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Activity and XPS Studies of Sulfur Poisoning Effect on Pt–Cu/γ-Al_2O_3 Oxidation Catalysts

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The effect of sulfur poisoning on the CO oxidation activity of alumina-supported bimetallic as well as monometallic Pt and Cu catalysts has been studied. The activity of the fresh catalysts increased with increasing Pt content. A strong decrease in the CO oxidation activity was observed after poisoning with SO_2. The bimetallic catalysts exhibited some resistance to sulfur poisoning. In fact, one bimetallic catalyst (8Cu 92Pt, total metal loading is 1 wt%) was more active than monometallic Pt after sulfur poisoning. The poisoned catalysts could be partially regenerated by heating in oxygen at 350°C followed by reduction in H_2 at the same temperature. Surface analysis of these catalysts by X-ray photoelectron spectroscopy (XPS) revealed slightly Cu-enriched surfaces. We found that the sulfur content on the surface was significantly lower on the bimetallic catalysts than on the monometallic counterparts. The S 2p photoelectron spectra of the reactor used poisoned catalysts, indicated predominance of adsorbed sulfate (SO_4^{2-} species). The monometallic Pt catalyst showed a lower valence sulfur species.

INTRODUCTION

The catalytic oxidation of carbon monoxide on transition metal catalysts, relevant to automobile exhaust emission control, has received much attention in recent years. The use of supported bimetallic catalysts, consisting of noble and base metals, is a possibility which merits further study since both components have good oxidation activity in monometallic form. A key factor in the evaluation of such bimetallic catalysts is their tolerance to sulfur poisoning.

Oudar (*1*), in an excellent recent review paper, has summarized the literature on sulfur adsorption on catalytic surfaces as well as the fundamental aspects of gas–metal–sulfur interactions. Shelef *et al.* (*2*) reviewed the literature about deactivation of automotive catalysts by poisons such as lead, phosphorus, and sulfur.

Sulfur poisoning of base metal oxides and noble metals during CO and hydrocarbon oxidation has been reported by several authors (*3–5*). A common finding is that SO_2 affects more the CO oxidation activity than the hydrocarbon oxidation activity. Farrauto and Wedding (*3*) suggested that SO_2 poisoning of metal oxide catalysts such as CuO occurred via sulfate formation which could not be easily regenerated. Yu Yao (*4*) observed that CuO and $CuCr_2O_4$ are more tolerant to sulfur poisoning than Co_3O_4 and that the extent of poisoning increased with decreasing temperature. Summers and Baron (*6*) found that, on a Pt catalysts, SO_2 decreased CO oxidation activity under net reducing conditions. However, small amounts of O_2 converted SO_2 to SO_3 which diminished the poisoning effect. Kummer (*5*) compared SO_2 poisoning of Cu-treated Pt/Al_2O_3 catalyst and monometallic Pt/Al_2O_3 catalysts and observed that the former suffered larger activity loss than the latter.

In addition to the effect of sulfur on the active agent, the support can also play a significant role on sulfur adsorption (*7*, *8*). Chang (*7*) studied the chemisorption of SO_2 on γ-Al_2O_3 and found that it was affected by the catalyst temperature and number of hydroxyl groups present. SO_2 chemisorbed

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more readily on a well dehydrated alumina and the uptake decreased as temperature increased.

Supported bimetallic catalysts have been extensively used in many catalytic processes because of improved activity and selectivity. The surface composition of bimetallic catalysts often differs from the bulk composition. Synergistic interactions between the two metals to improve sulfur tolerance have been reported in various catalysts: Pt–Ni catalyst in NO reduction by Katzer *et al.* (*9*), Ni–Ir methanation catalyst by Wise *et al.* (*10*), and Ni–Mo by Fowler and Bartholomew (*11*).

The kinetics and CO oxidation activity of a series of Pt–Cu/γ-Al_2O_3 bimetallic catalysts have been studied in a previous work (*12*). Here we address the question of SO_2 poisoning of these catalysts. CO activity measurements for fresh and poisoned catalysts are correlated with results obtained by X-ray photoelectron spectroscopy (XPS or ESCA) and chemisorption measurements.

EXPERIMENTAL METHODS

Catalysts. The platinum–copper bimetallic catalysts employed in this work were prepared by coimpregnation of γ-alumina (Harshaw-Chemical, 200 mesh powder, 192 m^2/g BET) with chloroplatinic acid and copper nitrate solution at the proper concentration to obtain the desired Pt/Cu ratio. Bimetallic catalysts containing 8, 25, 60, 100 wt% Cu of a *total* metal content (Cu + Pt) of 1% by weight were prepared. Table 1 summarizes the catalysts composition used, in weight and atomic percent, as well as the manufacturer's data on γ-alumina itself. The catalysts were dried in argon for 6 hr at 110°C and reduced in flowing hydrogen for 12 hr at 500°C.

TABLE 1

Catalyst Properties

γ-Alumina properties	
Powder size (Mesh)	200
BET area (m^2/g)	192
Total pore volume (cm^3/g)	1.079
Range of pore radii (Å)	60 ~7600
Powder density (g/cm^3)	1.22
Impurities (wt%)	<0.02
Catalysts Composition	
Weight %	Atomic % Cu
100 Cu	100
60Cu 40Pt	82.2
25Cu 75Pt	50.6
8Cu 92Pt	21.1
100Pt	0

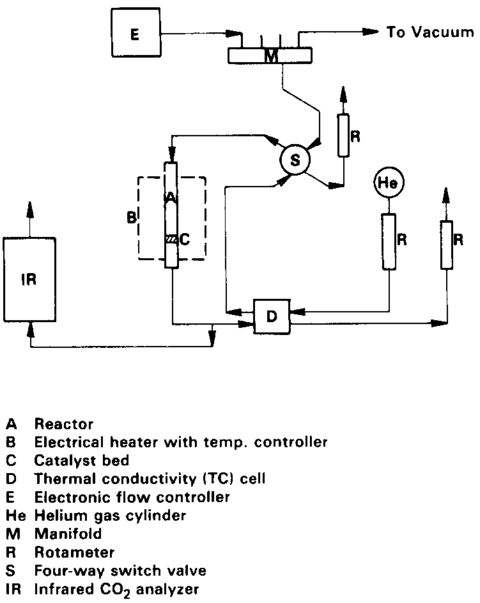

FIG. 1. Integrated reactor-adsorption apparatus.

Apparatus and experimental procedures. The experimental unit consists of an integrated reactor-chemisorption apparatus designed for kinetic studies and *in situ* measurement of SO_2 chemisorption by a breakthrough saturation technique. A schematic diagram of the equipment is shown in Fig. 1. It consists of a metering and mixing section for gases and a quartz tube flow reactor surrounded by an electrical heater with a temperature controller and a gas analysis section.

During SO_2 adsorption measurements, a step input of SO_2 diluted in ultrahigh purity helium (0.5%) was introduced into a He carrier gas stream by means of a four-way switching valve. SO_2 is adsorbed by the catalyst until saturation occurs, at which point it emerges (breakthrough) at the bed outlet where it is detected by a thermal conductivity cell (TC). Once breakthrough was completed, the feed is switched again to pure He. After purge of SO_2 from the system was completed, a second SO_2 step input is injected to account for line and reactor dispersion effects. The difference between the two breakthrough curves corresponded to SO_2 uptake. The adsorption experiments were conducted at room temperature; the SO_2–He stream flow rate was 60 cm^3/min.

Activity measurement were carried out by introducing a mixture of CO, 20% vol excess oxygen over CO, and He into the reactor containing 1 g of catalyst. An electronic flow controller (Linde FM-4530) was used to measure the carbon monoxide flow rate; the other gases were metered by fine valves through calibrated flow meters. The reaction product, CO_2, was analyzed continuously by an infrared analyzer (Beckman Model 865). Kinetic experiments, previously reported (*21*), were carried out by operating the reactor in a differential mode and varying the CO concentration from 0 to 2.5% by volume under isothermal conditions. The activity measurements reported here consisted of light-off temperature (LOT) experiments which were carried out at a constant 2% vol CO concentration while increasing the temperature from 70°C until total conversion was attained (up to 300°C). Due to the small size of the catalysts particles used, internal temperature gradients are not important (*21*). The catalyst bed temperature was measured by a thermocouple inserted in a thermowell imbedded in the catalyst bed. Total flow rate was kept constant during all experiments at 100 cm^3/min.

The catalysts were subjected to three different pretreatments. Catalysts were first used fresh after hydrogen reduction. Afterward the catalysts were poisoned with SO_2 until complete saturation was detected by the TC cell. SO_2 uptake measurements were calculated after the second step input of SO_2 was introduced. Activity measurements were carried out after SO_2 saturation, using a feed which contained 1500 ppm of SO_2 to offset any possible thermal desorption. Regeneration consisted of a calcination in oxygen at 350°C for 2 hr, to burn-off carbon residues and sulfur compounds, followed by reduction in flowing hydrogen for 3 hr. The calcination temperature was sufficiently low to avoid changes in crystallite sizes. Activity measurements of fresh and regenerated catalysts were carried out without SO_2 in the feed.

The XPS experiments were performed on a Hewlett–Packard 5950B spectrometer employing monochromatic Al$K\alpha$ X-rays ($h\nu$ = 1486.6 eV). The samples were analyzed as wafers (7 mm diameter, 1 mm thickness) mounted in gold-coated HP sample holders. The catalysts were kept under a dry N_2 atmosphere during sample preparation and insertion to prevent surface contamination. An electron flood gun was used to minimize sample charging. The photoelectron binding energies were referred against the C 1s line at 284.6 eV. Due to the low concentration of the active metals, up to 24 hr of analysis per sample was used. All XPS analysis reported in this paper refers to reactor used catalysts.

RESULTS

Activity and SO_2 Uptake

Conversion versus temperature curves (LOT) for five fresh catalysts of different Pt/Cu ratios, obtained at 2% CO concentration, are shown in Fig. 2. The fresh Pt catalyst is more active than the bimetallic catalysts and the monometallic Cu catalyst. The low temperature activity of the latter is slightly higher than the activity of the Pt–Cu catalysts; this trend reverses at higher temperatures ($T > 130$°C).

Each catalyst was poisoned in a flowing SO_2–He mixture following the saturation procedure previously described. Figure 3

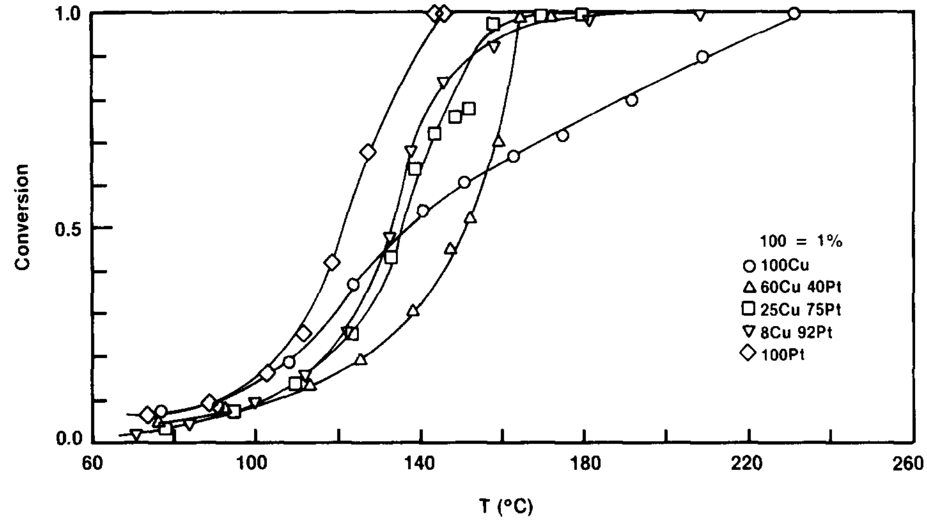

FIG. 2. LOT curves for five fresh catalysts (2% CO inlet).

shows the two breakthrough curves used to determine the SO_2 uptake. The lower curve is the response to the first injection, whereas the upper curve is the response to the second injection. The shaded area between these curves is the SO_2 uptake which is shown in Fig. 4 as function of bulk atomic % Cu. The results indicate that the 8Cu 92Pt bimetallic catalyst adsorbed less SO_2 than all other catalysts including Pt.

The LOT curves of the five poisoned catalysts are shown in Fig. 5. All catalysts suffered a significant activity loss, apparent from the temperature shift of about 70°C as compared with the data of Fig. 2. The monometallic Pt catalyst is no longer the most active catalyst but the 8Cu 92Pt catalyst exhibits now the lowest LOT except near complete conversion. The LOT curves of the other catalysts shift to higher temperatures as the Cu content increases.

The LOT curves of the regenerated catalysts, shown in Fig. 6, indicate that all catalysts recovered a significant fraction of their

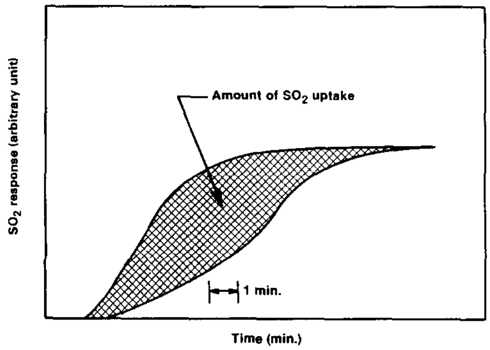

FIG. 3. SO_2 breakthrough saturation curves: lower boundary is first injection response and upper boundary is second injection response.

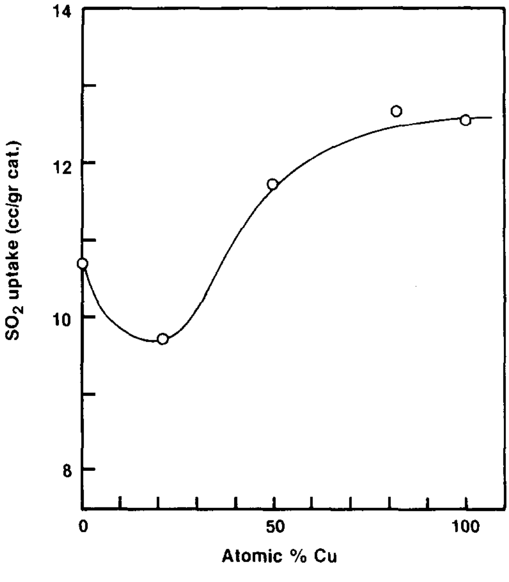

FIG. 4. SO_2 uptake results from breakthrough technique versus Cu bulk content.

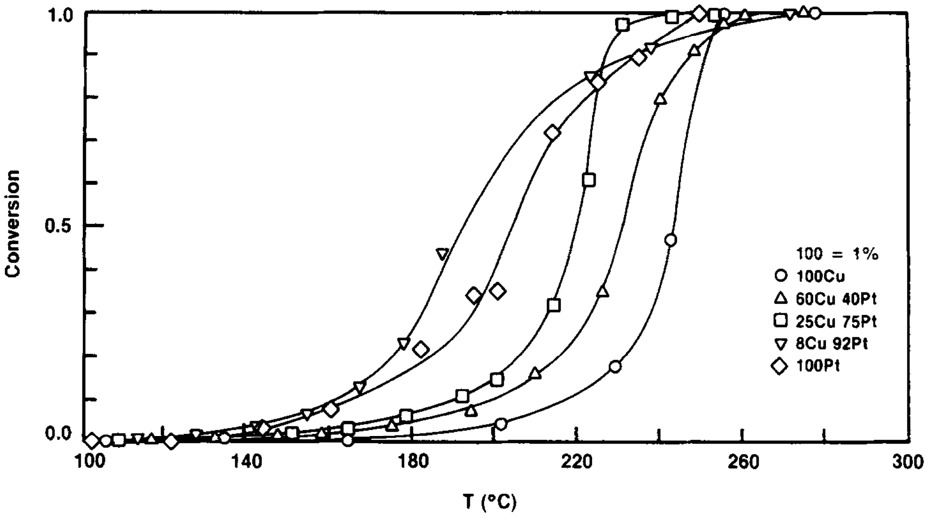

FIG. 5. LOT curves for five poisoned catalysts with 1500 ppm SO_2 in feed.

original activity. The monometallic Pt catalyst is only slightly less active than in fresh form, and monometallic Cu is the least active among the five catalysts. The LOT of the bimetallic catalysts fall between the monometallic components in order of increasing Cu content. The fact that the regenerated catalysts do not recover their original activity indicates that not all the S is removed on regeneration.

X-Ray Photoelectron Spectroscopy

The photoelectron peak areas were corrected for instrumental parameters, photoionization cross-sections (*13*), and for differences in electron mean free path (*14*). The atom fraction of Cu in the surface region of an assumed homogeneous Pt–Cu alloy $I_{Cu}/(I_{Cu} + I_{Pt})$ is plotted in Fig. 7 versus the atomic Cu bulk content of the catalyst for the fresh and poisoned samples. The results indicate that the Cu surface concentration is higher than the bulk concentration. The Cu enrichment is larger in the poisoned catalysts than in the fresh catalysts except for the 25Cu 75Pt catalyst. A

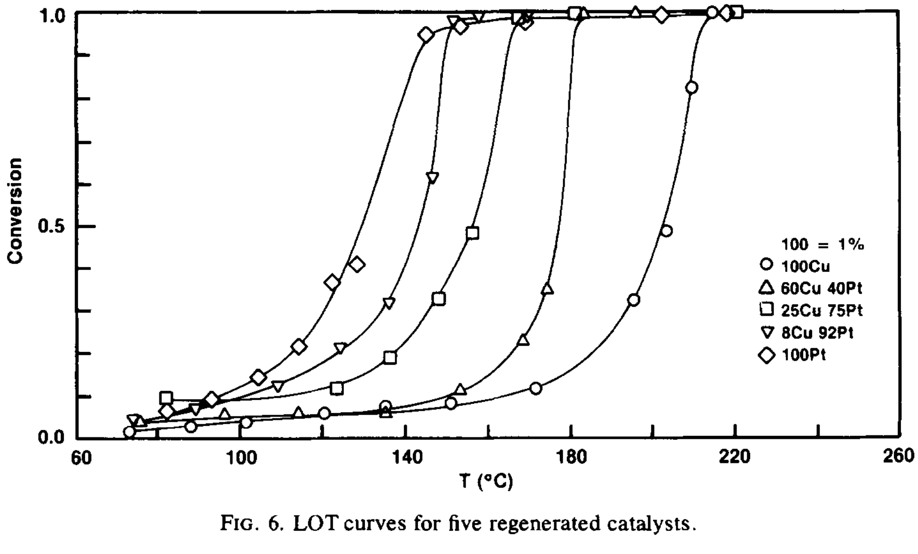

FIG. 6. LOT curves for five regenerated catalysts.

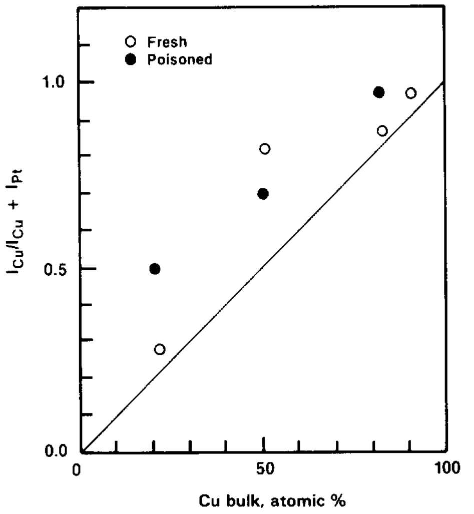

FIG. 7. Atom fraction of Cu on Pt–Cu cluster surface as obtained from XPS data versus Cu content in bulk for poisoned and fresh catalysts.

detailed discussion about the nature of the bimetallic entities formed in these catalysts has been presented previously (*21*).

Figure 8 shows XPS sulfur data in terms of average sulfur concentration versus Cu bulk atomic percent. The sulfur atomic percent shown in Fig. 8 is calculated from the corrected XPS signal of C, O, Al, Cu, and Pt. These results indicate that the surface sulfur content on the bimetallic catalysts is lower than on both monometallic catalysts. The S 2p photoelectron lines of four catalysts are shown in Fig. 9. There is a shift in the binding energy from 168.8 ± 0.2 eV for the Cu and Pt–Cu catalysts to 167.0 ± 0.2 eV for monometallic Pt. This latter sulfur species also appears as a shoulder on the low binding energy side of the 8Cu 92Pt catalyst.

DISCUSSION

The results obtained show that Pt–Cu bimetallic catalysts are poisoned by SO_2 as it has been documented for Pt/γ-Al_2O_3 (*7*), copper oxide (*3*, *4*), and copper chromite (*4*) catalysts. However, the extent of poisoning and regeneration observed on the supported bimetallic catalysts differs with the findings reported for the monometallic counterparts.

The activity results show that one bimetallic catalyst, the 8Cu 92Pt catalyst, exhibits higher activity than monometallic Pt. Another significant result is that activity recovery can be attained in all catalysts. The extent of activity recovery increases with Pt content; furthermore, monometallic Cu also shows partial activity recovery.

XPS measurements show three characteristic trends: (a) Cu average surface composition is higher than the bulk composition in both poisoned and unpoisoned catalysts, (b) average sulfur concentration on the bimetallic catalysts is lower than on monometallic Pt and Cu, and (c) the S 2p binding energy on the poisoned Cu catalyst (168.8 ± 0.2 eV) is characteristic of sulfate SO_4^{2-}) adsorbed species, whereas on poisoned Pt, the binding energy is 167.9 ± 0.2 eV which is characteristic of SO_2 and SO_3^{2-} adsorbed species (*18–20*). Bimetallic catalysts show predominantly SO_4^{2-} species. The 8Cu 92Pt catalyst shows additional intensity in the 167 eV region.

XPS results indicate clearly that the bimetallic catalysts have Cu-enriched surfaces and that adsorbed sulfur has SO_4^{2-} characteristics typical of SO_2 adsorption on

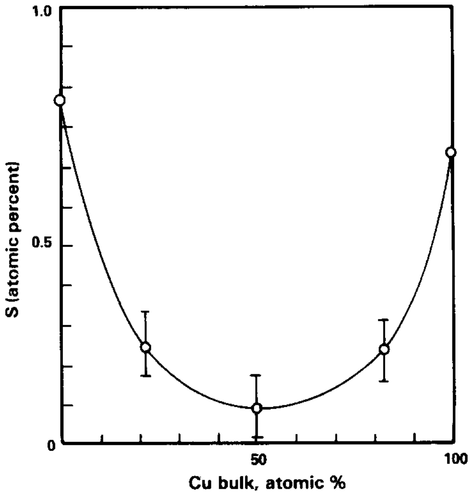

FIG. 8. Average sulfur surface content as obtained from XPS data versus Cu bulk content.

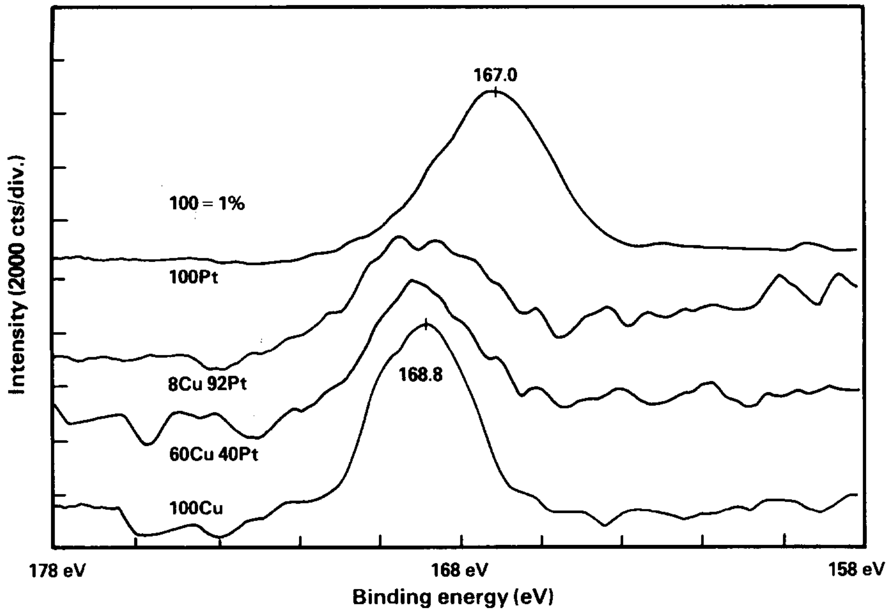

FIG. 9. XPS S 2p photoelectron lines for four catalysts.

monometallic Cu. The SO_4^{2-} species are apparently formed by oxidation during reaction since all the XPS analysis reported here refer to reactor used catalysts. Farrauto and Wedding (*3*) suggested that SO_2 poisoning on Cu oxide and copper chromite catalysts occurred via sulfate formation which showed little regenerability. In our case, however, the bimetallic catalysts exhibit regenerability and lower average sulfur signal than monometallic Pt and Cu. Thus, even though the surface is Cu rich, it exhibits some of the Pt activity characteristics. These results lead us to speculate that interaction between Pt and Cu not only weakens the bonding strength of the adsorbed sulfur decreasing its surface concentration but also increases catalyst regenerability. Further evidence for Pt–Cu interaction comes from the observation that sulfur poisoning of the bimetallic catalysts is less severe that it would be in mechanical mixtures of the monometallic components. Total SO_2 uptake is lowest on the 8Cu 92Pt catalyst which, therefore, exhibits the highest activity after sulfur poisoning. Since most of the SO_2 uptake occurs in the γ-Al_2O_3 matrix (*7, 17*) no good agreement could be observed between SO_2 adsorption data (Fig. 4) and surface sulfur determination by XPS (Fig. 8). However, we speculate that, since the XPS results were obtained in reactor used catalysts, these results reflect S associated with the metal components instead of the support. No SO_4^{2-} was detected on the Al_2O_3 support.

Kummer (*5*) compared effects of SO_2 deactivation during CO oxidation between Cu impregnated Pt/Al_2O_3 (0.15% Cu/0.35% Pt) and monometallic Pt catalyst and observed that the former was less active than the latter. However, reduction of the Cu-treated catalyst at high temperature showed that, in the presence of SO_2, its activity was comparable with that of monometallic Pt. It was also suggested by this author that formation of intermetallic Pt–Cu compounds could be responsible for this behavior. Several authors (*9–11*) have also reported that bimetallic interaction has enhanced the catalyst ability to resist sulfur poisoning.

Bonzel and Ku (*15*) found that on Pt (110), CO_2 production is virtually stopped when sulfur surface coverage reaches 0.28

even though CO can still be absorbed. It was suggested that on the poisoned catalysts, O_2 dissociation was inhibited. Chang (*16*) used ir to study the nature of sulfur poisoning on $Pt/\gamma\text{-}Al_2O_3$, and found that SO_2 competes with CO for Pt sites. SO_2 chemisorption on Pt, however, is relatively weak and SO_2 is replaced by CO at $T >$ 160°C. At 300°C, SO_2 is reduced by CO to form CO_2 and sulfur. In our catalysts it appears that competitive interaction of CO and O_2 with SO_4^{2-} adsorbed species is more significant than in the case of monometallic Cu or CuO (*3*, *4*).

In summary, we observe a sulfur poisoning resistance of supported Pt–Cu bimetallic catalysts. In fact, one bimetallic catalyst (8Cu 92Pt) shows less deactivation than monometallic Pt. XPS analysis shows that bimetallic surfaces are Cu enriched. The S 2p photoelectron spectra indicate predominance of absorbed SO_4^{2-} species after SO_2 poisoning and reaction. It appears that interaction of Pt–Cu modifies the bonding strength of adsorbed S species which decreases the extent of deactivation on the bimetallic catalysts. The sulfur poisoning is reversible making the poisoned catalysts regenerable.

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