

## Laboratory Experiments Evaluating the Effects of S and Cu on a Pt-Al<sub>2</sub>O<sub>3</sub> Auto Exhaust Oxidation Catalysts

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Copper impregnation substantially increases the ethylene oxidation activity in a laboratory gas stream of a Pt-Al<sub>2</sub>O<sub>3</sub> catalyst, while it decreases CO oxidation activity. SO<sub>2</sub> decreases the activity of untreated Pt-Al<sub>2</sub>O<sub>3</sub> catalyst for both CO and C<sub>2</sub>H<sub>4</sub> oxidation. The Cu-treated Pt-Al<sub>2</sub>O<sub>3</sub> catalyst shows a decrease in ethylene oxidation activity due to SO<sub>2</sub> about equal to or less than the untreated catalyst, whereas the Cu-treated catalyst shows a larger decrease in CO oxidation activity due to SO<sub>2</sub> than the untreated material. Reduction of the Cu-treated catalyst greatly increased the CO activity and decreased the ethylene activity.

The designation PTX has been given by Englehard Minerals and Chemicals Corp. to a catalytic unit used to oxidize CO and hydrocarbons in automobile exhaust to CO<sub>2</sub> and water. The catalytic unit is in the form of a ceramic honeycomb onto which has been deposited a transition alumina. Into the pores of this alumina have been deposited small crystallites of platinum. The weight percent of the honeycomb that is platinum is ~0.35 wt%. This unit is essentially a Pt-Al<sub>2</sub>O<sub>3</sub> catalyst in a physical form (honeycomb) that permits ready access of gases to the catalyst surfaces.

Analytical examination of deactivated PTX units that have been used downstream from a Monel NO removal catalyst has revealed relatively high (0.15%) copper content (J. Larson, Ford personal communication) which has led to speculation that Cu may deactivate the Pt-Al<sub>2</sub>O<sub>3</sub> catalyst. In view of this suggestion, it was thought desirable to carry out laboratory experiments designed to determine the effect of small amounts of copper on the activity of Pt towards the oxidation of CO and ethylene. Because the oxidation activ-

ity of Cu is susceptible to sulfur poisoning, it was felt necessary to explore the effect of this poison on the Al<sub>2</sub>O<sub>3</sub>-Pt-Cu system.

### EXPERIMENTAL METHODS

A portion of a PTX unit (American Lava honeycomb) was broken up, sieved, and the fraction 16-32 mesh (1-1.5 mm) was used for all the experiments. One half of this material (25 g) was used as a blank. The other half (25 g) was treated with a dilute cupric nitrate solution (5.2 g/liter) until it was just saturated with the solution. This resulted in the sample containing 0.15 wt% Cu. The wet sample was treated with hydrogen gas at room temperature for several days. It was hoped that the Pt on the catalyst would catalyze the reduction of the cupric ion by hydrogen so that the copper would be precipitated in the vicinity of the Pt particles. The pronounced effect of the small amount of Cu on the Pt activity towards ethylene oxidation, as shown below, seems to bear this out. Our laboratory experiments have shown that the catalytic activity of Pt towards the oxidation of ethylene under the conditions of

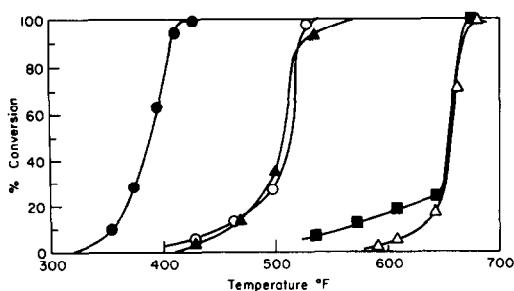


FIG. 1.  $C_2H_4$  Oxidation (0.2%  $C_2H_4$ , 1.8%  $O_2$ , 3%  $H_2O$ ). All units pretreated 19 hr at 1100°F in air, space velocity 80,000  $hr^{-1}$ . (○) PTX; (●) PTX + 0.15 wt% Cu; (△) PTX + 66 ppm by vol of  $SO_2$  in inlet (1000 ppm S in fuel); (▲) PTX + 0.15 wt% Cu + 66 ppm by vol  $SO_2$  in inlet; (■) PTX + 0.25% NO in inlet.

this test is  $\sim 20$  times larger than CuO per unit surface area and that the presence of 66 ppm of  $SO_2$  will completely deactivate CuO at 300°C. The assumption of separated phases of CuO and Pt are not in accord with the data shown (for example Fig. 3). The sample was then dried rapidly at 200°C. Portions of both the copper-treated and the untreated PTX material were heat treated in air for 19 hr at 1100, 1500, and 1800°F, respectively, before use as a catalyst.

For the activity measurements a helium gas stream containing premixed 1% CO or 0.2% ethylene was, after the addition of  $\sim 2\%$   $O_2$ , passed over the sample (0.13 g in a quartz tube  $\sim 2$  mm i.d., sample depth 4 cm) in a furnace. The inlet gas stream was

saturated with water vapor at room temperature ( $\sim 3\%$   $H_2O$ ). The exhaust concentration of  $CO_2$  and other constituents was continuously monitored by a mass spectrometer. The furnace temperature was programmed to increase in steps of 20°C with a time between steps of 10 min. The  $SO_2$  was added as a mixture in argon (1000 ppm) and the concentration was monitored by measuring the A peak. The space velocity used was 80,000  $hr^{-1}$ .

## RESULTS

### Ethylene Oxidation

Figures 1–3 indicate that, under these laboratory conditions, the presence of copper (most likely as the oxide after heat treatment in air) greatly increases the activity of the PTX unit toward ethylene oxidation. This is so for units calcined in air at 1100, 1500, and 1800°F, and surprisingly enough even in the presence of  $SO_2$ , where one should expect poisoning of the copper. Upon removal of the  $SO_2$  at the 50% conversion temperature, there is a rapid partial recovery of the activity, followed by a slow recovery to the original activity. When first used, the Cu–PTX units and, to a lesser extent, the PTX units themselves that had been calcined in air at 1800°F exhibited an abnormally high activity which decreased with time to a

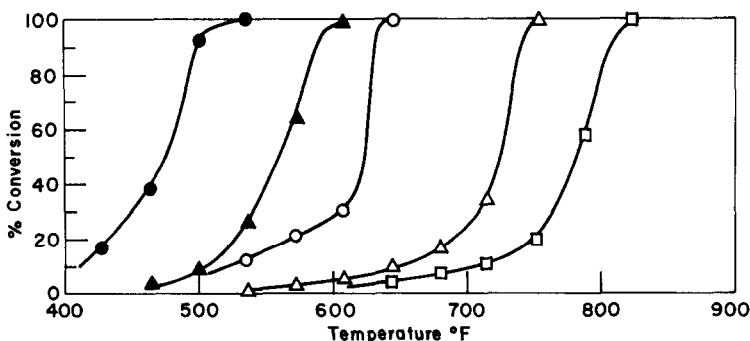


FIG. 2.  $C_2H_4$  Oxidation (0.2%  $C_2H_4$ , 1.8%  $O_2$ , 3%  $H_2O$ ). All units pretreated 19 hr at 1500°F in air, space velocity 80,000  $hr^{-1}$ . (○) PTX; (●) PTX + 0.15 wt% Cu; (△) PTX + 20 ppm by vol of  $SO_2$  in inlet (300 ppm S in fuel); (□) PTX + 60 ppm by vol of  $SO_2$  in inlet (900 ppm S in fuel); (▲) PTX + 0.15 wt% Cu + 66 ppm by vol  $SO_2$  in inlet.

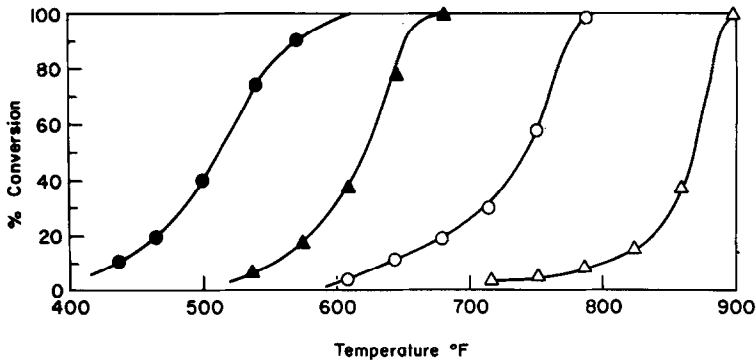


FIG. 3. C<sub>2</sub>H<sub>4</sub> Oxidation (0.2% C<sub>2</sub>H<sub>4</sub>, 1.8% O<sub>2</sub>, 3% H<sub>2</sub>O). All units pretreated 19 hr at 1800°F in air, space velocity 80,000 hr<sup>-1</sup>. (○) PTX; (●) PTX + 0.15 wt% Cu; (Δ) PTX + 66 ppm by vol SO<sub>2</sub> in inlet (1000 ppm in fuel); (▲) PTX + 0.15 wt% Cu + 66 ppm by vol SO<sub>2</sub> in inlet.

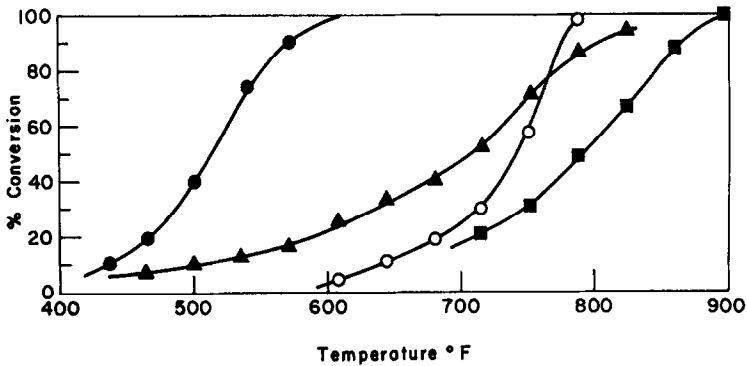


FIG. 4. C<sub>2</sub>H<sub>4</sub> Oxidation (0.2% C<sub>2</sub>H<sub>4</sub>, 1.8% O<sub>2</sub>, 3% H<sub>2</sub>O). All units pretreated 19 hr at 1800°F in air, space velocity 80,000 hr<sup>-1</sup>. (○) PTX; (●) PTX + 0.15 wt% Cu; (▲) PTX + 0.15 wt% Cu reduced 16 hr 1500°F (or 1100°F); (■) PTX + 0.15 wt% Cu reduced 16 hr 1500°F + 66 ppm by vol of SO<sub>2</sub> in inlet.

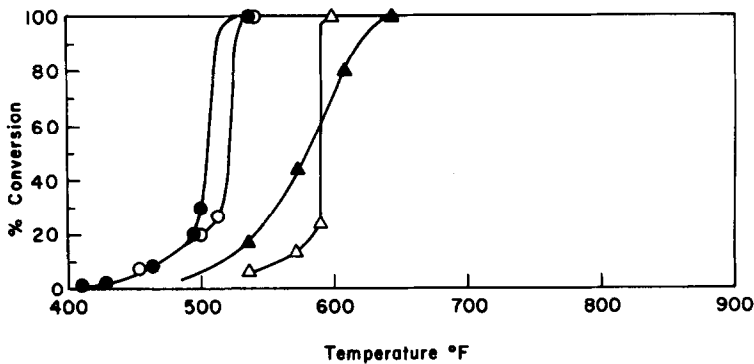


FIG. 5. CO Oxidation (1% CO, 1.8% O<sub>2</sub>, 3% H<sub>2</sub>O). All units pretreated 19 hr at 1100°F in air, space velocity 80,000 hr<sup>-1</sup>. (○) PTX; (●) PTX + 0.15 wt% Cu; (Δ) PTX + 66 ppm by vol SO<sub>2</sub> in inlet (1000 ppm in fuel); (▲) PTX + 0.15 wt% Cu + 66 ppm by vol SO<sub>2</sub> in inlet.

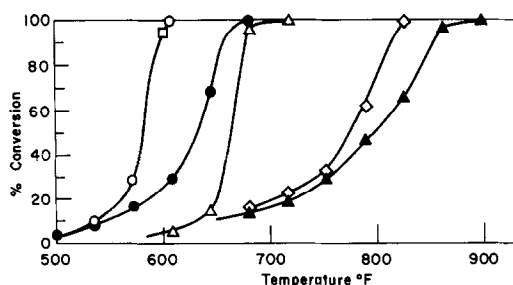


Fig. 6. CO Oxidation (1% CO, 1.8% O<sub>2</sub>, 3% H<sub>2</sub>O). All units pretreated 19 hr at 1500°F in air, space velocity 80,000 hr<sup>-1</sup>. (○) PTX; (●) PTX + 0.15 wt% Cu; (△) PTX + 66 ppm by vol SO<sub>2</sub> in inlet; (□) SO<sub>2</sub> off 2 hr; (▲) PTX + 0.15 wt% Cu + 66 ppm by vol SO<sub>2</sub> in inlet; (◇) SO<sub>2</sub> off 2 hr, run repeated without SO<sub>2</sub>.

steady activity. The structural surface changes that cause this behavior are not known.

When the sample that had been calcined at 1800°F in air (or at the other temperatures) was reduced in hydrogen at 1500°F, which could form the PtCu alloy, it exhibits much less activity for ethylene oxidation than the sample before reduction, and about the same activity as the PTX without copper (Fig. 4). Reoxidation can restore activity.

#### CO Oxidation

Figures 5–7 indicate that under these laboratory conditions the presence of copper decreases the activity for CO ox-

TABLE I

	PTX + 0.26 wt% Ag	PTX
Temp for 50% CO conversion (°F)	716	520
Temp for 50% C <sub>2</sub> H <sub>4</sub> conversion (°F)	430	514

idation of PTX units that have been calcined in air at 1500 and 1800°F and produced little change in the sample calcined at 1100°F. For CO oxidation the PTX units containing copper were more sensitive to SO<sub>2</sub> than those without copper. This is in line with the observation of others that CO oxidation over most base metal catalysts is more sensitive to sulfur than ethylene oxidation. Unlike C<sub>2</sub>H<sub>4</sub> oxidation, the Cu-PTX units when poisoned by S for CO oxidation showed only a small recovery when the SO<sub>2</sub> was removed at reaction temperature (~800°F) (Fig. 6).

As shown in Fig. 7, the activity of the Cu-PTX units, calcined in air, for CO oxidation was large and decreased with time to a steady value. This occurred to a lesser extent with the PTX unit containing no copper. As with ethylene oxidation, the surface rearrangements that cause this behavior are not known, although it may represent the transition from a higher to a

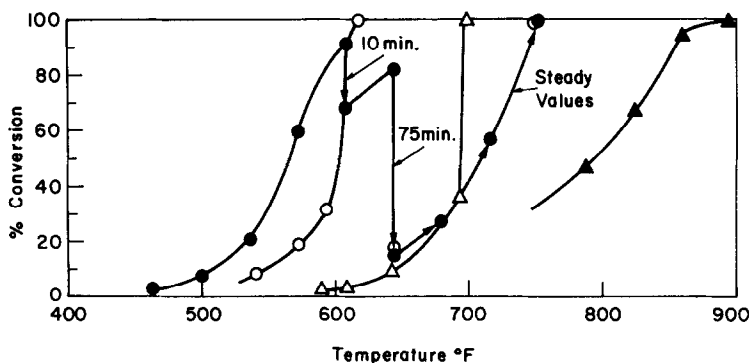


Fig. 7. CO Oxidation (1% CO, 1.8% O<sub>2</sub>, 3% H<sub>2</sub>O). All units pretreated 19 hr at 1800°F in air, space velocity 80,000 hr<sup>-1</sup>. (○) PTX; (●) PTX + 0.15 wt% Cu; (△) PTX + 66 ppm SO<sub>2</sub> in inlet (1000 ppm SO<sub>2</sub> in fuel); (▲) PTX + 0.15 wt% Cu + 66 ppm SO<sub>2</sub> in inlet.

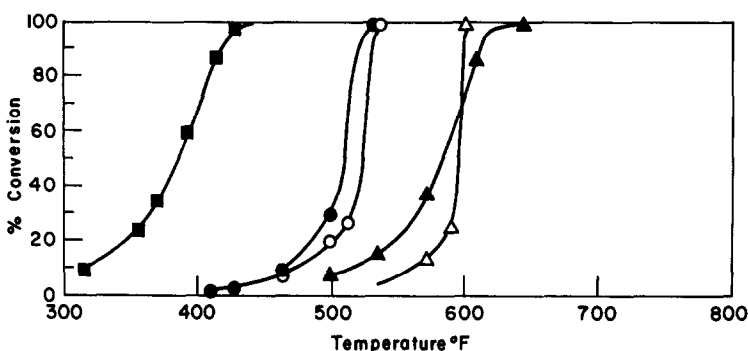


FIG. 8. CO Oxidation (1% CO, 1.8% O<sub>2</sub>, 3% H<sub>2</sub>O). All units pretreated 19 hr at 1100°F in air. (○) PTX; (●) PTX + 0.15 wt% Cu; (■) PTX + 0.15 wt% Cu reduced 16 hr, 1500°F; (▲) PTX + 0.15 wt% Cu reduced 16 hr, 1500°F + 66 ppm by vol SO<sub>2</sub> in inlet (1000 ppm in fuel); (△) PTX + 66 ppm by vol SO<sub>2</sub> in inlet.

lower oxidation state. Figures 8 and 9 show that the reduction of the Cu-PTX units greatly increased the CO oxidation activity of these units (as contrasted to the C<sub>2</sub>H<sub>4</sub> oxidation activity, which decreased).

The use of PTX + 0.26 wt% Ag after calcination for 19 hr at 1100°F in air has led to similar results as the Cu experiments, as shown by Table 1.

### CONCLUSION

Apparently the phase formed during the high temperature reduction is similar to the PTX without copper in activity for CO and C<sub>2</sub>H<sub>4</sub> oxidation. It is, however, more sensitive to S. The samples calcined in air are more active for C<sub>2</sub>H<sub>4</sub> oxidation and less active for CO oxidation than the untreated PTX. It is interesting to speculate

what the structure of the air-calcined material is. The copper is probably oxidized and may have formed a mixed oxide with PtO or with PtO and Al<sub>2</sub>O<sub>3</sub>. (Compounds such as PtCoO<sub>2</sub>, CuRhO<sub>2</sub>, PdCoO<sub>2</sub>, PdCrO<sub>2</sub>, CuCoO<sub>2</sub>, and CuAlO<sub>2</sub> are known (1); but no reference to PtCuO<sub>2</sub> has been found.)

The chemisorption characteristics of the mixed oxide toward CO, O<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> would be expected to be different from the metal and may well be the origin of the increased C<sub>2</sub>H<sub>4</sub> and decreased CO activity.

In actual automotive practice, with S present in the fuel one might expect, by extrapolation of the laboratory results, a copper-poisoned PTX to be less active for CO oxidation and more active for hydro-

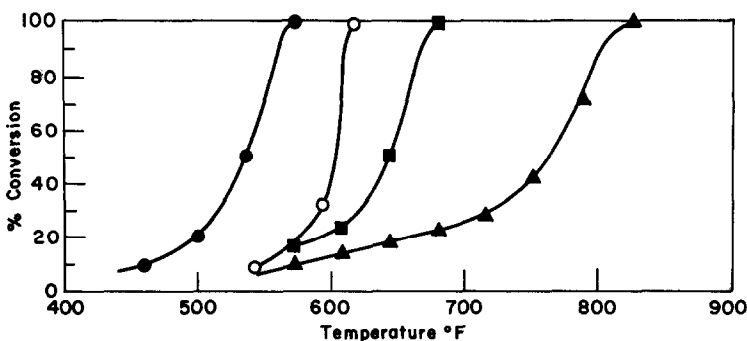


FIG. 9. CO Oxidation (1% CO, 1.8% O<sub>2</sub>, 3% H<sub>2</sub>O). All units pretreated 19 hr at 1800°F in air. (○) PTX; (●) PTX + 0.15 wt% Cu reduced 16 hr, 1100°F; (■) PTX + 0.15 wt% Cu reduced 17 hr, 1500°F; (▲) PTX + 0.15 wt% Cu used for CO oxidation in the presence of 66 ppm SO<sub>2</sub>, then reduced 4 hr, 1020°F.

carbon activity (if it follows  $C_2H_4$  activity) than the nonpoisoned PTX. Since the CO oxidation produces heat and a corresponding temperature rise which is useful during a cold start, one would expect the loss of CO activity in this period to be det-

rimental to the performance of the catalyst in the vehicle.

#### REFERENCES

1. Shannon, R. D., Rogers, D. B., and Prewitt, C. T., *Inorg. Chem.* **10**, 713 (1971).