The Effects of SO_2 on the Oxidation of Hydrocarbons and Carbon Monoxide over Pt/γ-Al$_2$O$_3$ Catalysts

Noble metals have been used since 1975 in the automotive exhaust catalysts to control hydrocarbon and carbon monoxide emissions. Small amounts of SO_2 (10 to 60 ppm) present in the exhaust gas are known to poison noble metal catalysts even though the poisoning is considerably less severe than base metal catalyst poisoning (*1–6*). Although the mechanism for the poisoning of noble metal catalysts is not known (*2*), it has been suggested that the severe poisoning of the base metal catalysts is due to the formation of surface sulfate on the base metal oxide, which decomposes in the temperature range of 500–700°C (*3, 4*). Therefore, a catalyst operating temperature greater than 500°C can alleviate, to some extent, SO_2 poisoning. This work is aimed at understanding the effects of SO_2 on the oxidation of saturated and unsaturated hydrocarbons and of carbon monoxide over Pt/γ-Al$_2$O$_3$ catalysts. Propane (C$_3$H$_8$) and propylene (C$_3$H$_6$) were selected as representative saturated an unsaturated hydrocarbons, respectively.

EXPERIMENTAL

The granular catalysts were made by agglomerating Dispal-M-γ-Al$_2$O$_3$ (Conoco Chemical) powder by wetting, drying at 300°C, crushing, and sieving. The 0.5- to 1.0-mm-diameter fraction was impregnated with aqueous H$_2$PtCl$_6$ solution of the desired concentration, dried, and calcined in air at 500°C. The surface areas and the compositions of the catalysts are shown in Table 1.

The apparatus for the activity measurements is described in Ref. (*7*). All flow reactor experiments were run at 60,000 hr^{-1}

space velocity. The reactant concentration was typically 0.1–0.15% hydrocarbons (as C), 0.5% carbon monoxide, and 2% oxygen. A Beckman infrared analyzer Model 865 was used for total hydrocarbon and carbon monoxide analyses, respectively.

Infrared spectra were obtained using a dual-purpose all-Pyrex cell equipped with KBr windows (*8*). The sample wafers were prepared by pressing about 150 mg of the catalyst in a 2.96-cm metal die and cutting to a size of 6 × 20 mm. By tilting the cell, the wafer could be moved out of its position in the optical path to the opposite end for *in-situ*, high-temperature treatment in static or flowing gases. The spectra were recorded in a double-beam mode with a Perkin–Elmer 180 spectrometer under normal setting.

During the oxidation of C$_3$H$_8$ and C$_3$H$_6$ mixtures in the presence of SO_2, samples of the reaction gas mixtures were collected at various time intervals and analyzed by a Fourier transform infrared (FTIR) spectrometer which consists of a scanning Michelson interferometer linked to a PDP 11/40 on-line computer (*9*). In that way the percentage conversion of C$_3$H$_8$ and C$_3$H$_6$ could be separated.

RESULTS AND DISCUSSION

1. Activity Measurements

Percentage conversion as a function of temperature for C$_3$H$_8$ oxidation over three Pt/γ-Al$_2$O$_3$ catalysts of different Pt concentrations is shown in Fig. 1. Two different feed gases are used: one is SO_2-free and the other contains 20 ppm SO_2. For the SO_2-free feed gas, the results indicate that the catalyst activity increases with Pt concen-

TABLE 1

Sample	BET area (m²/g)	Pt loading	
		wt%	μmol/m² (BET)
1	162	0.03	0.01
2	156	0.60	0.20
3	150	4.91	1.68
4	137	7.10	2.62

FIG. 1. Percentage conversion as a function of temperature for C_3H_8 oxidation over three Pt/γ-Al$_2$O$_3$ catalysts of different Pt concentrations.

tration. In the presence of 20 ppm SO_2 in the feed gas, the activity of all three catalysts is enhanced to a maximum activity regardless of the Pt concentration. Similarily, percentage conversion as a function of temperature for C_3H_6, CO, and C_3H_8 oxidation over a 0.03 wt% Pt catalyst is shown in Fig. 2. Again, two different feed gases are used. For the SO_2-free feed gas the oxidation activity is in the order: CO > C_3H_6 $\gg$ C_3H_8. In the presence of 20 ppm SO_2 in the feed gas, C_3H_8 oxidation is strongly promoted, while both C_3H_6 and CO oxidations are moderately inhibited. Under this condition, the oxidation activity is in the order: CO > C_3H_8 > C_3H_6.

In separate experiments, a 1 : 1 mixture of C_3H_6 and C_3H_8 is oxidized in the absence and presence of 20 ppm SO_2. Percentage conversion as a function of temperature is
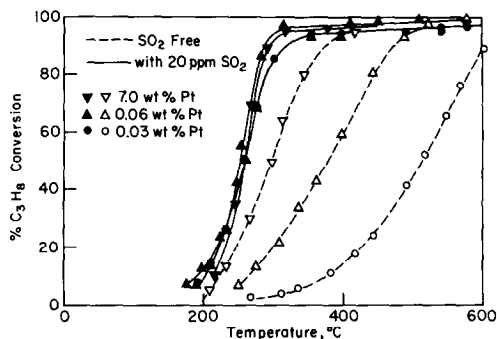
plotted in Figs. 3 and 4. In the absence of SO_2 in the feed gas, as expected, C_3H_6 is far more reactive than C_3H_8 and is completely oxidized as the temperature reaches 270–280°C, while oxidation for C_3H_8 starts at about 270°C. This indicates strong inhibition of C_3H_8 oxidation by C_3H_6. In the presence of SO_2, such inhibition is not shown; the two oxidations occur simultaneously with a higher activity for C_3H_6 oxidation (Fig. 4). Oxidation of a mixture of 0.45% CO and 0.29% C_3H_8 is studied also in the absence and presence of 20 ppm SO_2. Percentage conversion as a function of temperature is plotted in Fig. 5. In the

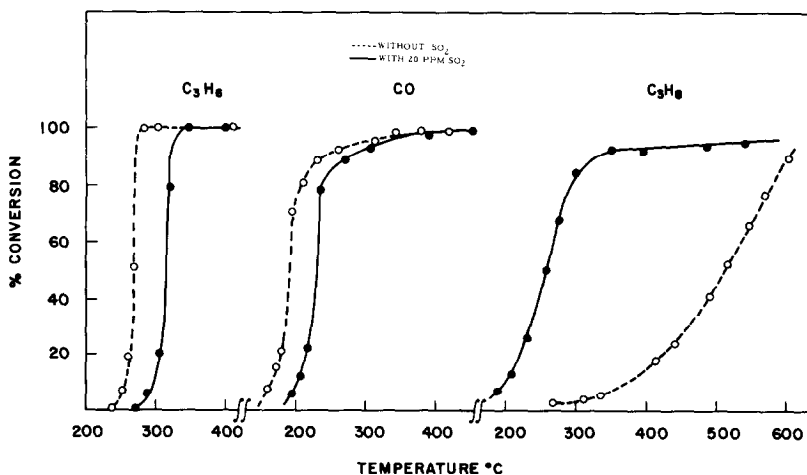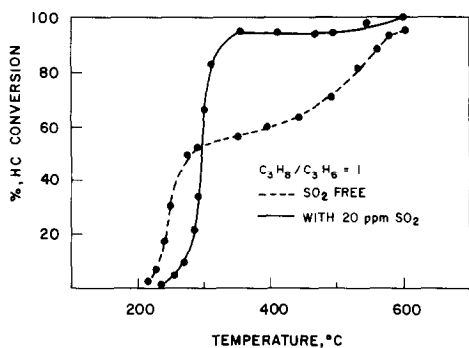FIG. 2. Percentage conversion as a function of temperature for C_3H_6, CO, and C_3H_8 oxidation over a 0.03 wt% Pt catalyst.

FIG. 3. Percentage conversion as a function of temperature for the oxidation of a 1 : 1 mixture of C_3H_6 and C_3H_8.
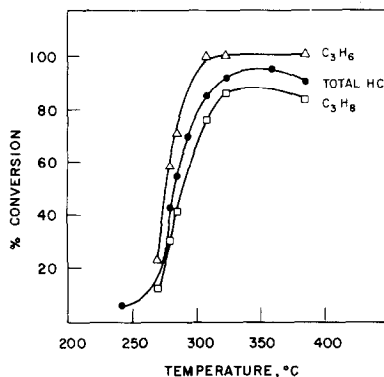

FIG. 4. Percentage conversion as a function of temperature for the oxidation of a 1 : 1 mixture of C_3H_6 and C_3H_8 with 20 ppm SO_2. Data analyzed by FTIR.

absence of SO_2, CO is more reactive than C_3H_8. At about 280°C, CO oxidation is nearly complete and C_3H_8 conversion rapidly increases. In the presence of 20 ppm SO_2 in the feed gas, the CO oxidation activity decreases, while the C_3H_8 oxidation activity increases significantly, and the temperatures for 50% conversion of these two reactants become very close (Table 2).

2. *Infrared Study of Surface Sulfate Formation on γ-Al_2O_3 and on Pt/γ-Al_2O_3*

The formation of surface sulfate groups on γ-Al_2O_3 by SO_2 chemisorption followed by oxidation has been reported by Chang (10) and is restudied herein to understand

the effect of SO_2 on the oxidation activity of γ-Al_2O_3-supported Pt catalyst. Infrared spectra (Fig. 6) of SO_2 adsorbed on γ-Al_2O_3 were taken after a sequence of treatments of the sample: (A) clean γ-Al_2O_3 sample, (B) after SO_2 adsorption at 25°C, (C) after degassing at 25°C, (D) after heating in air at 500°C, and (E) after degassing at 500°C. Upon adsorption of SO_2 on γ-Al_2O_3 (Fig. 6B), absorption bands at 1630, 1338–1372, 1148, and 1065 cm^{-1} appear. The band at 1630 cm^{-1} is due to the bending vibration of adsorbed water molecules (10) and can be removed by degassing at 500°C. The bands at 1338–1372 and 1148 cm^{-1}, which can be removed by degassing at 25°C, are assigned to the reversibly adsorbed SO_2 molecules. The band at 1065 cm^{-1} is attributed to the surface sulfite,

TABLE 2

Temperature for 50% Conversion, $T_{50\%}$°C over 0.03 wt% Pt/γ-Al_2O_3 Catalyst

Reactions	$T_{50\%}$°C	
	Without SO_2	With 20 ppm SO_2
C_3H_6 + O_2	265	310
CO + O_2	190	230
C_3H_8 + O_2	510	250

Note. Feed gas concentrations: C_3H_6 = 1500 ppm as C_1; CO = 0.5%; C_3H_8 = 1500 ppm as C_1; O_2 = 2.3%; SO_2 = 0 or 20 ppm; N_2 = balance. Space velocity: 60,000 hr^{-1}.
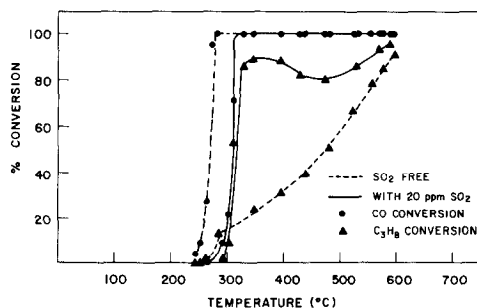

FIG. 5. Percentage conversion as a function of temperature for the oxidation of 0.45 wt% CO and 0.029% C_3H_8 mixture.
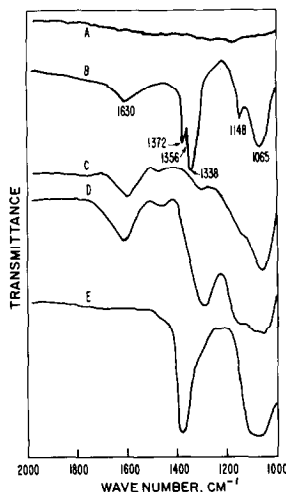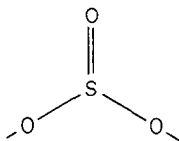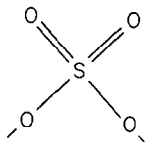
FIG. 6. Infrared spectra of (A) γ-Al₂O₃; (B) after SO₂ adsorption; (C) after degassing at 25°C; (D) after heating in air at 500°C; (E) after degassing at 500°C.

formed after chemisorption of SO₂ on γ-Al₂O₃. After heating in air at 500°C, it is oxidized to surface sulfate,

which gives two bands at 1290 and 1080 cm⁻¹ (Fig. 6D). After degassing at 500°C, these bands shift to 1380 and 1130 cm⁻¹ (Fig. 6E). According to Bellamy and Williams (11) the bands at 1380 and 1130 cm⁻¹ are the antisymmetric (ν_3) and symmetric (ν_1) stretching vibrations, respectively, of the surface sulfate groups. The shift in frequency is due to the presence of water molecules which can be either adsorbed on the surface sulfate groups or on γ-Al₂O₃ and bonded to the sulfate through hydrogen bonding (10). The band at 1130 cm⁻¹ is rather broad and indicates some sulfite remains. These sulfate and sulfite groups are stable and can be removed only after heat-

ing under vacuum at about 800°C or in flowing H₂ at about 700°C.

The formation of the surface sulfate groups appears the same on Pt/γ-Al₂O₃ as on γ-Al₂O₃. The only difference is that the presence of Pt lowers the oxidation temperature from 500°C required for γ-Al₂O₃ to 200°C for Pt/γ-Al₂O₃ and makes the oxidation more complete (sharper band at 1130 cm⁻¹). Apparently the Pt catalyzes the oxidation of sulfite to sulfate on γ-Al₂O₃ at a lower temperature.

3. C_3H_8, C_3H_6, and CO Chemisorption on γ-Al_2O_3 and Pt/γ-Al_2O_3, with and without the Surface Sulfate Groups

Infrared spectra taken after adsoprtion of C₃H₈, C₃H₆, and CO on γ-Al₂O₃ and subsequently degassed at 25°C show no evidence of chemisorption of these molecules. On γ-Al₂O₃ with surface sulfates (after SO₂ chemisorption and oxidation at 500°C) only strong chemisorption of C₃H₆ is found (Fig. 7A). The bands at 2980, 2940, and 2880 cm⁻¹ are the stretching vibration bands of chemisorbed C₃H₆.

Infrared spectra taken after adsorption of C₃H₈, C₃H₆, and CO on Pt/γ-Al₂O₃ and subsequently degassed at 25°C show no chemisorption of C₃H₈ but strong chemisorption of C₃H₆ and CO (Figs. 7B and C). The bands at 2960, 2920, and 2880 cm⁻¹ are
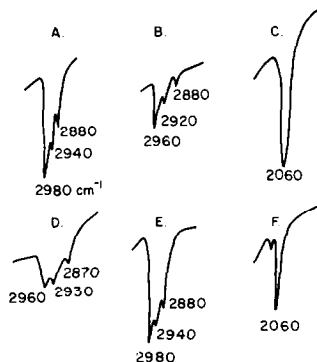

FIG. 7. Infrared spectra of (A) C₃H₆ chemisorbed on γ-Al₂O₃ with surface sulfates; (B) C₃H₆ and (C) CO chemisorbed on Pt/γ-Al₂O₃; and (D) C₃H₈, (E) C₃H₆, and (F) CO chemisorbed on Pt/γ-Al₂O₃ with surface sulfates.

the stretching vibration bands of chemisorbed C_3H_6 and the band at 2060 cm^{-1} is that of chemisorbed CO. On Pt/γ-Al$_2$O$_3$ with surface sulfate groups (after SO$_2$ chemisorption and oxidation at 200°C), ir spectra taken after the adsorption of C_3H_8, C_3H_6, and CO show the chemisorption of all three reactants (Figs. 7D, E, and F). Compared to the ir spectra of chemisorbed C_3H_8, C_3H_6, and CO on Pt/γ-Al$_2$O$_3$ without the surface sulfates, it indicates that both C_3H_8 and C_3H_6 chemisorptions are increased but the CO chemisorption is significantly decreased in the presence of surface surfates on γ-Al$_2$O$_3$.

4. Effect of Surface Sulfates on Oxidation of C_3H_8, C_3H_6, and CO

In the absence of SO$_2$ in the feed gas, the $T_{50\%}$ (Table 2) for C_3H_8 oxidation is much higher than that for C_3H_6 and CO oxidation, indicating considerably higher activity of Pt/γ-Al$_2$O$_3$ for CO and C_3H_6 than for C_3H_8. We attribute this difference to the stronger chemisorption of CO and C_3H_6, compared to that of C_3H_8, on Pt. The ir data, which show strong C_3H_6 and CO chemisorption on Pt, support this interpretation.

The presence of SO$_2$ in the feed gas changes the oxidation activity of Pt/γ-Al$_2$O$_3$ for all three reactants. The oxidation activity for C_3H_8 sharply increases while that for C_3H_6 and CO moderately decreases. This change of activity is attributed to the effect of surface sulfates, formed by SO$_2$ adsorption and followed by oxidation at 200°C, on the chemisorption capacities of Pt for each reactant. As shown in the ir study, the surface sulfates promote the dissociative adsorption of C_3H_8 on Pt, which results in higher activity for C_3H_8 oxidation. It also shows that the surface sulfates inhibit the associative chemisorption of CO on Pt, which results in lower activity for CO oxidation. The reason for the decrease in oxidation activity for C_3H_6 when surface sulfates are added to Pt/γ-Al$_2$O$_3$ is uncertain at present. Infrared studies show that C_3H_6 chemisorption on

Pt/γ-Al$_2$O$_3$ is increased by surface sulfates on γ-Al$_2$O$_3$, but this increase occurs mainly on the γ-Al$_2$O$_3$. On the other hand, opposing this effect is an expected decrease in adsorption of C_3H_6 on Pt because of an increased repulsive force from the surface sulfates and from the increase in C_3H_6 adsorbed on the γ-Al$_2$O$_3$. If the repulsive effect is dominant, then the lower activity for C_3H_6 oxidation over Pt/γ-Al$_2$O$_3$ in the presence of SO$_2$ can be attributed to the decrease in the associative C_3H_6 chemisorption on Pt in the presence of surface sulfates on the γ-Al$_2$O$_3$.

CONCLUSION

The results obtained from a flow reactor indicate that SO$_2$ in the feed gas enhances propane oxidation but suppresses both propylene and carbon monoxide oxidations over a Pt/γ-Al$_2$O$_3$ catalyst. These results are interpreted on the basis of the infrared data, which show the formation of the surface sulfates on γ-Al$_2$O$_3$ after the SO$_2$ adsorption and oxidation, and the effects of the surface sulfates on the chemisorption properties of a Pt/γ-Al$_2$O$_3$ catalyst. It is suggested that the surface sulfates on γ-Al$_2$O$_3$ enhance C_3H_8 oxidation by increasing the dissociative C_3H_8 adsorption on Pt and suppress both CO and C_3H_6 oxidations by decreasing the associative CO and C_3H_6 adsorptions on Pt.

REFERENCES

1. Shelef, M., Otto, K., and Otto, N. C., in "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 27, p. 311. Academic Press, New York/London, 1978.
2. Summers, T. C., and Baron, K., *J. Catal.* 57, 380 (1979).
3. Yao, Y. F. Yu, *J. Catal.* 36, 266 (1975); 39, 104 (1975).
4. Fishel, N. A., Lee, R. K., and Nilhelm, F. C., *Environ. Sci. Technol.* 8, 260 (1974).

5. Callagher, P. K., Johnson, D. W., Jr., Vogel, E. M., and Schrey, F., *Mater. Res. Bull.* **10**, 623 (1975).

6. Kummer, J. T., *J. Catal.* **38**, 166 (1975).

7. Gandhi, H. S., Piken, A. G., Shelef, M., and Delosh, R. G., *in* "SAE Transactions," Section 2, Vol. 85, paper 760201 (1976).

8. Yao, H. C., and Rothschild, W. G., *J. Chem. Phys.* **68**, 4774 (1978).

9. Niki, H., Maker, P. D., Breitenbach, L. P., and Savage, C. M., *Chem. Phys. Lett.* **57**, 596 (1978).

10. Chang, C. C., *J. Catal.* **53**, 374 (1978).

11. Bellamy, L. J., and Williams, R. L., *J. Chem. Soc.*, 863 (1975).

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