



Hydrogenation and Hydrodeoxygenation of 2-methyl-2-pentenal on supported metal catalysts

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ARTICLE INFO

Article history:

Received 11 March 2009

Revised 4 May 2009

Accepted 10 May 2009

Available online 3 June 2009

Keywords:

Hydrogenation

Deoxygenation

Decarbonylation

Hydrogenolysis

Methyl-pentanal

Pt

Pd

Cu

C=C hydrogenation

C=O hydrogenation

Conjugated carbonyl

ABSTRACT

Platinum, palladium, and copper catalysts supported on precipitated silica have been studied for the hydrodeoxygenation and hydrogenation of 2-methyl-2-pentenal in the 200–400 °C temperature range. The activity follows the order Pt > Pd > Cu. It has been found that at low temperatures, Pt and Pd are primarily active for the hydrogenation of the C=C bond to make 2-methyl-pentanal, with some decarbonylation, yielding *n*-pentane and CO as products. Decarbonylation increases at higher temperatures. Cu catalyzes hydrogenation of both C=C and C=O bonds. In both cases, the initial products are further hydrogenated to form 2-methyl-pentanol at higher space times. At higher temperatures on Cu, the hydrogenolysis of 2-methyl-pentanol takes place, giving 2-methyl-pentane (and H₂O) as the dominant product while no decarbonylation is observed.

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1. Introduction

This study investigates the performance of Pt, Pd, and Cu supported on precipitated silica catalysts for the hydrodeoxygenation of 2-methyl-2-pentenal. This aldehyde represents a molecule with reactive functional groups (C=C double bond and C=O) that are typical in the oxygenate fractions of bio-oils produced from pyrolysis. Such molecules are potential feedstocks for fuels and chemicals, but are too reactive to include as fuel components themselves and must be refined to remove the active oxygen and the unsaturation [1–3]. This molecule is also produced from the aldol condensation of glycerol, a low value by-product of biodiesel production. Pt and Pd are well known for their ability to hydrogenate C=C double bonds in preference to carbonyls [4–10]. Hydrogenolysis of fatty acid methyl esters to form alcohols is also an important reaction in the production of detergents that can be catalyzed by copper-based catalysts [11–14]. While most metals show higher activity for C=C in preference to C=O bonds [7–10], Cu has been shown to be an exception [15,16]. The potential for the hydrogenation of the C=O bond, leaving the unsaturated C=C bond, is also of interest in the production of fine chemicals [17].

The objective of this study is to gain an understanding of the catalytic pathways for selective hydrodeoxygenation reactions over different catalysts and operating conditions. Fig. 1 shows various products that can be obtained from the hydrogenation and hydrodeoxygenation of 2-methyl-2-pentenal on metals. In general, for fuel utilization, removal of oxygen from biomass-derived fuels is necessary to improve the stability of the fuel and to reduce water solubility. As an initial screening tool, research octane number (RON) of individual molecules is one of the important indicators to determine whether a molecule has potential as a gasoline component. However, for many oxygenated biomass-derived molecules, no such property measurements have been made. Substantial previous work [18] has been done to show that a database of octane number (and other relevant fuel properties) may be used to develop a predictive capability for molecules of similar type with useful reliability. The octane number values of product molecules found in this study were predicted for the alcohol products using QSAR models [19,20] that correlate molecular descriptors, i.e., numerical values calculated from the molecular structure, to specific properties of the corresponding compounds (in this case, octane number). Molecular descriptors involve geometric, steric, and electronic aspects of the molecule. In Fig. 1, it may be seen that the octane numbers predicted for the alcohols obtained from the hydrogenation of 2-methyl-2-pentenal are quite

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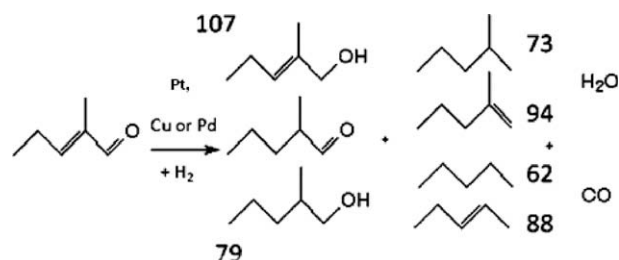


Fig. 1. Research octane numbers (RONs) for products of 2-methyl-2-pentenal conversion. Alcohols predicted by QSAR, hydrocarbons from the literature [18].

Table 1
Dispersion of Pt, Pd, and Cu from chemisorption and average d_{TEM} measurements.

Metal	Pt 0.5%	Pd 0.5%	Cu 5%
Dispersion CO/M	0.038	0.15	0
d_{TEM} (nm)	12 ± 3	3.6 ± 0.3	2.7 ± 0.5

high. At the same time, they have vapor pressures within the range of gasoline. Within the hydrocarbon products *n*-pentane has the lowest octane number. While 2-pentene has a good octane number, the concentration of this product is very low since, in excess of H_2 , equilibrium favors pentane. Olefins are typically undesirable components in gasoline. Note that the octane numbers for the aldehyde compounds are not shown since these are highly reactive and are undesirable molecules for fuels.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation of the metal precursor on precipitated silica (HiSil 210 obtained from Pittsburg Plate Glass Co.) having a BET surface area of $135 \text{ m}^2/\text{g}$. The metal loading in each catalyst was calculated based on the amount of metal precursor incorporated in the catalyst by impregnation. The liquid/solid ratio used to achieve incipient wetness was 1.26 ml/g. The precursors of Pt, Pd, and Cu metals were H_2PtCl_6 , $\text{Pd}(\text{NO}_3)_2$, and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, respectively, which were purchased from Sigma Aldrich. After impregnation, the catalysts were dried overnight in an oven, and then calcined in air at 400°C for 4 h. For the catalytic measurements, catalysts (0.05–0.15 g) were loaded in a tubular reactor and reduced in situ in flowing H_2 at 400°C for 2 h, then cooled down to the reaction temperature at 200°C . In this study, each catalyst sample is identified by the type of metal and weight percent loading.

2.2. Catalyst characterization

CO chemisorption was used to determine dispersion of the Pd and Pt catalysts. It was conducted in a dynamic chemisorption unit, including a pulse system with an SRI Model 310C Gas Chromatograph equipped with a Thermal Conductivity Detector (TCD). All the catalysts were reduced in H_2 heating to 400°C with a ramp rate of $10^\circ\text{C}/\text{min}$, held for 1 h, then flushed in He for 30 min and cooled down to room temperature before injecting CO. A pre-mixed gas of 5% CO in He was used for pulse injection with a 0.1 ml loop size. CO adsorption on the blank SiO_2 was carried out at room temperature to subtract any adsorption on the support. However, no CO adsorption was detected. Likewise, no CO adsorption was observed on the Cu catalyst at this temperature. The results of CO chemisorption on Pt and Pd are reported in Table 1.

The average particle size for all pre-reduced catalysts was obtained by TEM. The TEM images were obtained on a JEOL JEM-2000FX TEM. For this analysis, a suspension in ethanol was made by stirring the solid sample in an ultrasonic bath for 10 min. A few drops of the resulting suspension were deposited on a TEM grid and were subsequently dried and evacuated before the analysis. To estimate average particle size, the particles were considered spherical, and the average diameter (d_{TEM}) was obtained using the expression [21].

$$d_{\text{TEM}} = \frac{\sum n_i \cdot d_i^3}{\sum n_i \cdot d_i^2}$$

where n_i is the number of particles with diameter d_i .

2.3. Catalyst testing

Catalytic activity measurements were carried out in a continuous flow system that includes a syringe pump delivering the 2-methyl-2-pentenal to a heated line into a stream of H_2 that feeds to a 20-in long 3/8 in OD stainless steel tube within an electric furnace. Loads of 50–150 mg of catalysts were used, with the appropriate flow rate to achieve the desired space time (W/F). Operating conditions were 200°C and atmospheric pressure. Experiments were continued for 2–3 h. No significant changes in activity or selectivity were observed over these reaction times, indicating a very low extent of catalyst deactivation. All the lines were heated with heating tapes to maintain the feed and products in gas phase. The carrier gas, H_2 , was used to reduce the catalyst and also during reaction with the 2-methyl-2-pentenal at a relative molar ratio 12:1. Quantitative product analysis was made by on-line gas chromatography using a HP 6890A with a flame ionization detector. A Shimadzu GCMS-QP2010S was used for product identification. The light gas products were monitored by online gas chromatography using a Carle series 400 AGC with TCD.

2.4. Model fitting

Pseudo first-order models were fitted to the data for the tested catalysts over the low W/F range (0–0.35 h). These simple models therefore assume that at low W/F (low conversion), competitive adsorption of products on the surface is not significant. For each catalyst, all product yield and conversion data were simultaneously fitted for a plug flow reactor model and the results are shown as the solid lines in the figures, together with the experimental data points.

3. Results and discussion

The overall conversion of 2-methyl-2-pentenal on the metals is compared over the same range of space time W/F (0–0.33 h). The observed catalytic activity order under the conditions investigated is $\text{Pt} > \text{Pd} > \text{Cu}$. To quantify the intrinsic activity of the different metals, turnover frequencies (TOFs) were calculated from the initial linear conversion region per surface metal atom and are shown in Table 2. For Pt and Pd, the percent metal exposed was estimated from the CO chemisorption values; for Cu, it was estimated from the metal particle sizes observed in TEM.

Table 2
Turnover frequencies over different catalysts at 200°C , H_2 : feed ratio = 12:1.

Catalyst	Pt	Pd	Cu
Loading (wt.%)	0.5	0.5	5
TOF (s^{-1})	341	39	1.3

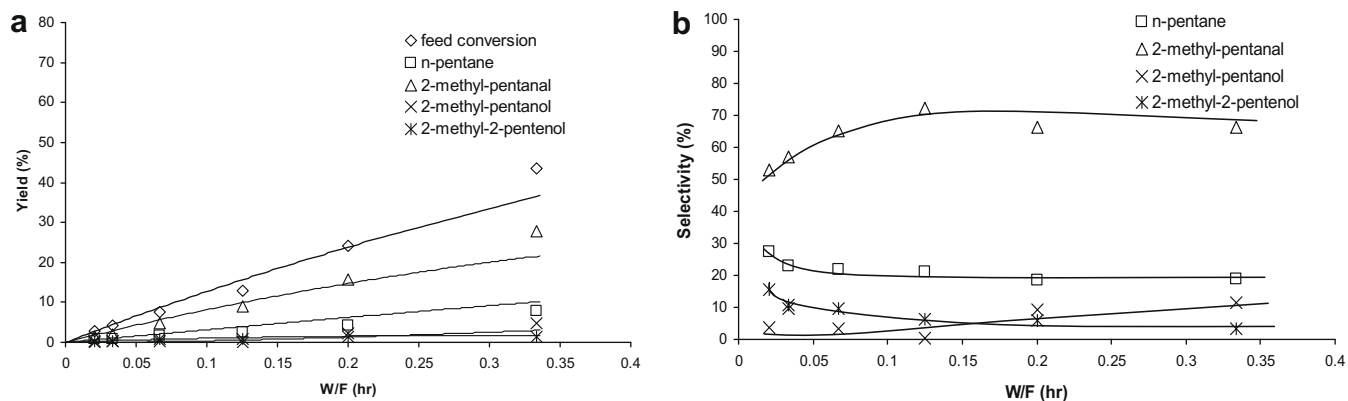


Fig. 2. (a) Conversion and product yield of 2-methyl-2-pentenal on 0.5 wt.% Pt/SiO₂ at 200 °C at different W/F. H₂:feed ratio = 12:1. (b). Selectivity of 2-methyl-2-pentenal conversion on 0.5 wt.% Pt/SiO₂. Solid lines in (a) represent fits for first-order models for each reaction pathway shown in Fig. 4. Solid lines in (b) are added to show the trends.

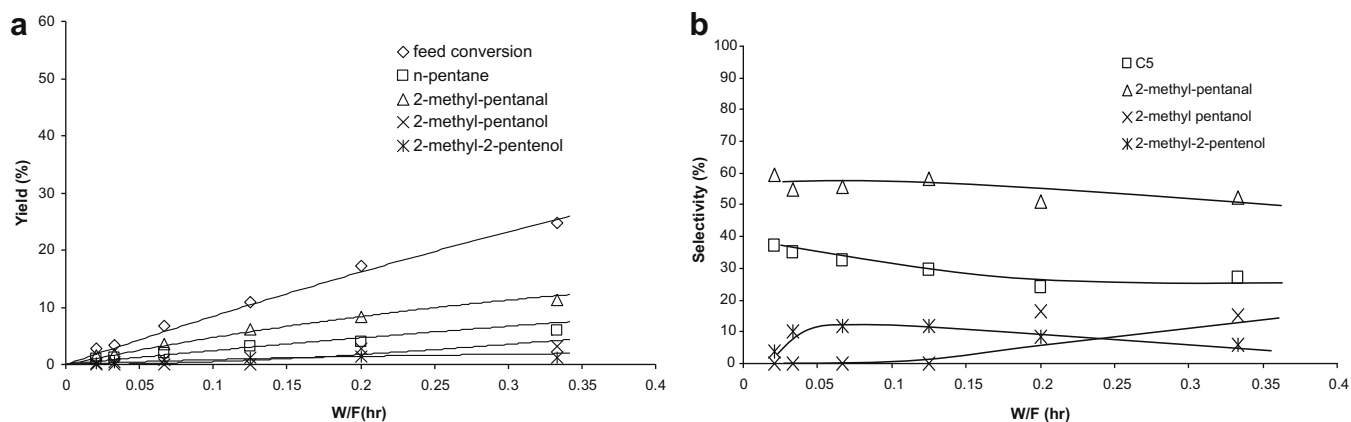


Fig. 3. (a) Conversion and product yield of 2-methyl-2-pentenal on 0.5 wt.% Pd/SiO₂ at 200 °C at different W/F. H₂:feed ratio = 12:1. (b) Selectivity of 2-methyl-2-pentenal conversion on 0.5 wt.% Pd/SiO₂.

Interesting differences among the three catalysts were observed in the product distribution. From analyzing the slope at W/F = 0, one can differentiate the primary from the secondary products. For example, on the 0.5 wt.% Pt/SiO₂ catalyst, three primary products were observed, as shown in Fig. 2a: 2-methyl-pentanal, with smaller amounts of *n*-pentane (any 2-pentene formed would be rapidly hydrogenated under these conditions) and 2-methyl-2-pentenal. 2-Methyl-pentanal is the dominant product arising from the hydrogenation of the C=C bond, 2-methyl-2-pentenal is formed by the hydrogenation of the C=O bond, and *n*-pentane is the primary product of the decarbonylation of 2-methyl-2-pentenal. The by-product CO was also observed. In this figure, the lines represent the fits obtained with the first-order models for the reaction pathways discussed below.

2-Methyl-pentanol is observed as a secondary product, resulting from the hydrogenation of either 2-methyl-pentanal or 2-methyl-2-pentenal. In Fig. 2b, it may be observed that the selectivity of 2-methyl-2-pentenal decreases and that of 2-methyl-pentanol increases as W/F increases which indicates that 2-methyl-pentanol mainly comes from the hydrogenation of 2-methyl-2-pentenal in this range of W/F. In Fig. 2b, the lines are not results of the fitting, but simply show the trends.

In Fig. 3a and b, the results for 0.5 wt.% Pd/SiO₂ are shown. The solid lines in Fig. 3a represent the first-order model fits. It is clear that conversion is significantly lower over Pd than over Pt over the same range of W/F. The data show that in comparison to Pt, the yield of 2-methyl-pentanal on Pd is particularly reduced relative to the yields of other products.

To better visualize the relative trends for the different reaction pathways over the two catalysts, a plot of yield of *n*-pentane vs. yield of 2-methyl-pentanal is shown in Fig. 4. This graph allows a direct comparison of each catalyst's relative activity for decarbonylation compared to the hydrogenation of the C=C bond. The higher slope of the curve for Pd indicates that it has a stronger preference for decarbonylation than Pt at a given overall activity level.

Compared to Pt and Pd, the 0.5 wt.% Cu/SiO₂ catalyst shows a much lower activity at the same weight loading. Therefore, to get

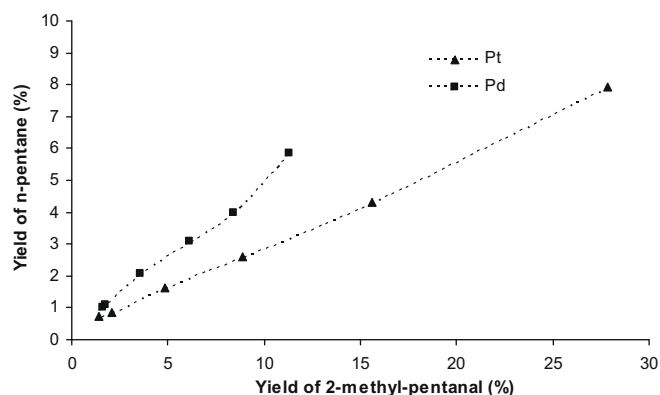


Fig. 4. Yield of *n*-pentane vs. yield of 2-methyl-pentanal to compare activity of decarbonylation with hydrogenation of C=C bond on Pt and Pd catalysts.

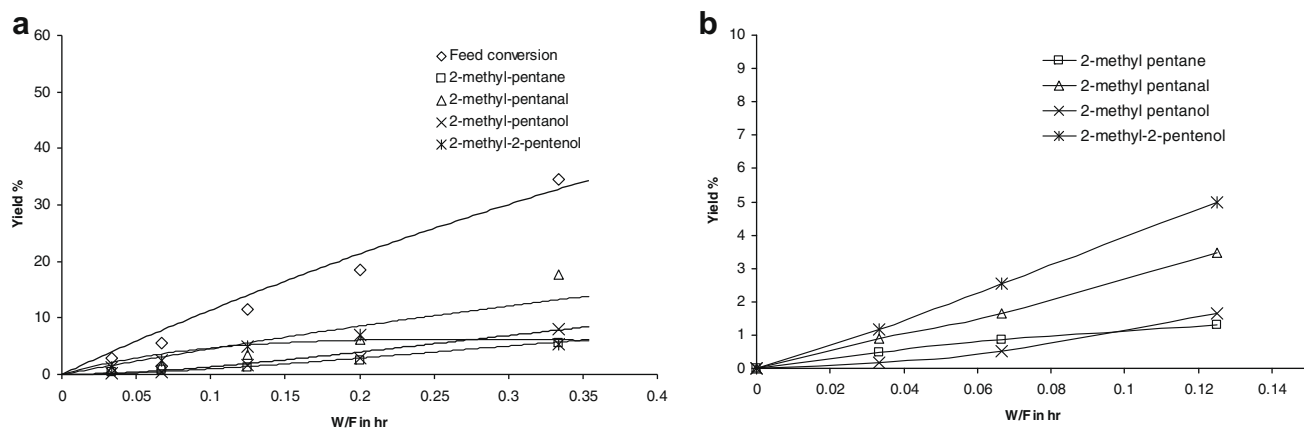


Fig. 5. (a) Conversion of 2-methyl-2-pentenal and product yield on 5 wt.% Cu/SiO₂ at 200 °C at low W/F. H₂:feed ratio = 12:1 and (b) product yields in the low W/F region.

a comparable range of conversions, Cu/SiO₂ was tested at a higher metal loading (5 wt.%). Fig. 5.a shows the different product yields at conversions up to 33% with the lines representing the first-order model fits. 2-Methyl-pentanal is again the most abundant product at higher conversion, but essentially no *n*-pentane is observed. In Fig. 5b, the scale is expanded to show the low W/F region. It may be seen that, initially, the yield of 2-methyl-2-pentenol is the highest, but it goes through a maximum at about W/F = 0.2 and decreases at higher W/F, while the secondary product 2-methyl-pentanol increases.

Thus, it is clear that on the Cu catalyst, the hydrogenation of the C=O bond is faster than that of the C=C bond, which is the opposite trend to that observed on Pt and Pd. The only hydrocarbon observed is 2-methyl-pentane with no *n*-pentane (or CO) as observed over the Pt and Pd catalysts. C₆ is primarily formed by the hydrogenolysis of 2-methyl-2-pentenol that yields 2-methyl-2-pentene, which is then rapidly hydrogenated to 2-methyl-pentane (initially, a small amount of 2-methyl-2-pentene is also observed). Thus, the methyl-pentane is not a primary product, but is formed by the pathway shown in Fig. 6.

The schematic conversion of 2-methyl-2-pentenal on Pt, Pd, and Cu in H₂ is summarized in Fig. 6. Each reaction is labeled with the corresponding *k* values from the fits of the pseudo first-order models. The fitting results are shown as solid lines in Figs. 2a, 3a, and 5a. In all cases, the fittings are very good. For Pd and Pd, the dominant product in the W/F range 0–0.33 h is 2-methyl-pentanal. *n*-Pentane comes from both 2-methyl-2-pentenal and 2-methyl-pentanal but mainly from the latter. At longer contact times, the dom-

inant product is expected to be *n*-pentane as 2-methyl-pentanal is consumed by the decarbonylation reaction. Under the conditions of the study, the yields of 2-methyl-pentanol and 2-methyl-pentanal shift toward the aldehyde because of the favorable equilibrium. Although 2-methyl-pentanol is favored as W/F becomes higher, ultimately (W/F = 2.4, 100% feed conversion) the decarbonylation of the 2-methyl-pentanal to make *n*-pentane becomes the dominant product even at 200 °C.

The *k* values summarized in Table 3 are reported on the basis of the estimated surface atom density. Note that for Pt and Pd catalysts, no C₆ hydrocarbon product was formed, and therefore, both *k*₆ and *k*₈ are listed as zero. Conversely, on Cu, there was no C₅ hydrocarbon product, so *k*₇ is zero. The relative rate of hydrogenation of C=C bond vs. C=O bond is best reflected by the ratio of *k*₁/*k*₂ for all three catalysts. For Pt and Pd, the *k*₁/*k*₂ ratio is about 6, that is, these metals are much more selective for C=C hydrogenation. On Cu, it is about 10 times lower, 0.65, indicating that on this metal, hydrogenation is much less selective. This behavior is clearly illustrated in Fig. 7 showing the yield of 2-methyl-2-pentenol (C=O hydrogenation) vs. yield of 2-methyl-pentanal (C=C hydrogenation). Fig. 7 shows that while Pt and Pd are highly selective for C=C hydrogenation to form the saturated pentanal, Cu is much less selective, but hydrogenates C=O with a preference over C=C. At higher conversions, secondary reactions may mask this effect.

The *k*₇/*k*₁ ratios give an indication of the relative rates of decarbonylation and C=C bond hydrogenation. As shown above, these values illustrate the slightly stronger tendency of Pd toward decarbonylation compared to Pt and quantify the trend shown in Fig. 4. By contrast, Cu shows no decarbonylation activity.

Results from experiments at higher W/F on 5 wt.% Cu/SiO₂ are shown in Fig. 8. These experiments were conducted to see the predominant products at high conversion at 200 °C. At W/F ≥ 1 h,

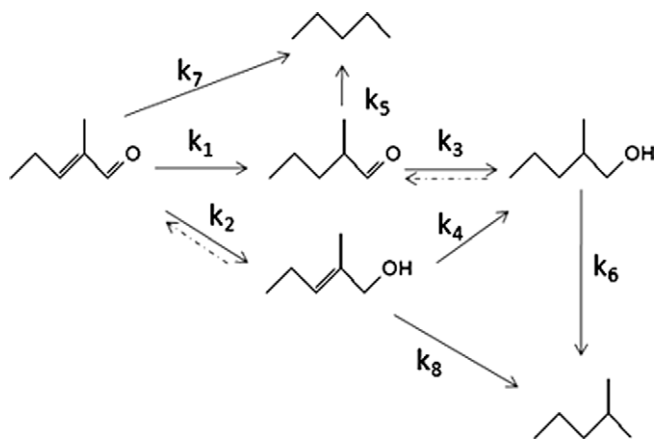


Fig. 6. Schematic conversion of 2-methyl-2-pentenal on Pt, Pd, and Cu.

Table 3
First-order model rate constants (s⁻¹ on a per surface atom basis).

Metal	Pt	Pd	Cu
Loading (wt.%)	0.5%	0.5%	5%
<i>k</i> ₁	2.65	0.20	0.01
<i>k</i> ₂	0.41	0.04	0.01
<i>k</i> ₃	0.29	0.44	0.00
<i>k</i> ₄	19.64	1.12	0.09
<i>k</i> ₅	0.29	0.02	0
<i>k</i> ₆	0	0	0.01
<i>k</i> ₇	0.93	0.10	0
<i>k</i> ₈	0	0	0.02
<i>k</i> ₁ / <i>k</i> ₂ ratio	6.50	5.67	0.65
<i>k</i> ₇ / <i>k</i> ₁ ratio	0.35	0.47	0

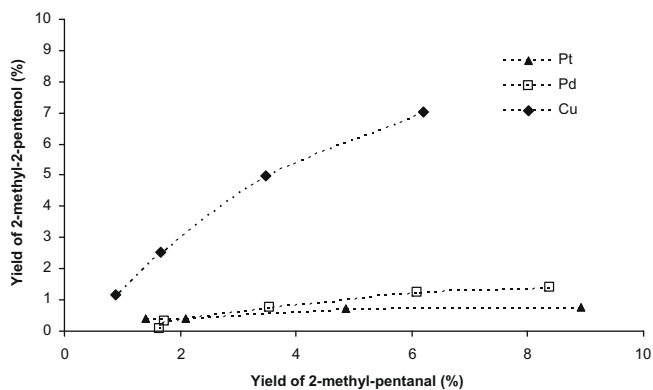


Fig. 7. Yield of 2-methyl-2-pentanol vs. yield of 2-methyl-pentanal on Pt, Pd, and Cu catalysts, comparing C=O vs. C=C hydrogenation activity.

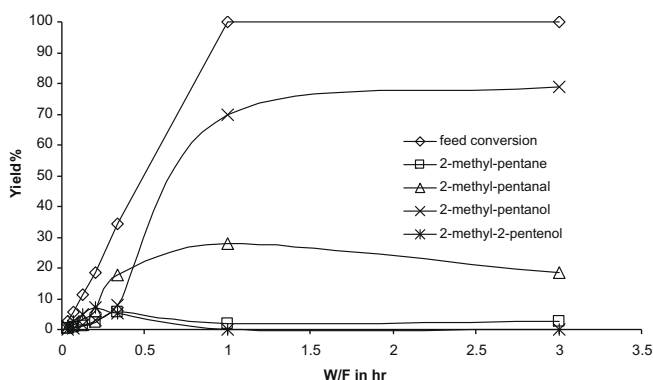


Fig. 8. Conversion and product yield of 2-methyl-2-pentenal on 5 wt.% Cu/SiO₂ at 200 °C at different W/F. H₂:feed ratio = 12:1.

conversion of 2-methyl-2-pentenal was 100%. The highest selectivity was for 2-methyl-pentanol followed by 2-methyl-pentanal. No 2-methyl-2-pentenal was observed, showing complete hydrogenation of 2-methyl-2-pentenal to 2-methyl-pentanol. However, the hydrogenation of 2-methyl-pentanal to 2-methyl-pentanol is not complete, due to equilibrium limitations. Equilibrium experiments were carried out by feeding 2-methyl-pentanal in H₂ with molar ratio 1:12 at 200 °C at high W/F (1–3 h). At W/F = 2–3 h, there is no change in product selectivity so equilibrium is presumably reached. The equilibrium constant K is defined as a ratio of partial pressures $[\text{alcohol}]/[\text{aldehyde}] \times [\text{H}_2]$. From the data, the equilibrium constant was calculated to be $K = 2.71$. As shown in Fig. 8, at 200 °C and this range of W/F, only small amounts of the hydrocarbon 2-methyl-pentane are observed.

On 5 wt.% Cu/SiO₂, it is interesting that at higher W/F, 2-methyl-pentanol and 2-methyl-pentanal are the main products. Further increasing W/F does not change the product ratios since equilibrium is approached. Fig. 9 shows the effect of temperature on selectivity over the Cu catalyst at W/F of 1 h. Under these conditions, the conversion of 2-methyl-2-pentenal is 100% in the entire temperature range. At the lowest temperature (200 °C), selectivity is determined predominantly by the equilibrium between 2-methyl-pentanol and 2-methyl-pentanal. At 300 °C, this equilibrium is shifted toward the aldehyde 2-methyl-pentanal since the hydrogenation reaction (aldehyde + H₂ → alcohol) is exothermic. Also at 300 °C, selectivity to the hydrocarbon product 2-methyl-pentane has increased as the rate of hydrogenolysis becomes significant. As the temperature increases, the equilibrium ratio of alcohol/aldehyde decreases further. At the highest temperature, the hydrogenolysis reaction is fast, with selectivity to 2-methyl-

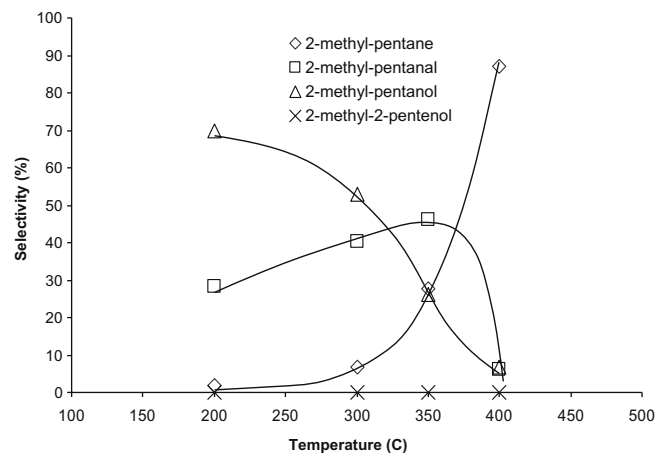


Fig. 9. Selectivity of 2-methyl-2-pentanal conversion on 5 wt.% Cu/SiO₂ at W/F = 1, X = 100%. H₂:feed ratio = 12:1.

pentane approaching 90%. High temperature experiments were also conducted on the Pd catalyst and the results showed high selectivity to *n*-pentane as a function of temperature. Decarbonylation is thus predominant at elevated temperatures on Pd.

Based on experimental results at 200 °C, the equilibrium constant for the reaction 2-methyl-pentanal + H₂ ↔ 2-methyl-pentanol was determined. Values at higher temperatures were calculated using heat of reaction data [22] and Van't Hoff's equation for the range of 200–400 °C. Fig. 10 shows the equilibrium OH/AL ratio together with experimental OH/AL values. The experimental ratio of alcohol and aldehyde (Exp OH/AL) tracks the equilibrium ratio from 200 °C to 250 °C, then deviates above 250 °C as secondary hydrogenolysis becomes dominant. The advantage of C–OH hydrogenolysis that occurs on Cu is the retention of the original carbon chain length whereas the C–C hydrogenolysis that occurs on Pd and Pt shortens the chain length, losing carbon as CO.

In agreement with the results shown here, previous studies have reported that on Pd catalysts, hydrogenation of the C=C bond is generally more favored than C=O [23]. It is believed that when a molecule containing both functional groups adsorbs on a metal surface, activation of the π -bond of C=C is preferred, and once on the surface, this interaction may hinder activation of the C=O group. The C=C activation occurs via two possible modes: (1) π -complex and (2) di- σ bond with the metal. Poniec [23] and Delbecq and Sautet [24] have shown that for a conjugated system, the adsorption on Pd and Pt usually occurs involving both π -bonds. In this adsorption mode, the molecule then transforms into an enol

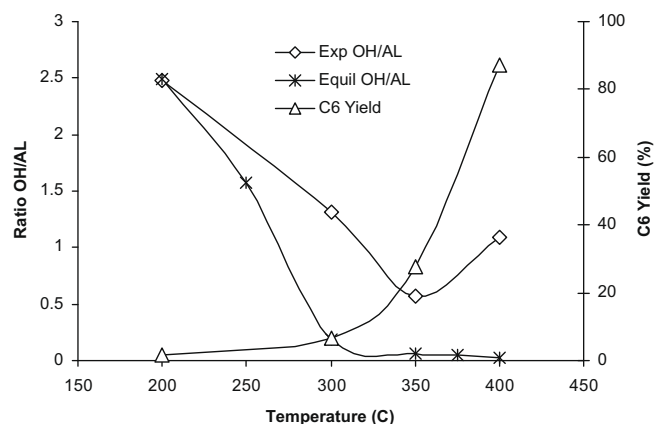


Fig. 10. Ratios of alcohol: aldehyde from experiments and equilibrium, and yield of C6 with temperature.

that isomerizes to a saturated aldehyde, which is the same result as a direct C=C hydrogenation. This preference for C=C hydrogenation when both groups are present has also been reported by other authors [29–31]. This trend is consistent with the results observed in this study, that on Pd (and also on Pt), the major primary product is 2-methyl-pentanal, which comes directly from C=C hydrogenation of 2-methyl-2-pentenal. The 2-methyl-pentanol is initially low, but slowly increases with W/F due to further hydrogenation of 2-methyl-pentanal and 2-methyl-2-pentenal.

Crotonaldehyde has been a popular probe molecule to study competitive hydrogenation on metals [25–28]. As 2-methyl-2-pentenal, crotonaldehyde is an α , β unsaturated aldehyde, however, it does not have a methyl substituent group. The results reported for this molecule also indicate differences in Cu compared to Pt catalysts. It has been reported that the selectivity toward the unsaturated alcohol is lower than the selectivity toward the saturated aldehyde. On Pt the selectivity for C=C hydrogenation is 88% while on Cu it is only 59%. Comparison among different metals, Ag, Au, Co, Cu, Ir, Ni, Pt, and Ru, shows that the selectivity for C=O hydrogenation on crotonaldehyde is lowest on Ni, Ir, and Pt. By contrast, the highest selectivities are seen on Ag, Au and Co catalysts.

As discussed above, Mertens [26] shows that without the methyl group, crotonaldehyde has only moderate selectivity for the hydrogenation of C=O on Cu ($S = 41\%$ [26]). The presence of the methyl substituent group at the α -carbon may affect the selectivity for the hydrogenation of C=O. In our study, the unsaturated aldehyde feed is 2-methyl-2-pentenal, with a methyl substitution at the α -position. The methyl group may hinder C=C hydrogenation, resulting in the observed $S = 61\%$ (from the k_1/k_2 ratio in Table 3), a higher C=O hydrogenation selectivity compared to that for crotonaldehyde in [26]. Mertens [26] also found, for Au and Ag catalysts, a small increase in selectivity for C=O hydrogenation when an α -methyl is added to crotonaldehyde (tiglic aldehyde) with about half of the reactivity. Their results suggest that the improvement in C=O bond hydrogenation selectivity on Cu observed in this study may be due in part to the presence of the α -methyl group.

4. Conclusions

The conversion of 2-methyl-2-pentenal was studied over Pt, Pd, and Cu supported on precipitated silica at 200 °C. On all catalysts, hydrogenation activity was observed for both C=C and C=O bonds. 0.5 wt.% Pd, and Pt showed strong hydrogenation of the C=C bond to form primarily 2-methyl-pentanal. At very low conversion, 5 wt.% Cu/SiO₂ showed strong initial hydrogenation activity of C=O to form primarily 2-methyl-2-pentenal that is converted to 2-methyl-pentanol in equilibrium with 2-methyl-pentanal at higher conversion. On Pt and Pd catalysts, decarbonylation leads to *n*-pentane via C–C cleavage, becoming significant at higher W/F or at higher temperature. On Cu, 2-methyl-pentane via C–O hydrogenolysis was observed on Cu as a minor product at 200 °C, but

became the dominant product on Cu as the temperature was increased to 400 °C.

From the practical point of view, it may be desirable to produce the 2-methyl-pentanol using the Cu catalyst at lower temperatures, since these alcohols are stable and have fairly good octane numbers. At higher temperatures, Cu is a good catalyst for total removal of oxygen without loss of carbon. The high selectivity for C=C hydrogenation on Pt and Pd offers no advantage in producing the more desirable alcohol and despite much higher activity, the loss of carbon (and molecular size) via decarbonylation is a distinct disadvantage when building small molecules to useful fuel range molecules is the objective.

Acknowledgments

Support from the Oklahoma Secretary of Energy and the Oklahoma Bioenergy Center is gratefully acknowledged. The assistance of Steven Crossley in performing the QSAR octane estimates is greatly appreciated.

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