THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

INFLUENCE OF CARBON MONOXIDE IN CHEMOSELECTIVE HETEROGENEOUS
CATALYTIC REACTIONS

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Abstract

The activity for the hydrogenation of crotonaldehyde and selectivity to butyraldehyde and crotyl alcohol was studied in the absence and presence of a small molecule, carbon monoxide at low pressures (19.1, 10, and 2 mTorr). The addition of small amounts of carbon monoxide to the reaction (9 Torr crotonaldehyde, 160 Torr H_2, 373 K) decreased conversion and decreased the overall selectivity to crotyl alcohol, while exerting very little influence on the turnover frequency for butyraldehyde. It was determined that the active sites responsible for the formation of crotyl alcohol are also responsible for the formation of n-butanol because the selectivity to both the unsaturated alcohol and saturated alcohol decreased with increasing CO partial pressure or increasing time-on-stream with a constant pressure of carbon monoxide. This is direct evidence that CO competes for the active sites responsible for crotyl alcohol and n-butanol formation. It was also found that carbon deposits from extended time-on-stream experiments (~20 h) inhibit the formation of crotyl alcohol. The addition of CO shortened the time to achieve steady-state by 25% for the formation of butyraldehyde and 31% for the formation of crotyl alcohol which was presumably due to elimination of the most active sites for decomposition of crotonaldehyde. The apparent activation energies are as follows: 41.8 kJ/mol for the formation of butyraldehyde in the absence of CO, 76.0 kJ/mol for the formation of butyraldehyde in the presence of 19.1 mTorr CO, and 33.1 kJ/mol for the formation of crotyl alcohol in the absence of CO. Increasing the temperature from 353 to 373 K increased the TOF for butyraldehyde by ~2 fold (from 0.3 – 0.54 x 10^{-3} s^{-1} to 0.6 – 1.2 x 10^{-3} s^{-1}), increased the TOF for crotyl alcohol ~1.2 times (from 0.12 – 0.20 x 10^{-3} s^{-1} to 0.14 – 0.24 x 10^{-3} s^{-1}), and decreased the selectivity to crotyl alcohol from 28% to 18%. The TOF decreased to its steady- value faster when more CO was added for both butyraldehyde and crotyl alcohol. It was found that the Pt(3.6 nm)/SBA-15 (3.6 nm represents the average particle size) catalyst changed during use and an amorphous Pt/SiO_2 catalysts worked initially, but then stopped producing crotyl alcohol. Currently, we do not known reason for this behavior. Further research should focus on surface studies of the Pt(3.6 nm)/SiO_2 catalyst during reaction, varying the partial pressure of carbon monoxide to compare the activity and selectivity of Pt/SiO_2 versus Pt/SBA-15 catalysts, and comparing the effects of varying amounts of carbon monoxide on Pt catalysts of varying nanoparticle size.

Table of Contents

1.   Introduction

Heterogeneous catalysis describes a catalytic reaction in which the catalyst is of a different phase than the reactants and products. The most common type consists of a solid catalyst and either a fluid (gas or liquid) phase. In order for a reaction to occur, reactants must diffuse to the catalyst surface and adsorb onto it. The reaction occurs on the surface and the products then desorb from the surface and diffuse into the bulk. Hence, a catalytic reaction is cycle because the catalytic surface is regenerated after desorption and capable of subsequent reactions.   In addition, the rate of reaction can be diffusion-limited or rate-limited, and the catalyst properties and reaction conditions determine what the rate-liming step is.

There are two main factors to help determine the catalyst's performance, activity and selectivity. Activity is defined as how quickly and efficiently a catalyst can produce product and, is typically reported using turnover frequency (TOF). Turnover frequency is the number of molecules reacting per active site per time, where the number of active sites is assumed equal to the total number of surface atoms, which is inversely related to the size of a spherical particle. The surface-to-volume ratio increases with decreasing particle size. Selectivity is defined as the amount of desired product produced relative to the amount of undesired product made [1]. The control of the selectivity is considered more important than the control of other variables such as conversion (which is related to activity). The most important variable to optimize for an industrial catalyst is yield, defined as selectivity × conversion.

The selective hydrogenation of α,β-unsaturated carbonyl compounds has many benefits in fragrance chemistry and in pharmaceuticals. Favorable thermodynamics allows the reaction to proceed at relatively low temperatures [2]. The reactant studied in this paper is an α,β-unsaturated aldehyde, crotonaldehyde, because hydrogenating an α,β-unsaturated ketone produces very little product with a hydrogenated C=O bond. Chemoselectivity is the preferential reaction of a chemical reagent with one of two or more different functional groups [1]. In this case, the chemoselectivity of the catalyst can be studied because there are two unsaturated bonds (C=C and C=O). There are several properties of the catalyst that can affect activity and selectivity to certain products; some of which include the type of metal, amount of metal exposed, adsorbed ligands, and promoters [3, 4]. The amount of metal exposed is the surface area of the active metal available for reactants to adsorb. A promoter is a substance that can increase the catalytic activity [1]. The molecular structure of the α,β-unsaturated aldehyde can

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affect selectivity. If the molecule has a bulky side group at or near the double bond, steric hindrance can lower the selectivity to hydrogenate that bond. Molecules such as 3-methylcrotonaldehyde and cinnamaldehyde both have higher selectivity to the unsaturated alcohol because of steric hindrance near the C=C bond [3].

There are some challenges regarding the control of reaction selectivity. Crotonaldehyde is a four carbon α,β-unsaturated aldehyde that can be hydrogenated to produce either butyraldehyde, by hydrogenation of the C=C bond, or crotyl alcohol, by hydrogenation of the C=O bond. If the reaction proceeds further, both primary products can be further hydrogenated to form n-butanol. At higher temperatures, crotonaldehyde can decarbonylate to produce propene and CO which can then be further hydrogenated into propane. The reaction scheme is shown below in Figure 1. Hydrogenated C=O bonds (C-OH bonds) are important because alcohols are useful as both final products and as intermediates to other reactions.
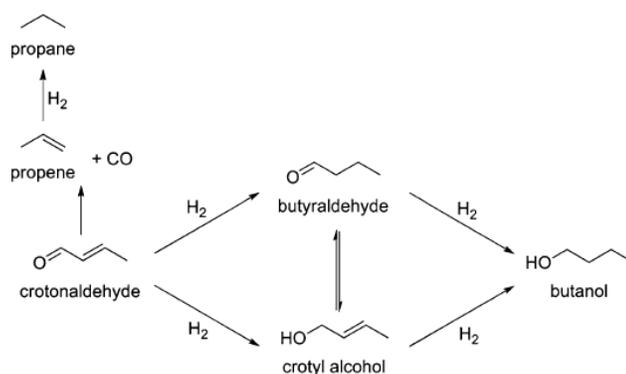

Figure 1. Reaction Pathway for the Hydrogenation of Crotonaldehyde

For this experiment, a silica-supported Pt(X) catalyst, either amorphous (Davidson) or mesoporous (SBA-15) where X is the average diameter of the platinum nanoparticles, determined from chemisorption measurements of catalyst dispersion. Dispersion is the fraction of atoms of a material exposed (located at the surface) to the total number of atoms (volume of nanoparticle) [1]. Dispersion is an important in heterogeneous catalysis because only atoms that are exposed at the surface are available to participate in catalytic surface reactions. Therefore, it is important to quantify this value, which is inversely proportional to crystallite size and is approximately unity when the crystallite diameter is about 1 nm. Under normal operating conditions, when only crotonaldehyde and hydrogen present, this catalyst has a selectivity that

favors the production of butyraldehyde. However, there is an interest to find a way to increase this catalyst's selectivity to crotyl alcohol because it has more potential to be used in industry.

It may be possible to alter selectivity by using a small molecule that can adsorb to the catalyst and compete for sites that favor the undesired product by geometrically or electronically changing the environment to favor production of the desired product [5]. In this experiment, the small molecule of choice is carbon monoxide. An example of this was studied by Rioux et al. in the hydrogenation of ethylene poisoned by CO [6]. In this experiment, addition of CO decreased the rate of reaction and increased the activation energy. Borodzinski and Bond reported an increase in the selectivity to ethene and a decrease in selectivity to ethane when adding CO to the hydrogenation of an ethyne/ethene mixture [7]. In this paper, the effects of carbon monoxide on the activity and selectivity of the hydrogenation of crotonaldehyde over a Pt(3.6)/SBA-15 catalyst will be studied.

2.   Experimental Setup

The 3.6 nm Pt nanoparticles were synthesized by taking a 2.9 nm Pt nanoparticle solution (H_2O/MeOH (1:9), 100 mL) and mixing it with 6 mM $H_2PtCl_6 \cdot 6H_2O$ (10 mL) and MeOH (90 mL). The mixture was refluxed for 3 hours, purified, and separated in 3 mM solutions by sequential precipitation/redispersion. The 3.6 nm Pt nanoparticle solution (27 mL) was mixed with Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF, 2.5 g in 50.5 mL H_2O). This solution was mixed at 313 K for 1 hour. Tetramethyl orthosilicate (TMOS, 98%, Aldrich, 3.91 mL) and sodium fluoride (99.99%, Aldrich, 0.5 M, 0.375 mL) were immediately added to the solution and the mixture was stirred at 313 K for 1 day. The resulting slurry was aged for 1 day at 373 K, centrifuged, washed with ethanol, dried at 373 K, and calcined at 723 K for 1 day under O_2 flow. TEM, XRD, SAXS, BET N_2 adsorption, and chemisorption experiments were all performed to characterize the catalyst.

Catalytic reactions were carried out in a stainless steel (1/4 in.) flow reactor system equipped with mass flow controllers (Tylan FC-260 Instruments) for He, H_2, O_2 and CO (ultra-high purity (UHP), UHP, 20% in He, 51.2 ppm in He), controller box (Tylan), and an inline Pyrex saturator for the introduction of crotonaldehyde (Sigma-Aldrich, 99.9%, predominantly *trans*) into the feed. The catalyst was calcined at 673 K for 1 h in 20% O_2/He (40 mL/min). The catalyst and reactor were flushed for 1 h with He. The catalyst was then reduced at 673 K for 1 h in H_2 (160

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Torr)/He at a total flow rate of 70 mL/min. The reaction was initiated by introducing a flow of He (20 mL/min) through the saturator containing crotonaldehyde held at room temperature (~298 K). This flow was mixed with a flow of H_2/He to create a flow of 9 Torr crotonaldehyde, 160 Torr H_2, and balance He (70 mL/min) (See Appendix for vapor pressure data derived from the Antoine equation for crotonaldehyde.).

The catalyst was placed atop a quartz frit in a ½ in. O.D. Pyrex U-tube reactor. The reactor was loaded with ~15-40 mg of catalyst that had been diluted with ~5 times as much glass microbeads (Ferro). This mixture was loaded into the reactor between beds of ~500 mg of the same microbeads used to dilute the catalyst. The reactor effluent stream was analyzed by gas chromatography (Agilent 7890A) using a flame ionization detector for analysis of organic concentrations. The reaction was started at 353 K for ~2.5 h. The reaction temperature was then changed to 373, 343 and back to 353 K, being left at each temperature for ~1.5 h. The initial and final temperatures were the same in order to observe the extent of catalyst deactivation.

CO poisoning experiments were carried out at 373 K for ~15 h. The reactor feed contained an additional flow of 51.2 ppm CO in He controlled with a mass flow controller with partial pressures of CO corresponding to 19.1, 10 and 2 mTorr. The total flow rate was fixed at 70 mL/min.

The turnover frequency (TOF) was calculated by normalizing the reaction rate to the number of surface Pt atoms based on TEM measurements and the Pt loading determined by ICP-OES. Selectivity values were calculated by dividing the TOF of a certain product by the total TOF, which is the rate of disappearance of reactant.

3.   **Results and Discussion**

A TEM micrograph, in Figure 2, shows that ordered silica structures encapsulate the Pt nanoparticles and the Pt nanoparticles are isolated and randomly distributed throughout the entire silica framework with minimal aggregation. XRD analysis shows a broad amorphous SiO_2 signal at $2\theta = 27.4°$ (XRD diffraction pattern not shown). Estimation of the nanoparticle size based on XRD was not successful because of the low signal-to-noise ratio of the peaks. SAXS analysis showed peaks corresponding to SBA-15 (100), (110), and (200). BET N_2 adsorption measurements showed that the catalyst had a surface area of 523 m^2/g, a pore volume of 1.42 mL (STP)/g (STP = standard temperature (273 K) and pressure (1 atm), and a pore diameter of 11.3

nm. Finally, chemisorption studies showed a dispersion of 0.27 and a nanoparticle diameter of 4.2 nm, slightly bigger than the number-average size determined from TEM [8].
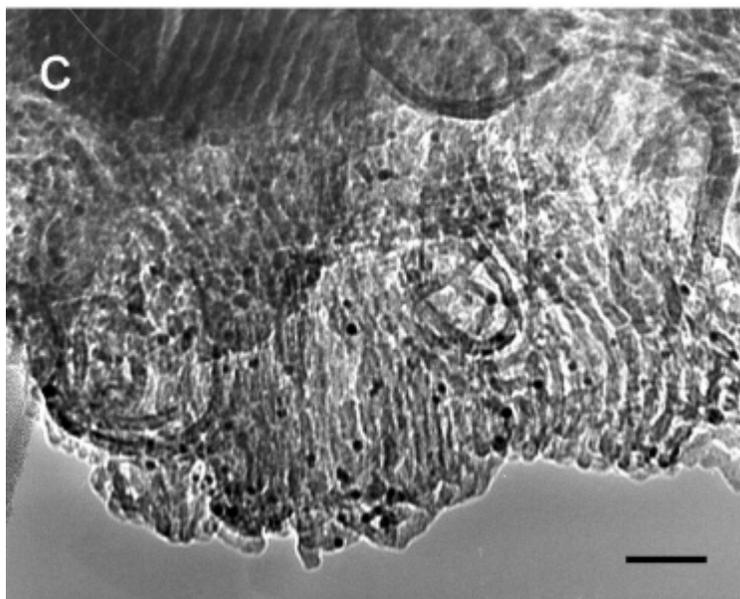

Figure 2. TEM image of Pt(3.6)/SBA-15 catalyst. The scale bars represent 40 nm. [8]

Butyraldehyde is the major product of crotonaldehyde hydrogenation over all temperatures and partial CO pressures studied, which forms by the hydrogenation of the C=C bond. The minor products are crotyl alcohol (the second most abundant product, formed by the hydrogenation of the C=O bond), butanol (complete hydrogenation of C=C and C=O), and propene/propane (decarbonylation) (see reaction scheme, Figure 1). Decarbonylation pathways were detected at all temperatures, indicating the formation of CO.

The TOF data shows an initial deactivation period for the formation of all products without added CO. It is documented that this deactivation is caused by CO from the decarbonylation reaction, which adsorbs to the surface of the catalyst and by carbon depositing on the catalyst surface [4]. For the reactions without added CO, this deactivation period is ~60 minutes long for butyraldehyde and ~275 minutes long for crotyl alcohol and butanol. These times become shorter, ~45 minutes for butyraldehyde (25% decrease) and ~190 minutes for crotyl alcohol and butanol (31% decrease) when any amount of CO is added to the reaction. This reinforces the idea that adsorbed CO is the main cause of the initial deactivation and not carbon deposits on the catalyst surface.

For both butyraldehyde and crotyl alcohol, at 353 K without any added CO, the steady-state TOF values are ~80% of the initial TOF values. At 373 K and the same pressures, the steady-state TOF values for butyraldehyde and crotyl alcohol are only ~40% of the initial TOF values. This implies that at higher temperatures, more decarbonylation occurs leading to the production of more CO which adsorbs on the catalyst surface and increases the initial deactivation. There appears to be strong temperature dependence for the hydrogenation reaction at for all studied CO partial pressures. Therefore an Arrhenius relationship was used to determine the activation energies were determined for butyraldehyde in the presence and absence of 19.1 mTorr CO and for crotyl alcohol in the absence of CO. There were not enough valid data points to obtain a value for crotyl alcohol in the presence of 19.1 mTorr CO. The apparent activation energies are: 41.8 kJ/mol for the formation of butyraldehyde in the absence of CO, 76.0 kJ/mol for the formation of butyraldehyde in the presence of 19.1 mTorr CO, and 33.1 kJ/mol for the formation of crotyl alcohol in the absence of CO. The linearized Arrhenius plot used to determine the apparent activation energies is presented in Figure 3. These values can be used for kinetic work in future experiments.
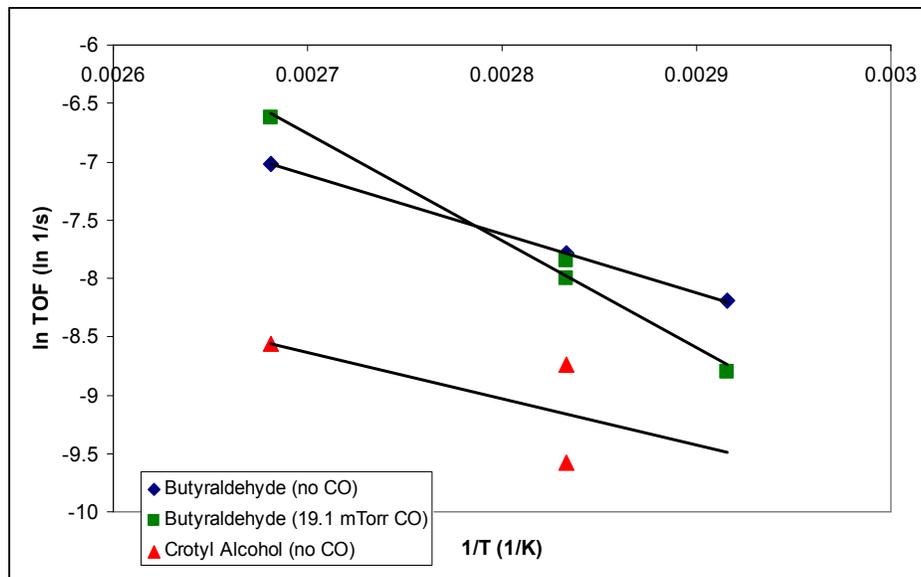

Figure 3. TOF for the formation of butyraldehyde and crotyl alcohol as an Arrhenius plot. The pressures of crotonaldehyde, hydrogen, and carbon monoxide were 9 Torr, 160 Torr, and 19.1 mTorr respectively, with a total pressure of 760 Torr. The apparent activation energies are 41.8 kJ/mol for butyraldehyde without CO, 76.0 kJ/mol for butyraldehyde for butyraldehyde with CO, and 33.1 kJ/mol for crotyl alcohol without CO.

Increasing the temperature from 353 to 373 K caused the steady-state TOF values for both butyraldehyde and crotonaldehyde increased (with no added CO) by ~2 times (from $0.3 - 0.54 \times 10^{-3}$ s^{-1} to $0.6 - 1.2 \times 10^{-3}$ s^{-1}) for butyraldehyde and ~1.2 times (from $0.12 - 0.20 \times 10^{-3}$ s^{-1} to $0.14 - 0.24 \times 10^{-3}$ s^{-1}) for crotyl alcohol. Decreasing the temperature from 353 to 343 K (with no added CO) caused the steady-state values for butyraldehyde to decrease by ~2/3 fold (from $0.3 - 0.54 \times 10^{-3}$ s^{-1} to $0.2 - 0.36 \times 10^{-3}$ s^{-1}). Crotyl alcohol was produced at 343 K, but in amounts too small for accurate analysis (below the detection limit of the FID). From this result, it was determined that butyraldehyde is the favored product, which was confirmed by looking at the steady-state TOF values of butyraldehyde in the presence of CO (19.1 mTorr). The TOF of butyraldehyde increased ~3 fold (from 0.39×10^{-3} s^{-1} to 1.3×10^{-3} s^{-1}) after the temperature was increased from 353 to 373 K and decreased ~ 2 fold (from 0.39×10^{-3} s^{-1} to 0.15×10^{-3} s^{-1}) when the temperature was reduced to 343 K. The presence of CO made analysis of the steady-state crotyl alcohol TOF invalid. This data is shown in Figures 4 and 5. The selectivity data also confirms that butyraldehyde is the thermodynamically controlled product; at 353 K, the selectivity to crotyl alcohol is ~28%, while at 373 K, the selectivity is ~18%.
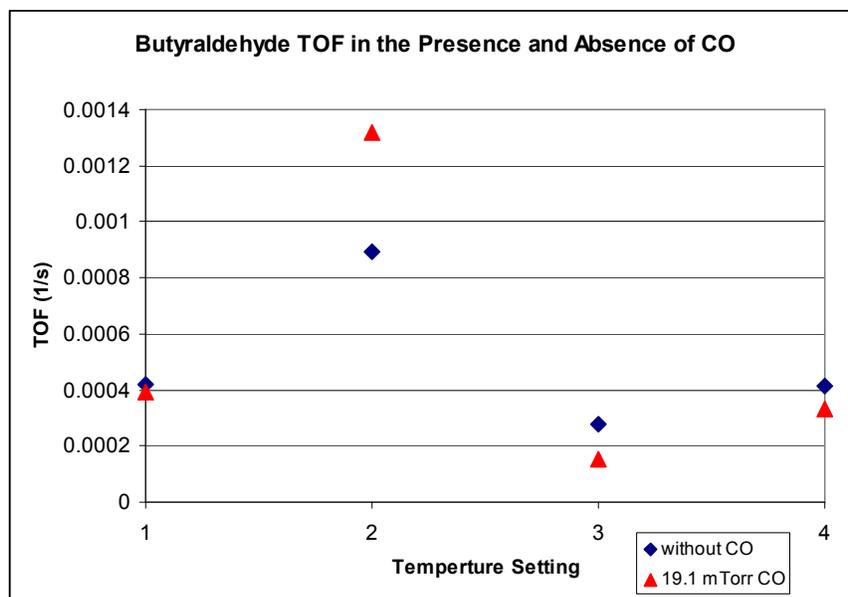

Figure 4. Steady-state TOF values for butyraldehyde in the presence and absence of CO (19.1 mTorr) as a function of temperature. Settings 1, 2, 3, and 4 correspond to 353, 373, 343, and 353 K, respectively.

Figure 5. Steady-state TOF values for crotyl alcohol in the presence and absence of CO (19.1 mTorr) as a function of temperature. Settings 1, 2, 3, and 4 correspond to 353, 373, 343, and 353 K, respectively.
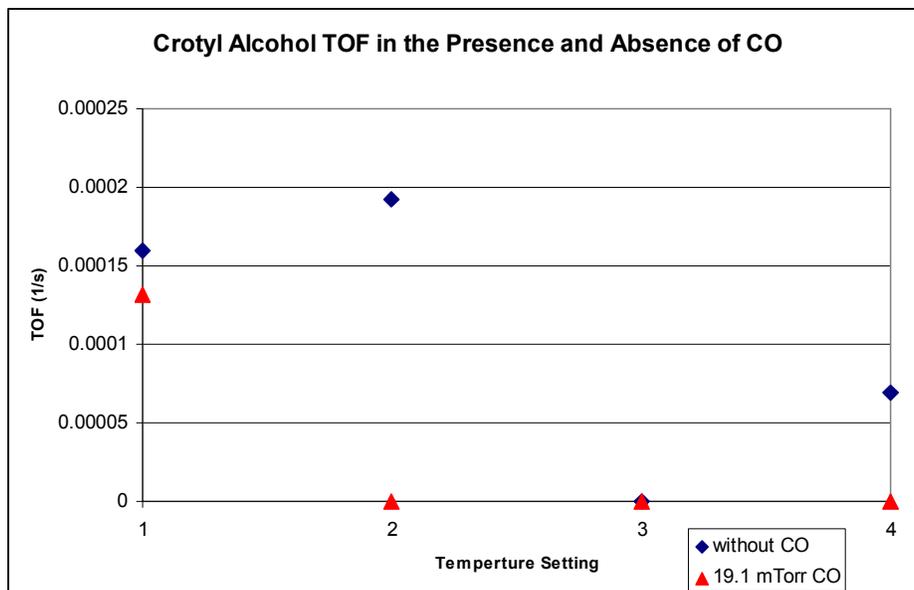
There was no significant decrease in the TOF for butyraldehyde when the temperature was returned to 353 K, but there was a significant decrease in the TOF for crotyl alcohol (decreased by ~1/2). This implies that the carbon deposits block the active sites responsible for the formation of crotyl alcohol. The effect of this is also seen in the selectivity to crotyl alcohol. For the first experimental run at 353 K, the selectivity to crotyl alcohol is ~28%, while for the second experimental run at 353 K, the selectivity is ~20%.

A major effect seen by adding CO to the reaction is in the selectivity data. Without the addition of CO, the selectivity to crotyl alcohol at 373 K is ~18%. However, for partial pressures of CO of 19.1, 10 and 2 mTorr, the selectivity to crotyl alcohol is 12.6%, 11.9%, and 9.0%, respectively. This trend, shown in Figure 6, was not expected since the addition of CO to the reaction lowered the selectivity to crotyl alcohol. Since it is believed that the catalyst changed over time, thus providing inaccurate data, the addition of CO to the reaction should increase the selectivity to crotyl alcohol and the more CO that is present, the higher the selectivity to crotyl alcohol, up to some limit.
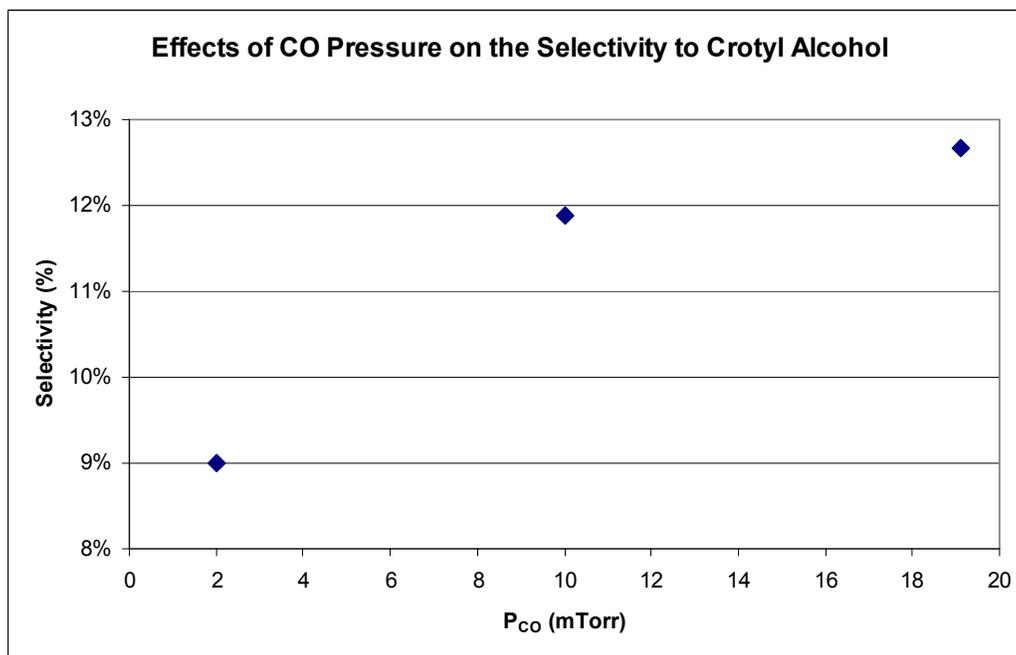
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Figure 6. Selectivity to crotyl alcohol as a function of partial pressure of CO at 373 K. The selectivity increased with larger CO pressure, though the selectivity was lower than the reaction without CO at the same temperature. The pressure of crotonaldehyde and hydrogen were 9.09 Torr and 160 Torr, respectively.

The TOF data shows that the addition of CO causes a faster decrease in TOF for both butyraldehyde and crotyl alcohol. The rates of decay of the TOF for butyraldehyde at 2, 10, and 19.1 mTorr are 1.10×10^{-7}, 4.07×10^{-7}, and 8.16×10^{-7} (1/s min^{-1}), respectively. The rates of decay of the TOF for crotyl alcohol at 2, 10, and 19.1 mTorr are 5.12×10^{-7}, 8.37×10^{-7}, and 1.13×10^{-6} (1/s min^{-1}), respectively. The rates of decay for crotyl alcohol are consistently higher than those for butyraldehyde, which implies that CO is more likely to compete for active sites that are responsible for the formation of crotyl alcohol, which is reinforced because for all pressures of CO, butyraldehyde reached a steady-state TOF, while the crotyl alcohol TOF decreased until there was not enough to analyze accurately.

Pt/SiO$_2$ (Dispersion, D = 0.05 and D = 1.0) catalysts were also used in this study (under identical reaction conditions) but did not show signs of formation of crotyl alcohol or butanol. Initially ~16 mg of the D = 0.05 (particle diameter, d = 22 nm) catalyst was used and there were signs of crotyl alcohol formation; however, all formation ceased. Various amounts of the D =0.05 catalyst were used (~20 – 60 mg). The total flow rate was kept constant but the crotonaldehyde pressures were varied from 2 to 9 Torr, H$_2$ pressures were varied from 40 to 320

Torr, and the reactor temperature was varied from 353 to 473 K. These changes brought about different areas for the peaks of propene/propane, butyraldehyde, and crotonaldehyde with varying conversions, but neither crotyl alcohol nor butanol was formed. These catalysts were not calcined before use but were reduced for 2 h under the conditions mentioned in the experimental section. Approximately 40 mg of a catalyst with D = 1.0 (particle diameter, d ≈ 1 nm) was loaded and reduced, but produced the same results as the previous catalyst. It is unknown as to why the first catalyst stopped producing crotyl alcohol and why new loadings or different dispersions of the same catalyst did not produce crotyl alcohol.

4.   Conclusions

The hydrogenation of crotonaldehyde over a Pt(3.6)/SBA-15 catalyst was studied in the absence and presence of CO (2, 10 and 19.1 mTorr). Addition of CO shortened the time for the catalyst to achieve steady-state by 25% for the formation of butyraldehyde and 31% for the formation of crotyl alcohol. The apparent activation energies are as follows: 41.8 kJ/mol for the formation of butyraldehyde in the absence of CO, 76.0 kJ/mol for the formation of butyraldehyde in the presence of 19.1 mTorr CO, and 33.1 kJ/mol for the formation of crotyl alcohol in the absence of CO. At higher temperatures (373 K), the steady-state TOF values were 40% of the initial TOF value. At 353 K, this value was 80%, indicating more CO is produced at higher temperatures, causing more deactivation. It was seen that increasing the temperature from 353 to 373 K increased the TOF for butyraldehyde by ~2 fold (from $0.3 - 0.54 \times 10^{-3}$ s^{-1} to $0.6 - 1.2 \times 10^{-3}$ s^{-1}), increased the TOF for crotyl alcohol ~1.2 times (from $0.12 - 0.20 \times 10^{-3}$ s^{-1} to $0.14 - 0.24 \times 10^{-3}$ s^{-1}), and decreased the selectivity to crotyl alcohol from 28% to 18%. It was found that at longer run times, the formation of crotyl alcohol was hindered by carbon deposits, as noted by the selectivity to crotyl alcohol decreasing from 28% to 20% at 353 K. Adding CO to the system decreased the selectivity of crotyl alcohol from 18% to 12.6% (19.1 mTorr), 11.9% (10 mTorr), and 9.0% (2 mTorr). An increase in the CO caused a faster decrease in TOF for both butyraldehyde and crotyl alcohol. The rates of decay of the TOF for butyraldehyde at 2, 10, and 19.1 mTorr are 1.10×10^{-7}, 4.07×10^{-7}, and 8.16×10^{-7} (1/s min^{-1}), respectively. The rates of decay of the TOF for crotyl alcohol at 2, 10, and 19.1 mTorr are 5.12×10^{-7}, 8.37×10^{-7}, and 1.13×10^{-6} (1/s min^{-1}), respectively. It was found that Pt(X)/SiO$_2$ catalysts worked initially, but then stopped producing crotyl alcohol. There is no known reason for this.

5.   Future Research

Further research should focus on surface studies of the Pt(3.6)/SiO$_2$ catalyst during the reaction; specifically studying the effects of other partial pressures of carbon monoxide, comparing the activity and selectivity of Pt/SiO$_2$ versus Pt/SBA-15 catalysts. The Pt/ SiO$_2$ catalysts can then be calcined and run again, comparing the effects of varying amounts of carbon monoxide on catalysts with different sized nanoparticles.

6.   References

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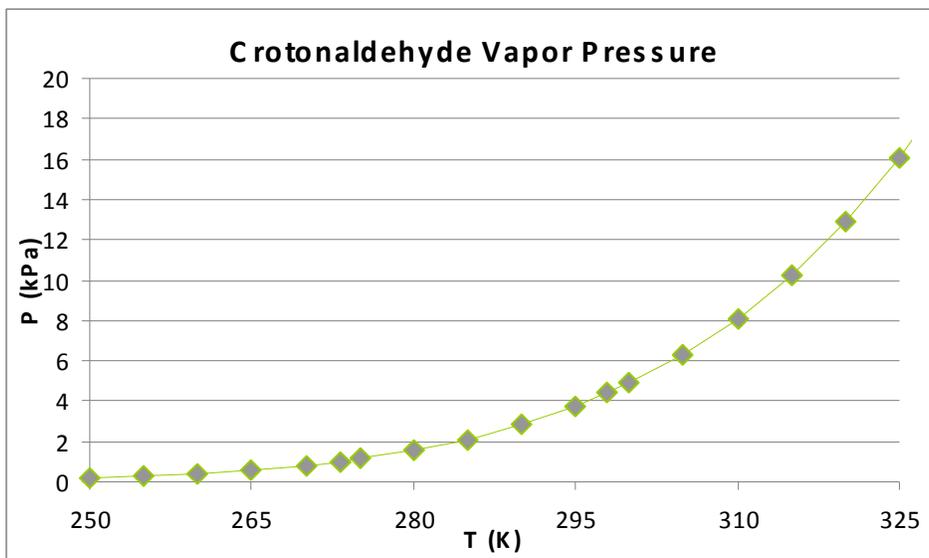**Appendix A - Partial Pressure Data for Important Products and Reactants**

Figure A1 – Partial pressure data of crotonaldehyde using the Antoine equation
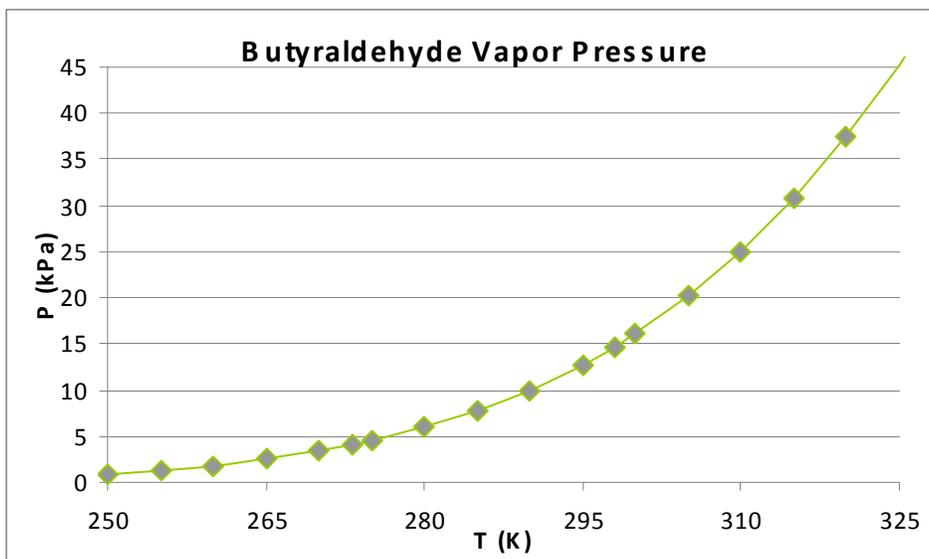

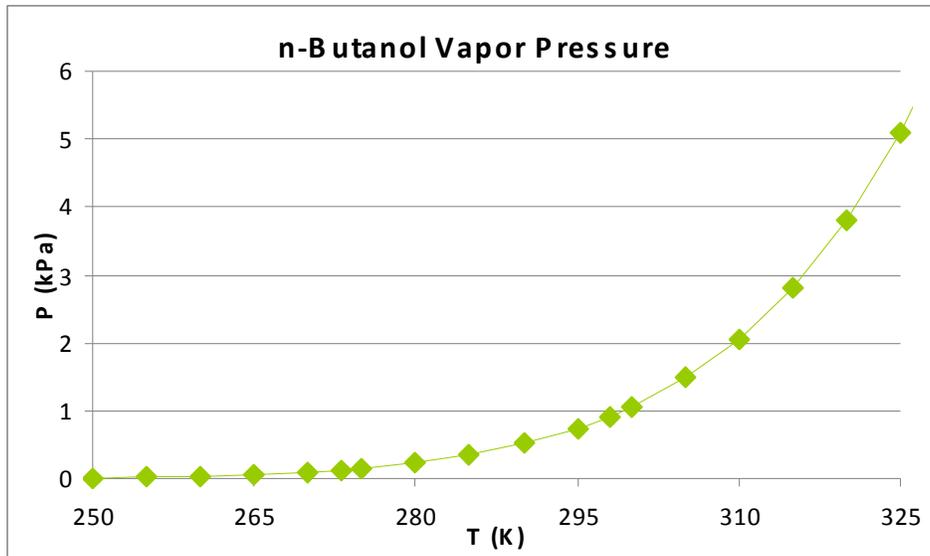**Figure A2** – Partial pressure data of butyraldehyde using the Antoine equation

Figure A3 – Partial pressure data of n-butanol using the Antoine equation

Appendix B – Procedure to Operate GC and Reactor System

Operating the Agilent 7890A GC System:
1. Start the program "Instrument 1 online" via the "Agilent ChemStation" program folder.
2. Go to "Instrument" at the top of the page, then down to "Edit Agilent 7890A Parameters".
3. Beneath the graph, there are icons to click on, starting on the far left (make sure all check boxes are unchecked and do not exit the box when finished):
    a. ALS – N/A (no injectors)
    b. Valves
        i. Valve #1 – Type: Gas Sampling Valve, On/Off: Blank, Position: N/A, Load Time: 0.5 min, Inject Time: 0.5 min
        ii. Valve #2-8 – Not installed
    c. Inlets
        i. PP-Front – Heater: 110 ^{o}C, Control Mode: Flow, Total Flow: 33 mL/min, Septum Purge Flow: 3 mL/min
        ii. SSL-Back – N/A
    d. CFT Settings
        i. Column 1 – Control Mode: Flow, Value: XX mL/min, Post Run: 30 mL/min
        ii. Column 2 – Control Mode: Pressure, Value: 0.5 psi, Post Run: 0.5 psi
        iii. Back SS Inlet – N/A
        iv. Aux EPC 2 – N/A
        v. Aux EPC 3 – N/A
    e. Oven – Value: XX ^{o}C, Hold Time: XX min, Post Run: XX ^{o}C, Post Run Time: 1 min
    f. Detectors
        i. FID-Front – Heater: 250 ^{o}C, H_2 Flow: 35 mL/min, Air Flow: 350 mL/min, Makeup Flow (He): 25 mL/min
        ii. TCD-Back – Heater: 150 ^{o}C, Reference Flow: 45 mL/min, Makeup Flow (He): 2 mL/min
    g. Aux Heaters – Initial: 110 ^{o}C
    h. Run Time Events – N/A
    i. Signals
        i. Front Signal (FID): 50 Hz/.004 min, Save
        ii. Back Signal (TCD): 50 Hz/.004 min, Save
    j. Configuration – N/A
    k. Backflush – N/A
    l. Diagnostic Counters – N/A
    m. Readiness – Check All
4. Set the values marked XX so that the displayed peaks are smooth, have symmetrical fronts and backs, and are not overlapping with each other. These set points will vary on a case-by-case basis.
5. Turn on the gas lines to the GC by the back wall (H_2 – GC, He – UHP) and make sure all valves in these lines and the air line are open.
6. Check the following boxes, then hit apply:

a. Inlets – PP-Front – Heater, Total Flow, Septum Purge Flow
b. CFT Settings – Column 1 and Column 2 – Control Mode On
c. Oven – Oven Temp On
d. Detectors
    i. FID-Front – Heater, Makeup Flow (He), Electrometer
    ii. TCD-Back – Heater, Reference Flow, Makeup Flow (He)
e. Aux Heaters – Thermal Aux 1 On
7. When the front detector reaches 250 ^{o}C and the back detector reaches 150 ^{o}C, check the boxes next to flame (on the FID tab) and filament (on the TCD tab), and hit apply, then hit ok. Turning on the flame will also turn on the H_2 and air flows.
turning these on before the detectors heat up will ruin the GC
8. Go to "RunControl" at the top, then "Sample Info".
9. Choose the location and name of where you want your samples to go and start the counter at 000001, also here you can add notes about your sample, hit ok when done.
10. Go to "Sequence" at the top, then "Sequence Parameters" and do the same thing.
11. Go to "Sequence" then "Sequence Table". Fill in the first 5 columns; choose how many samples you want in your sequence, hit ok.
12. Go to "Method", "Save Method As" and save your method. Go to "Sequence", "Save Sequence Template As" and save your sequence.
13. When the FID signal has leveled off at a value under 20, hit either F5 to run one sample or hit F6 to run the sequence.

Calcining the Catalyst
1. Note: the GC does not have to be on.
2. Turn on the O_2/He cylinder next to the reactor setup.
3. Set the temperature in the reactor to 400 ^{o}C using the temperature controller.
4. Make sure the saturator has no flow to it and the reactor does have flow to it.
5. Flow 40 mL/min over the catalyst using the file "Crotonaldehyde Hydrogenation" to obtain the proper MFC channel and set point.
6. Let the catalyst calcine for 1 hour.
7. When the time is up, turn down the reactor temperature (unless reduction is immediately following), turn off the O_2/He flow, and turn on a flow of ~20 mL/min He (from the cylinder by the reactor setup) for approximately 1 hour.

Reducing the Catalyst
1. Note: the GC does not have to be on.
2. Turn on the H_2 – UHP cylinder on the back wall and the He cylinder by the reactor setup.
3. Set the reactor temperature to 400 ^{o}C if it is not there already.
4. Make sure there is no flow to the saturator but that there is flow to the reactor.
5. Flow 70 mL/min of 160 Torr H_2/He over the catalyst using the file "Crotonaldehyde Hydrogenation" to obtain the proper MFC channels and set points.
6. Reduce for 1-2 hours.
7. Turn down the temperature of the reactor, and flow 5-15 mL/min He over the catalyst unless a reaction will immediately follow. If the reduction is immediately followed by a reaction, purge the line for ~10 minutes with He.

Running a Reaction

1. After the catalyst is loaded, calcined and reduced, turn the temperature controller on and set it to the desired temperature set point.
2. Obtain ~15 mL of crotonaldehyde and place in the saturator.
3. Making sure the line to the saturator is closed, place the saturator together and place a clamp on the top to hold it together.
4. If holding the crotonaldehyde at 273 K, obtain ice, place the ice with some water in a vacuum flask, and place the flask on a jack under the saturator and raise the jack so that the ice/water mixture completely covers the level of crotonaldehyde.
5. Make sure the lines to the reactor and saturator are both closed.
6. If not already opened, open the He (UHP) and H_2 (UHP) gas cylinders by the reactor setup and back wall, respectively.
7. Set the flow rates using the file "Crotonaldehyde Hydrogenation" to obtain set points and MFC channels.
8. Open the line to the saturator.
9. Start a sequence or individual runs until the crotonaldehyde areas reach a steady-state value.
10. Turn on the reactor (once reactor is at desired temperature).
11. To change the temperature of the reactor, do so manually using the temperature controller box.

Appendix C – Obtaining GC Response Factors

1. Obtain the area of a spectral peak for a substance making sure that the experimental conditions (T, P and flow rate) are identical to those in the column.
2. Divide the area of the peak by the volume of the substance to obtain the response factor.

Or

1. Obtain a spectral peak area of a known volume of a substance with a known response factor.
2. Find the corrected area for this known substance.
3. Obtain a spectral peak area for the same volume of an unknown substance.
4. Divide this spectral peak area by the corrected area from above to obtain the response factor for the unknown substance.

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