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# Catalytic oxidation of odorous organic acids

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## Abstract

Emissions of volatile organic acids is a significant problem in rural communities. So far no one has considered catalytic solutions to the problem but catalytic alternatives look quite reasonable. In this paper we present the results of the first study of the oxidation of a series of odorous organic acids on copper catalysts. We find that the organic acids are easily oxidized on commercial copper on alumina catalysts. Light-off temperatures vary from 180°C for *n*-butyric acid to 220°C for acetic acid. The rate of oxidation of acetic and *i*-butyric acid show simple power law dependence on the concentrations of the reactants. In contrast, the oxidation of *n*-butyric, *i*-valeric and *n*-valeric acids show rates which reach a maximum at intermediate oxygen concentrations. Analysis of the data indicates that the copper can exist in two different states: a more active and a less active state.

These results provide the first evidence that catalytic processes are viable for emissions control in rural communities.

*Keywords:* VOC oxidation; Cu/$Al_2O_3$; Catalytic oxidation; Organic acids; Acetic acid oxidation; Butyric acid oxidation; Valeric acid oxidation

## 1. Introduction

Emissions of ammonia and of volatile organic molecules from livestock production facilities is a significant national problem [1–8]. It has been estimated that in northern Europe, about 30% of the acid rain comes from livestock production [1–3]. In the United States, emissions from livestock production facilities are not included in the emissions inventories but the emissions are a significant nuisance [9–14].

According to recent studies, a cow or a hog might produce 200 g of volatile waste every day [15]. At present there are no published studies that indicate what fraction of the volatiles actually gets emitted from a typical facility. Still, a typical producer might have 1000–100,000 animals while a large producer might have as many as 2,000,000 animals. Therefore, the possibility of significant VOC emissions is quite high.

The composition of the emissions from animal production facilities has been examined previously [9–14]. Emissions include ammonia, alcohols, organic acids, esters, and some sulfur compounds. Table 1 gives a list of the compounds which are the most significant sources of odorous pollution from swine production facilities. Generally, more ammonia is emitted than anything else. However, organic acids have the highest nuisance value [9]. The organic acids travel for miles [16], and they have a distinguishing odor which can be readily detected at the parts-per-billion level.

One of the characteristics of livestock production facilities is that localized sources of emissions. Most of the VOC's come from two sources. About 80% comes from the ventilation stacks on the farm buildings, and the other 20% comes from the waste treatment sys-

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Table 1
The major odorous molecules being emitted from Swine facilities [39,40]

| | |
|---|---|
| Acetic acid | Ammonia |
| *n*-Butyric acid | Creosol |
| *i*-Butyric acid | Indole |
| *n*-Valeric acid | Phenol |
| *i*-Valeric acid | Skatole |
| *n*-Caproic acid | |

tem [9]. Both of these are essentially point sources of emissions so they are amenable to conventional emissions control.

We have been exploring possible catalytic solutions to the emissions problems. We are imagining combining a catalyst and an adsorbent. In unpublished work, we found that the organic acids in Table 1 are strongly bound to MgO. Therefore, we imagine a process where an MgO supported catalyst will be placed in the ventilation system of the production facility. The catalysts will adsorb volatile acids, and then the catalyst will occasionally be heated to be regenerated. The waste heat can be use to heat the farm buildings.

A search of the literature reveals that while there has been some published work [17–31] on the oxidation of acetic acid on platinum, ruthenium, silver, and copper, there is only one published paper [30] on any of the other acids in air. There is work on the oxidation of acids in aqueous solution using hydrogen peroxide or ozone as an oxidant.

In this paper, we will present a small part of that work: studies of the oxidation of organic acids on copper/alumina catalysts. Data for reactions on magnesia supported catalysts is complicated because the support plays an important role. Here, we will only provide data on the oxidation on alumina supported catalysts because that is simpler. We will also only present our steady-state data. The non-steady-state data is also interesting but there is insufficient room to consider it here.

## 2. Experimental

The experiments reported here were done as described elsewhere [32]. The catalyst was a commercial 13% copper-oxide on alumina catalyst (Aldrich) with a reported metal surface area of 5–20 $M^2$/g. We activated the catalyst by oxidizing in oxygen at 300°C for 4 h prior to each run. Then the reaction was started. The data in the figures are taken after the reaction reached steady-state.

The reactor was a simple one pass flow tube. A mixture of air, oxygen, nitrogen and organic acid was passed through a heated tube containing 10 g of catalyst. The composition at the entrance and the exit of the tube was measured with a gas chromatograph (GC). The reactor consisted of a thin walled quartz tube embedded in a thermostated in a copper block. The reactions examined here are 340–650 kcal/mole exothermic but the reactor was designed so that the catalyst bed was nearly isothermal during all of the steady-state runs. Experimentally, the exit temperature was never greater that 2°C, hotter than the inlet temperature in the runs reported here. The pellet temperatures were always within 1 K of the measured gas temperature at steady-state. During the experiments, transient temperature spikes were observed when the feed composition changed. However, the transient typically only lasted for 10 min or less. All of the data reported here was measured under steady-state conditions. The reactor was isothermal during these runs. Additional details are given in [32].

## 3. Results

Fig. 1 shows a plot of the acid conversion versus temperature for several of the organic acids. The data in Fig. 1 were measured by feeding an acid/air mixture onto a cold catalyst, heating the catalyst at 2 K/min and measuring the conversion versus time. All of the data were taken at a residence time of 1 s, an acid flowrate of 0.5 ml of liquid acid per hour and an oxygen partial pressure of 175 Torr.

Notice that the conversion of acetic acid increases gradually up to a temperature of 240°C, and then there is a sudden jump and the system goes to 100% conversion. At first we thought that the rapid increase in conversion was due to a temperature transient since the temperature of the catalyst bed rises during the transient experiment. However, we repeated the experiments under conditions where the catalyst temperature rose $<2$ K and still observed a rapid increase in conversion between 240 and 250 K. Evidently, there is a change in the state of the catalyst at about 240°C which leads to higher activity.

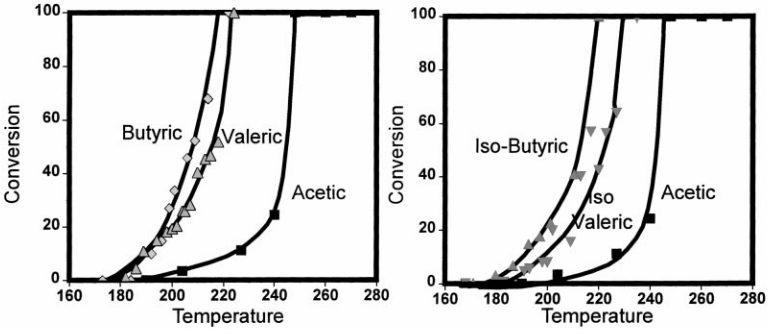

Fig. 1. The conversion vs. temperature for oxidation of a number of organic acids on 20 g of a copper on alumina catalyst. All of the runs were done by feeding an acid air mixture onto a cold catalyst, and then heating the catalyst at 2 K/min and measuring the conversion vs. time. All of the data were taken at a residence time of 1 s, at an acid flowrate of 0.5 ml of liquid acid per hour and an oxygen partial pressure of 175 Torr.

We have done similar measurements with several other acids, and the data is also given in Fig. 1. Generally, all the acids show similar behavior. The conversion is modest until we get to a critical temperature and then the conversion jumps to nearly 100%. The change in behavior appears to be associated with a change in the state of the catalyst since it is seen in both steady-state and transient experiments.

The temperature where the jump occurs varies with the acid as indicated in Table 2. Generally *n*-butyric acid has the lowest critical temperature, and acetic acid has the highest critical temperature. Both *n*- and *i*-butyric acid are oxidized at lower temperatures than either acetic, *n*-valeric or *i*-valeric acid. There are only small differences between the *n*- and *i*-isomers.

We have used a GC to analyze the composition of the composition of the gases leaving the reactor during the runs in Fig. 1. The GC analysis showed that there was $CO_2$, water and unreacted acid in the exit stream but surprisingly no partially oxidized products were detected.

Table 2
The temperature where the sudden increase in conversion occurs on a copper catalyst[a]

| Acid | Critical temperature |
|---|---|
| *n*-Butyric | 214–218 |
| *i*-Buteric | 215–218 |
| *n*-Valeric | 219–223 |
| *i*-Valeric | 227–230 |
| Acetic | 240–242 |

[a] The data was taken on 20 g of catalyst at an acid flow rate of 0.5 ml of liquid acid per hour and a residence time of 1 s and an oxygen partial pressure of 175 Torr.

Fig. 2 shows how the rate of acetic acid oxidation varies with the acid and oxygen pressure. Notice that the conversion of the acid increases monotonically with increases in the oxygen pressure and decreases monotonically with increasing acid concentration. This is integral reactor data, so if the reaction had been first order in the acid concentration the conversion would be independent of the acid concentration. The results on the left of Fig. 2 show that the reaction is less than first-order in the acid concentration.

Previous investigators have found that the oxidation of acetic acid on platinum and rhodium follow Langmuir behavior [17–22]. If the reaction followed a Langmuir rate law similar to those in references [17–22], then the conversion should level off at low concentrations and should show a maximum with increasing oxygen pressure. There is no evidence for that behavior in the data.

We have fit the data in Fig. 2 with (a) various Langmuir rate laws, (b) Frendlich rate laws, and power laws, and found the best agreement with a simple power law expression

$$r_{\text{acid}} = k(P_{\text{acid}})^m (P_{\text{O}_2})^n \tag{1}$$

Fig. 2 shows a plot of the conversion calculated with $k = 3.9 \times 10^{-9}$ mol/s g catalyst $(\text{Torr})^{0.6}$, $m = 0.12$, $n = 0.48$. Good agreement between experiment and calculations is observed.

Fig. 3 shows a plot of the conversion of *i*-butyric acid as a function of the acid and oxygen concentra-

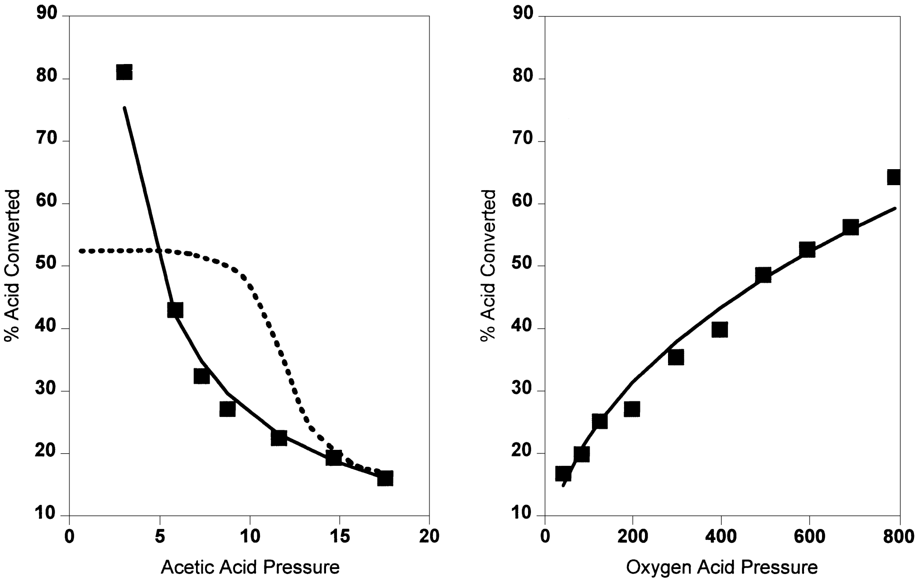

Fig. 2. The conversion of acetic acid as a function of the acid and oxygen pressure, measured on 20 g of a copper on alumina catalyst at a temperature of 240°C, a residence time of 1.26 s. The curve on the left was taken at a fixed feed oxygen pressure of 172 Torr, the curve on the right was taken at a fixed acid partial pressure in the feed of 7.04 Torr. Points: data, solid lines calculated with rate $= 3.9\times10^{-9}$ (mol/s g catalyst (Torr)$^{0.6}$)$(P_{\mathrm{acid}})^{0.12}(P_{\mathrm{oxygen}})^{0.48}$, dashed line expected from Langmuir rate law.

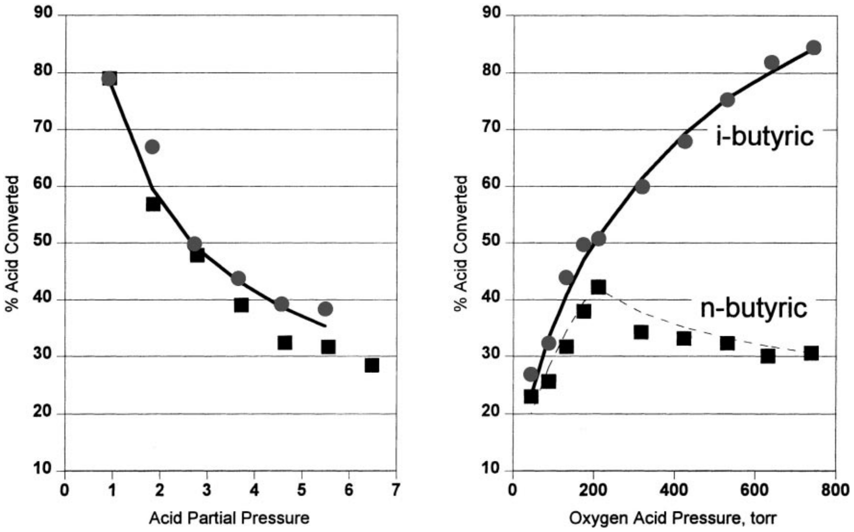

Fig. 3. The conversion of *n*-butyric and *i*-butyric acid as a function of the acid and oxygen pressure, measured on 20 g of a copper on alumina catalyst at a temperature of 200°C, a residence time of 1.17 s. The curve on the left was taken at a fixed feed oxygen pressure of 175 Torr, the curve on the right was taken at a fixed acid partial pressure in the feed of 3.77 Torr. Points: data, solid lines calculated with rate $= 1.31\times10^{-8}$ (mol/s g catalyst (Torr)$^{0.96}$)$(P_{\mathrm{acid}})^{0.46}(P_{\mathrm{oxygen}})^{0.5}$. Dashed line calculated with Eq. (2).

tion. The *i*-butyric data follows the same trends as in Fig. 2. The conversion increases monotonically with increasing oxygen pressure, and decreases monotonically with increasing acid concentration. We have fit the data with a number of expressions, and found that again the best agreement with a simple power law expression with $n = 0.46$, $m = 0.5$, $k = 1.31 \times 10^{-8}$ mol/s g catalyst (Torr)$^{0.96}$. A plot of the power law expression is also given in Fig. 3. Again good agreement is observed.

Fig. 3 also shows a plot of the conversion of *n*-butyric acid as a function of the acid and oxygen concentration. Unlike the results above, the conversion reaches a maximum at intermediate oxygen concentrations. We have tried to fit the data with a simple rate law and do not obtain any reasonable results. We could fit the data with a rate law of the form

$$r_{\text{acid}} = \begin{cases} 1.18 \times 10^{-8}\ (\text{mol/s g catalyst (Torr)}^{0.96})(P_{\text{acid}})^{0.46}(P_{\text{O}_2})^{0.5}, & \text{for } P_{\text{O}_2} < 200\,\text{Torr} \\ 6.03 \times 10^{-7}\ (\text{mol/s g catalyst (Torr)}^{0.21})(P_{\text{acid}})^{0.46}(P_{\text{O}_2})^{-0.25}, & \text{for } P_{\text{O}_2} > 200\,\text{Torr} \end{cases} \tag{2}$$

Fig. 4 shows comparable data for *n*-valeric and *i*-valeric acid. In this case both acids show the same type of behavior as with buteric acid. The rate shows a sharp maximum at intermediate oxygen concentrations. Again the results can be fit with Eq. (2).

We have also done work on platinum catalysts. Fig. 5 shows a the results of a run done by feeding an acetic acid air mixture onto a cold platinum on alumina catalyst, and then heating the catalyst at 2 K/min and measuring the conversion versus time. All of the data were taken at a residence time of 1 s, at an acid flowrate of 0.5 ml of liquid acid per hour and an oxygen partial pressure of 175 Torr. Notice that the rate shows a slow monotonic increase in conversion with increasing temperature. There is no evidence for a sudden increase in rate with increasing temperature.

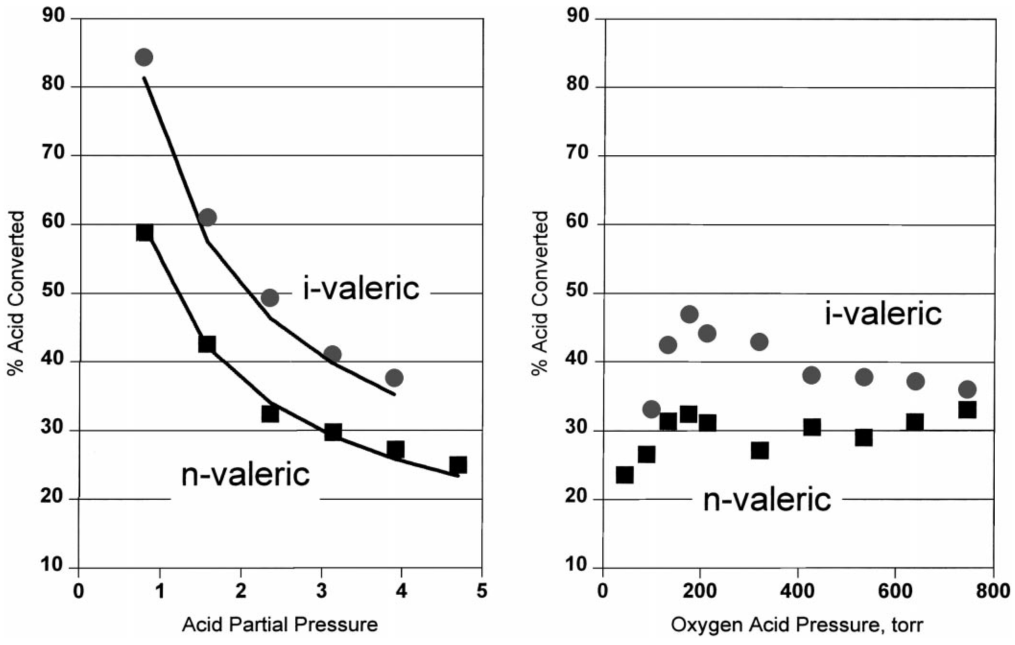

Fig. 4. The conversion of *n*-valeric and *i*-valeric acid as a function of the acid and oxygen pressure, measured on 20 g of a copper on alumina catalyst at a temperature of 200°C, a residence time of 1.27 s. The curve on the left was taken at a fixed feed oxygen pressure of 187 Torr, the curve on the right was taken at a fixed acid partial pressure in the feed of 2.40 Torr.

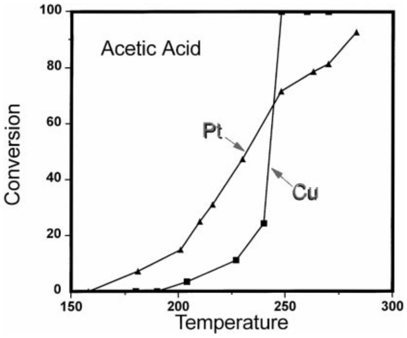

Fig. 5. The conversion of acetic acid on a platinum/alumina and copper/alumina catalyst. All of the runs were done by feeding an acid air mixture onto a cold catalyst, and then heating the catalyst at 2 K/min and measuring the conversion vs. time. All of the runs were done at an acid flow rate of 0.5 ml of liquid acid per hour and a residence time of 1 s and an oxygen partial pressure of 175 Torr.

## 4. Discussion

The data in Figs. 2–5 shows that catalytic processes have the potential for use in the farm environment. Organic acids are easily oxidized on a $Cu/Al_2O_3$ catalyst. Conversions are reasonable at modest temperatures. The light-off temperature is higher than we had hoped but within reach.

The kinetics of the process were different than one might have expected. For example, Fig. 2 when we slowly heat the catalyst to 240°C, the rate suddenly jumps to a much higher value. When we first did the experiments we considered the idea that the catalyst was just getting hot and that increased the rate. However, we observe an increase in rate even under conditions where we do not observe significant change in the external temperature of the catalyst pellets at steady-state. Further, we observe the sudden change in rate with copper on alumina catalysts but not platinum on alumina catalysts. If the main cause of the sudden increase in rate we observe on copper were associated with a temperature change, then we would expect to observe a similar effect in platinum. After all, everything is the same except the composition of the catalyst. The fact that we observe a sudden change in rate with copper but not with platinum is strong evidence that the change in rate is associated with a change in the copper, and not a heat transfer problem or other artifact.

We have observed similar changes in rate with all of the other acids we have examined but the critical temperature where the sudden increase in rate occurs varies with the acid. Butyric acid has the lowest critical temperature. Acetic and valeric acids show higher critical temperatures. If the change in rate were associated with a phase transition in the catalyst then the critical temperature should have been independent of the acid. One should observe a dependence on the acid, only if the acid were directly participating in the process that produces a more active catalyst. There we suggest that the acids are somehow interacting with the catalyst to produce a more active catalyst phase.

Our kinetic data is also consistent with this view. Notice that the slope of the butyric acid curve on the right of Fig. 3 shows a sudden change in slope at an oxygen pressure of 200 Torr. A similar change in slope is also seen in the valeric acid data in Fig. 4. This change in slope is strongly suggestive in a change in the characteristics of the catalyst.

In the previous literature, many workers have examined CO, methanol ammonia and formic acid oxidation on copper. Examples are given in [33–38]. Generally, the activity of the catalyst changes greatly according to how the catalyst is prepared. The catalysts can exist in several oxidation states. According to the previous literature [33–38] a partially oxidized copper phase is the most active. Fully oxidized or fully reduced copper phases are less active.

Our data suggests that it is possible to convert the copper from an inactive phase to an especially active phase or vice versa during the course of the reaction. We observe sudden changes in conversion and sharp changes in the slopes of the oxygen plot. These changes are strongly suggestive of a change in the active phase of the catalysts under reaction conditions. The data in Fig. 1 shows that as we raise the temperature, we shift from a less active copper phase to a more active copper phase. The data in Fig. 4 show that the less active copper phase in suppressed at high oxygen pressures.

There are some unexplained observations in the data. In particular, butyric and *i*-butyric acid show different behavior in the right side of Fig. 3. Evidently the active phase of the catalysts survives to higher oxygen pressures with *i*-buteric acid than with *n*-butyric acid. Still, the majority of our results can be explained if we assume that there is a dynamic equilibrium between a less active form and a more active form of our copper catalyst as suggested by previous investigators [33–38].

## 5. Conclusions

In summary then, the results in this paper show that catalytic processes have the possibility of being used to solve an important problem: the emissions of odorous molecules from animal production facilities [39,40]. We find that the odorous molecules are oxidized at reasonable rates on the catalyst, at reasonable temperatures. The kinetics of the reaction are unusual in that we have evidence for two different copper phases with different activities. Further, we observe evidence that the catalyst can change from an active form to an inactive form during the course of the reaction.

This is the first paper on the catalytic oxidation of many of the molecules considered here, so there is still much more work to be done. However, the results look interesting, and they may contribute to an important national problem.

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