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Research Article

Production of Butane from Methyl Ethyl Ketone over Pt/Al_2O_3

Zahraa Al-Auda[1],*, Keith L. Hohn[2]

[1]Department of Chemical Engineering, The University of Technology, Baghdad, 10066, Iraq.
[2]Department of Chemical, Paper, Biomedical Engineering, Miami University, 64 Engineering Building 650 E. High St, Oxford, OH 45056, USA.

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Abstract

Methyl ethyl ketone (MEK) was catalytically converted to butane directly in one step over platinum (Pt) supported on alumina (Al_2O_3). The reaction was performed in the gas phase in a fixed bed reactor. Conversion of MEK to butane was achieved by hydrogenation of MEK to 2-butanol, dehydration of 2-butanol to butene, and further hydrogenation of butene to butane. The results showed that butane can be produced with selectivity reaching 95% depending on the operating conditions. The highest selectivity for butane was obtained at 220 °C and a H_2/MEK molar ratio of 15.

Keywords: Hydrodeoxygenation; methyl ethyl ketone; butane; Pt/Al_2O_3

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1. Introduction

There is a considerable attention in investigating alternative pathways of converting biomass as a sustainable source to renewable chemicals and fuels to reduce the world's dependence on petroleum. Producing hydrocarbons from biomass requires biochemical and catalytic processes. The first processes convert biomass-derived sugars to beneficial intermediates while catalytic process convert these intermediates to renewable hydrocarbons and fuel.

MEK can be obtained from dehydration of 2,3-butanediol (2,3 BDO) [1,2], produced from biomass-derived sugars via a biochemical process [3–5]. It can serve as a platform chemical, used to construct a number of useful chemicals. For example, butene [6,7], C_{12} alkanes, Cyclic trimers [8], C_8 ketone [9,10], C_8 alkene [11]. Yet to be systematically studied is conversion of MEK to butane. Butane is important for production of maleic anhydride [12] (used mainly as a monomer for unsaturated polyester resin [13]), isobutane [14] (which is an intermediate towards producing high octane products), and 1,3-butadiene, a precursor for synthetic rubber [15]. Typically, the subsequent hydrodeoxygenation necessitates the presence of both a metal and a strong Brønsted or Lewis acidic catalyst [16–18]. Hydrodeoxygenation of MEK to butane proceeds through the removal of an oxygen atom from MEK via the hydrogenation of the C=O bond over metal sites to produce 2-butanol. This

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* Corresponding Author.
Email: alauda@ksu.edu (Z. Al-Auda);
Telp: +9647723419901

alcohol can be dehydrated to butene over acidic sites. Further hydrogenation of butene to butane can be achieved over the metal sites.

The hydrogenation reactions are catalyzed by many metals including Pt [19,20], Ru [21], Ni [22,23], and Cu [24,25]. Gerrit Waters *et al.* [26] studied the effect of different metals supported catalysts on the single-stage self-condensation and subsequent hydrogenation of acetone to methyl isobutyl ketone (MIBK) in the gas phase. They stated that platinum, palladium, nickel, and copper hydrogenation activity decreased in the order Pt > Pd > Ni > Cu at 1 MPa and 623 K. For hydrogenation of benzaldehyde to benzyl alcohol, platinum catalyst, noble metals demonstrated better activity compared to transition metal-based catalysts [27]. Szöllősi *et al.* [28] investigated hydrogenation of 3-penten-2-one on Ni, Cu, Ru, Rh, Pd and Pt supported on SiO_2 catalysts under the same experimental conditions. They mentioned that the activity of metals decreased in the order Pt > Pd $\geq$Rh >> Ru > Ni > Cu on the basis of the turnover yields. Selective hydrogenation of 3-penten-2-one produced 2-pentanone which was further hydrogenated to 2-pentanol on all catalysts, excluding on Pd/SiO_2.

Metal oxides are the traditional choice for catalysis of alcohol-dehydration [29–31]. TiO_2 can act as a dehydration and dehydrogenation catalyst. Rekoske *et al.* [32] investigated the decomposition of isopropanol on oxidized anatase. They noted ketone formation by dehydrogenation was favored at low temperatures, with selectivity near of 100%, while alkene formation by dehydration reaction increased to ~25% when temperature increased. Bahruji *et al.* [33] also studied thermal decomposition of alcohols on TiO_2. They mentioned to ether and alkene formation for reactions of methanol, ethanol and propanol, with no formation of ketone. Auroux *et al.* [34] tested a number of pure and modified ZrO_2 catalysts for 4-methyl 2-pentanol dehydration with different temperatures. The authors reported that surface composition is a key parameter in controlling the selectivity of the desired alkene product. Results showed that alkene selectivity above 80% can be achieved under higher-temperature conditions and a ratio of base to acid sites of ~1.2. Surface hydroxyl groups on γ-Al_2O_3 can exhibit both acidic and basic properties (Lewis and Brønsted) [35]. Kostestkyy *et al.* [36] investigated TiO_2, ZrO_2, and γ-Al_2O_3 oxides to catalyze the dehydration of 1-propanol, 2-propanol, and 2-methyl-2-propanol. They mentioned that γ-Al_2O_3 was more active than either TiO_2 or ZrO_2 in catalyzing the dehydration reactions.

Pham *et al.* [37] studied the effect of Pt, Pd, and Cu catalysts supported on precipitated silica on the hydrodeoxygenation and hydrogenation of 2-methyl-2-pentenal using temperature range 200–400 °C. Hydrogenation activity was observed for both C=C and C=O bonds on all catalysts, and it has been found that the activity of these metals was in the order Pt > Pd > Cu. They stated that at low temperatures, Pt and Pd are mainly active for the hydrogenation of the C=C bond to form 2-methyl-pentanal, and decarbonylation increases at higher temperatures to produce n-pentane. Cu catalyzes hydrogenation of both C=C and C=O bonds. On Cu, hydrogenolysis of C–O was observed to produce 2-methyl-pentane as a minor product at 200 °C but became the primer product on Cu when the reaction temperature increased to 400 °C. González *et al.* [38] investigated hydrodeoxygenation of acetophenone in the gas-phase over noble metal (Pt, Pd, Ru, and Rh) supported catalysts. They found that Pt/Al_2O_3 was the most active and stable catalyst at 325 °C and 0.5 MPa with the main products being ethylbenzene and styrene. Peng *et al.* [39] studied the catalytic hydrodeoxygenation of C_3 alcohols including 1- and 2-propanol, 1,2- and 1,3-propanediol, and glycerol on Pt/Al_2O_3 in the aqueous phase. They reported that the presence of water as solvent inhibits the dehydration for mono-alcohols by blocking of Lewis acid sites by water. The overall C_3 alcohol reactivities decrease in the order of 1,3-propanediol ≈ glycerol > 1,2-propanediol ≈ 1-propanol. Itagaki *et al.* [40] stated that a $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-supported platinum catalyst (Pt/CsPW) could act as an effective heterogeneous catalyst for hydrodeoxygenation of different types of compounds contained oxygen like ketones, ethers and phenols.

To the best of our knowledge, there is no researcher concerned on conversion of MEK to butane. This work focuses on producing butane from MEK (biomass-derived oxygenates) with high selectivity in the presence of hydrogen in a single-stage catalytic process. The process includes using a heterogeneous catalyst consisted of Pt supported on Al_2O_3 selected based on the above literature as a bifunctional catalyst. Furthermore, studying conversion of MEK to butane allows us to understand the interplay between chemistries on acid and metal sites. This study focuses on how operating conditions affect the selectivity of butane and the conversion of MEK over Pt/Al_2O_3.

2. Materials and Methods

2.1 Materials

MEK was purchased from Fisher Scientific Company. Both the Pt precursor (Tetraammineplatinum(II) nitrate $[Pt(NH_3)_4(NO_3)_2]$ and alumina (Catalyst support, high surface area, 1/8" pellet) were obtained from Alfa Aeser.

2.2 Supported Catalyst Preparation

The catalyst (platinum supported on alumina) was synthesized using the incipient wetness impregnation method as the previous work [41]. $[Pt(NH_3)_4(NO_3)_2]$ was used as a metal precursor after dissolving in a known amount of de-ionized water to fill the pores of amount of the Al_2O_3 as a support. Then, the precursor solution was added to the support by dropwise addition and was stirred at room temperature for 1 h. The resulting mixture was dried first in the oven overnight at 100 °C followed by drying at 110 °C for 2 h and then calcination at 550 °C for 4 h with a ramp rate of 2 °C/min up to 110 °C and 1 °C/min up to 550 °C. With respect to alumina, the pellet was ground and sieved to obtain a 100-mesh powder before loading platinum. After the calcination process, the catalyst was ground and sieved to $\leq$ 0.15 mm.

2.3 Catalytic Reaction

The catalytic conversion of MEK was conducted in a continuous flow fixed-bed reactor under atmospheric pressure. Before the reaction, 0.5 g of catalyst was reduced in the reactor with flow rates of hydrogen and nitrogen equal to 68.5 and 16.5 mL/min, respectively, at 300 °C for 1 h. Then, MEK was mixed with hydrogen and nitrogen in a preheater before flowing into the reactor. The MEK was fed through the reactor top at a feed rate of 1 (mL/h) together with H_2 and N_2 with flow rates of 68.5 and 16.5 mL/min, respectively by a micro pump. The outflowing product compositions were analyzed via an on-line gas chromatography (SRI 8610C) with an MXT-1 column (100% dimethyl polysiloxane (nonpolar phase), 60 m, ID 0.53 mm). FID and TCD detectors were used for the analysis of hydrocarbons and oxygenates. The products were identified by gas chromatography with a mass spectrometer (an Agilent 7890A GC-MS system equipped with an Agilent 5975C MS detector). The conversion of MEK and the selectivity for the products were determined using Equations (1) and (2):

$$Conversion\,\% = \frac{(Moles\ of\ MEK)_{in} - (Moles\ of\ MEK)_{out}}{(Moles\ of\ MEK)_{in}} \times 100 \quad (1)$$

$$Selectivity\,\% = \frac{(Moles\ of\ product)}{(Moles\ of\ total\ products)} \times 100 \quad (2)$$

Two repeat runs were performed for the experiments and the two trials were within 5% of each other. The carbon balances closed within 10% for all runs in this paper.

3. Results and Discussion

3.1. Effect of Reaction Temperature

The influence of temperature on the conversion of MEK and the selectivity of butane was investigated over 1% Pt/Al_2O_3 for a range of temperature between 160 and 280 °C. The results are shown in Figure 1. As seen in this figure, the conversion of MEK increased with increasing temperature. At low temperature, the main product was 2-butanol. As temperature increased, the selectivity of 2-butanol dropped from over 80% at 160 °C to close to zero by 220 °C. As this occurred, the selectivity to butane increased, reaching a maximum of 95% at 220 °C. That suggests that increasing the temperature of reaction induces the dehydration of 2-butanol to butene and hydrogenation of butene to butane. Beyond 220 °C, the selectivity to butane dropped, as notable amounts of 3-methyl heptane (C_8 alkane) were produced as a result of dimerization reaction of butene followed by

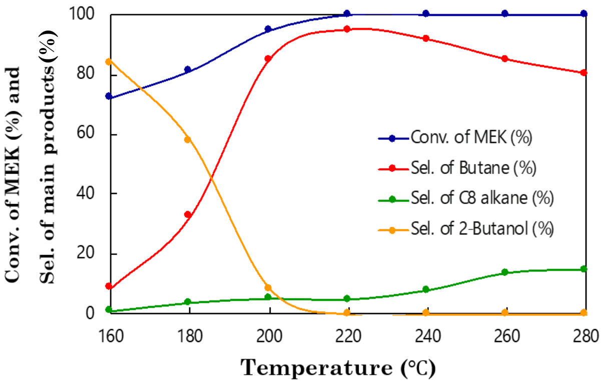


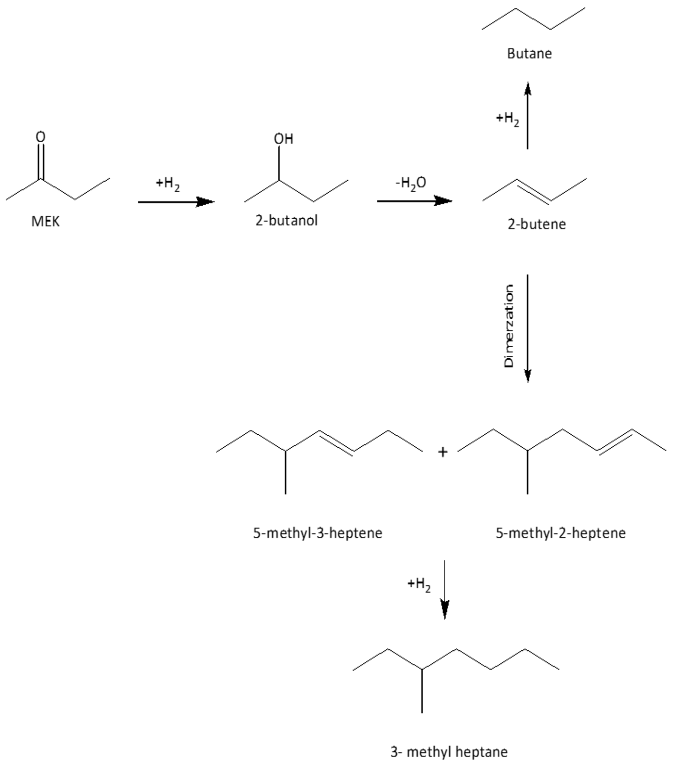
Figure 1. Catalytic results for the conversion of MEK with different temperature using 0.5 g of 1% Pt/Al_2O_3. The range of reaction temperature is from 160 to 280 °C, total flow rate of H_2 and N_2 = 85 mL/min, the flow rate of MEK is 1 mL/h and molar ratio of H_2/MEK is 15. The catalyst was reduced in the reactor at 300 °C for 1 h and flow rate of H_2 and N_2 are 68.5 and 16.5 mL/min, respectively.

hydrogenation of the C_8 alkene to C_8 alkane, as shown in Scheme 1. Minor amounts of ethylene and C_8 ketone were detected.

The results are consistent with a reaction mechanism where MEK is first hydrogenated to 2-butanol, which is then dehydrated to butene before being hydrogenated to butane. Interestingly, butene was not detected at these operation conditions, suggesting that hydrogenation of butene to butane was extremely fast relative to the other reactions. The presence of C_8 alkane can be explained by coupling between butene molecules over acid sites to produce C_8 alkenes which are then rapidly hydrogenated.

3.2 Effect of H_2/MEK Molar Ratio on Product Selectivity

The effect of changing the molar ratio of H_2 to MEK on the conversion of MEK and the selectivity of butane over 1% Pt/Al_2O_3 was studied at 220 °C, the temperature that gave the maximum butane selectivity in Figure 1. The results of these experiments are displayed in Figure 2. As exhibited in this figure, the selectivity of butane increased as the molar ratio of H_2/MEK increased at the expense of C_8 alkane. This is likely because the increased hydrogen motivated the hydrogenation of butene, preventing butene dimerization to C_8 alkene. Minor amounts of ethylene, C_8 ketone, and 3,5 dimethyl-phenol were formed.



Scheme 1. The mechanism of conversion MEK to butane and C_8 alkane.

3.3 Studying the Effect of Space Time

To better understand the reaction mechanism, the effect of space time (W/F_{A0}, where W is the weight of catalyst (g), and F_{A0} is the molar flow rate of MEK (mol.h^{-1}) was evaluated.

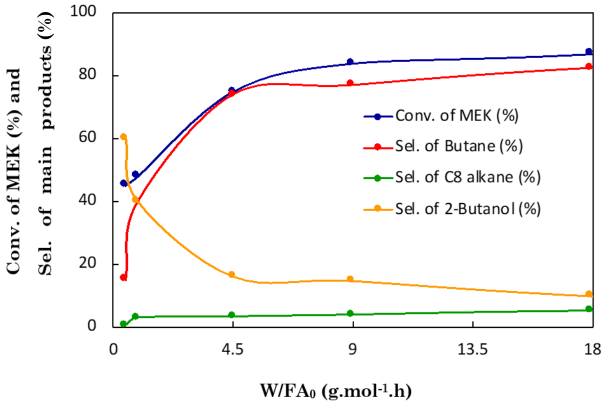


Figure 3. Catalytic results for the conversion of MEK to main products with different amounts of 1% Pt/Al_2O_3 catalyst. The temperature of reaction is 220 °C, total flow rate of H_2 and N_2 is 85 mL/min, the flow rate of MEK is 1 mL/h and molar ratio of H_2/MEK is 15. The catalyst was reduced in the reactor at 300 °C for 1 h and flow rate of H_2 and N_2 are 68.5 and 16.5 mL/min, respectively.

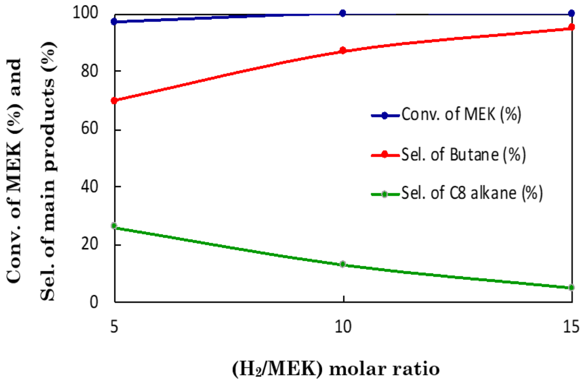


Figure 2. Catalytic results for the conversion of MEK with different H_2/MEK molar ratio using 0.5 g of 1% Pt/Al_2O_3. The temperature of reaction is 220 °C, total flow rate of H_2 and N_2 = 85 mL/min, the flow rate of MEK is 1 mL/h and molar ratio of H_2/MEK is varied from 2 to 15. The catalyst was reduced in the reactor at 300 °C for 1 h and flow rate of H_2 and N_2 are 68.5 and 16.5 mL/min, respectively.

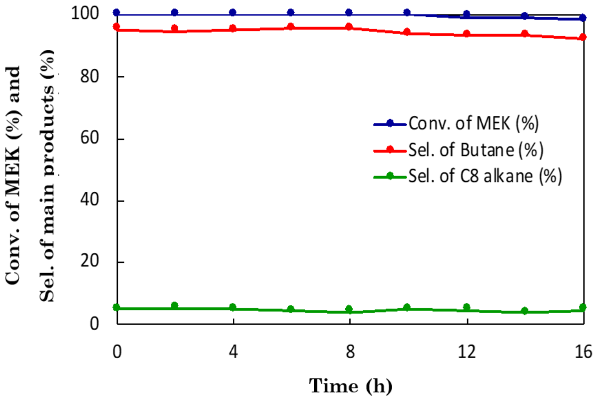


Figure 4. Catalytic results for the conversion of MEK with time using 0.5 g of 1% Pt/Al_2O_3. The temperature of reaction is 220 °C, total flow rate of H_2 and N_2 = 85 mL/min, the flow rate of MEK is 1 mL/h and molar ratio of H_2/MEK is 15. The catalyst was reduced in the reactor at 300 °C for 1 h and flow rate of H_2 and N_2 are 68.5 and 16.5 mL/min, respectively.

Results for 1% Pt/Al_2O_3 at 220 °C are shown in Figure 3, after 30 min from the reaction. As can be seen, the conversion of MEK increased with increasing space time from 45% at 0.5 g.mol^{-1}.h space time to 87% at 18 g.mol^{-1}.h space time. The selectivity to butane increased from 15% to 82%, while the selectivity for 2-butanol decreased from 60% to 10% when the space time increased from 0.5 to 18 g.mol^{-1}.h. Also, it can be noted that 1% Pt/Al_2O_3 produced primarily butane even at the smallest space times although a small amount of butene was detected at low space time. This indicates that the hydrogenation of butene to butane (C=C bond) was quite fast [11,42]. Formation of C_8 alkane increases slightly with increasing space time.

3.4 Stability of 1% Pt/Al_2O_3

The catalyst stability was studied for 1% Pt/Al_2O_3. The conversion of MEK and the selectivity of main products during 16h of reaction over 1% Pt/Al_2O_3 are shown in Figure 4 as a function of time on stream. As can be seen, the conversion was maintained near 100% for almost the entire time studied, with a slight decrease to 99 % at 12 h and 98.5% at 16 h. The selectivity for butane decreases slightly with time from 95% at the start of the reaction to 92% after 16 h and is associated with an increase in byproducts, such as ethylene, 2-butanol, 2,3 dimethyl butene and C_8 ketone. This is probably because of the deactivation of acid sites that are responsible for dehydration of 2-butanol to butene.

4. Conclusions

Hydrodeoxygenation of MEK to butane was examined using bifunctional catalysts composed of Pt loaded on Al_2O_3 to provide both dehydration and hydrogenation sites. 1% Pt/Al_2O_3 produced nearly all butane because Pt was a very active hydrogenation catalyst for C=C double bonds. Higher reaction temperatures had a significant impact on MEK conversion and selectivity for butane. These results are consistent with a pathway consisting of a series of reactions where MEK is hydrogenated to a 2-butanol on metal sites, dehydrated to butene on acidic sites, and further hydrogenated to butane. Higher H_2/MEK ratios also enhanced the selectivity to butane. Little catalyst deactivation over 16 h was noted for 1% Pt/Al_2O_3 catalyst as the conversion was maintained near 100% for nearly the entire time studied, with a slight decrease to 99 % at 12 h and 98.5% at 16 h.

CRediT Author Statement

Author Contributions: Zahraa Al-Auda: Conceptualization, Investigation, Resources, Writing, Review and Editing, Data Curation; Keith Hohn: Conceptualization, Writing, Review and Editing. All authors have read and agreed to the published version of the manuscript.

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