity obtained on catalysts loaded both active components. In presence of hydrogen by splitting the C–C bonds of the reactants lower concentration undesired methane and carbon monoxide gases are producing.

It is interesting that the reactant acetone can be fully reduced to isopropyl alcohol already below 200 °C, but after all alkylation is materialized. Using hydrogen, significant butanol formation can be detected. In situ formed butanol results in mimicking of ABE mixture. Gaseous, cracked by-products are formed in less quantity by applying hydrogen stream over the applied “bifunctional” catalysts which is only the advantage of H_2 use.

Based on products shown in Tables 1 and 2 and the traces detectable by GC-MS a complex reaction scheme can be recognized; the main variation of the alkylation reactions are presented (Scheme 1), but several products are forming in low concentration as well.

The yield of alkylated products is increasing at higher temperature, but at a lower temperature the production of useless gaseous by-products is less (Fig. 2). The efficiencies of the studied Pd/C catalysts ($5Pd,20K_3PO_4/AC$; $5Pd,20CsOH/AC$) applied in different medium (He and H_2) can be more easily compared in Fig. 2. The nature of different bases ($CsOH$ or K_3PO_4) seems to be not too important in contrast to the batch results.¹⁰ However, it is a great difference that in this work the reaction temperature was much higher and gas/solid interactions were studied resulting in higher reaction rates and productivity with more than one magnitude of order.

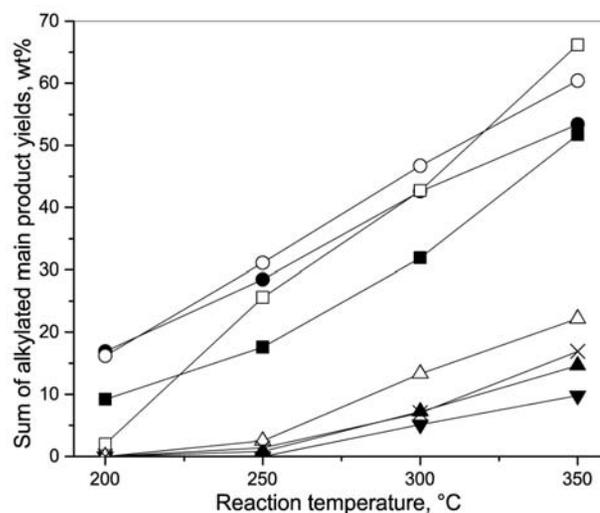


Figure 2. The sum of alkylated main product yields (■,□,●,○) and gaseous by-products (▼,▲,X,△) against the reaction temperature over $5Pd,20K_3PO_4/AC$ (■,□,▲,△) and $5Pd,20CsOH/AC$ (●,○,▼,X) in H_2 (solid) and He (open). ($WHSV=1\ g_{AE}\ h^{-1}\ g_{cat}^{-1}$; $p=21\ bar$; $A/E=1:2\ mol/mol$)

The di-alkylated products were formed in a consecutive reaction from mono-alkylated products as reflected in Figs. 3–4. Determination of optimal reaction conditions for the requested products needs compromise. Enhancement of the reaction temperature results in higher yields of the desired alkylates but with higher increase of gaseous by-products. Using longer catalyst bed or feeding less reactant by increasing the space time the yield for desired products are increasing with slow increase of gaseous by-products yield resulting in better selectivity.

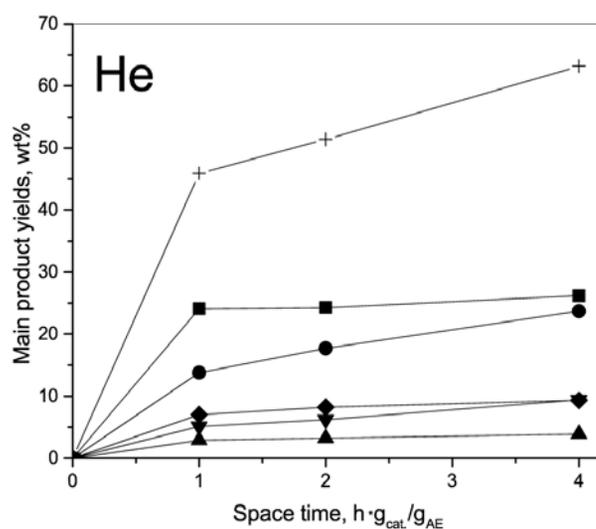


Figure 3. Yield of significant products (■ 2-pentanone, ● 4-heptanone, ▲ 2-heptanone, ▼ 4-nonanone, ◆ gas by-products, + sum of main alkylates) obtained over $5Pd,20CsOH/AC$ catalyst in helium as a function of space time. The reaction was carried out at 21 bar total pressure and 300 °C.

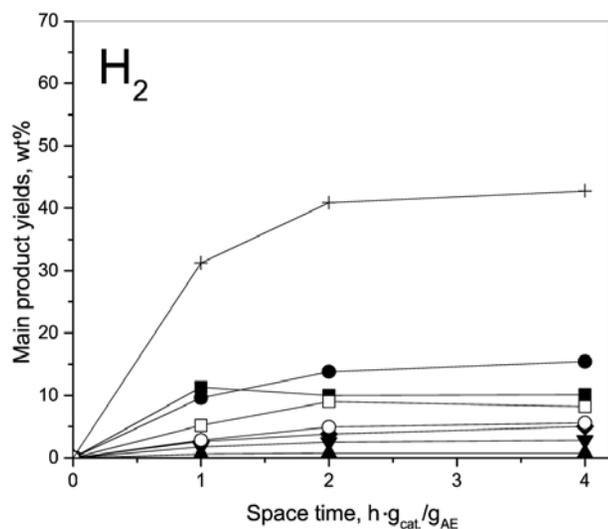


Figure 4. Yield of significant products obtained (■ 2-pentanone, ● 4-heptanone, □ 2-pentanol, ○ 4-heptanol, ▲ 2-heptanone, ▼ 4-nonanone, ◆ gas by-products, + sum of main alkylates) over 5Pd,20CsOH/AC catalyst in hydrogen as a function of space time. The reaction was carried out at 21 bar total pressure and 300 °C.

4. Conclusions

Alkylation of ABE mixture reveals an exciting synergy of the reacting compounds in a complicated reaction network resulting in a complex liquid product (longer ketones (and alcohols in H₂ atmosphere)) with decreased O-content and consequently with higher value. Guerbet alkylation is a green chemical process because water is the sole by-product. It proceeds in a reaction sequence of dehydrogenation-condensation-hydrogenation. In principle, the reaction does not require reducing agents (expensive hydrogen) for deoxygenation because great part of oxygen is removed in dehydration steps producing water. The catalyst initiates alcohol dehydrogenation (alcohol oxidation) aldol addition/condensation and hydrogenation of the obtained unsaturated ketone. The hydrogenation consumes the hydrogen obtained in the oxidation step, i. e., the metal sites catalyze the transfer dehydrogenation of alcohol and hydrogenation of condensation products as intermediates (hydrogen borrowing methodology). Pd/carbon catalysts have great potential for C-alkylation of ketones using alcohols via borrowing hydrogen route applied in batch or continuous processes equally. Working over fixed catalyst bed, presence of palladium and base crystallites together on well-defined activated carbon surface is advantageous resulting in high productivity, exceeding the cited results. Various mono- or dialkylated ketones were formed with high yields in inert, helium atmosphere and these products were found to be reducible selectively to alcohols over the same catalysts in hydrogen.

This study gives a good base for efficient processing of ABE mixture (obtainable from biomass degradation) to

fuel precursors in a continuous process using metal and alkaline loaded carbon supported catalysts (e.g. Pd,Cs-OH/AC).

5. Acknowledgements

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6. References

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Povzetek

Pridobivanja možnih goriv iz biomase z zveznim procesiranjem mešanice aceton-butanol-etanol (ABE) smo proučevali z alkilacijo acetona z etanolom kot modelnima reaktantoma. Da bi lahko zasledovali kompleksnost reakcijskega mehanizma, butanola kot reaktanta v raziskavo nismo vključili. Uporabili smo pretočni reaktor v temperaturnem območju 150–350 °C s pretokom inertnega He ali reducenta H₂. Reakcija je potekala ob prisotnosti katalizatorja, ki smo ga pripravili iz Pd in bazičnih (K₃PO₄ ali CsOH) kristalitov z uporabo komercialnega aktivnega ogljika. Katalizator smo predhodno tretirali v toku H₂ pri temperaturi 350 °C. Tako smo z visokim izkoristkom pridobili mono- in dialkilirane ketone ki se lahko reducirajo le do alkoholov.