JOURNAL OF CATALYSIS **105**, 258–262 (1987)

Formaldehyde Oxidation on Silica-Supported Platinum: Spectroscopic Evidence for Adsorbed Carbon Monoxide Intermediate

I. INTRODUCTION

The objective of this study was to gain further understanding of the surface reaction mechanism of formaldehyde (H_2CO) oxidation on platinum. A previous, related study by McCabe and McCready (MM) on Pt wires (*1*) provided kinetic evidence for an H_2CO oxidation mechanism involving dissociation of the adsorbed H_2CO to adsorbed carbon monoxide [CO(a)] and adsorbed hydrogen atoms [H(a)] followed by reaction with atomic oxygen to produce CO_2(g) and H_2O(g). The kinetic arguments were based principally on similarities observed between the kinetics of CO oxidation and H_2CO oxidation on the same Pt wires, thereby suggesting that the common aspect of a CO(a) intermediate in both reactions produces the kinetic similarities.

Although detailed kinetics were examined in the previous study, no corroborating spectroscopic experiments could be performed on the low-surface-area Pt wires. Thus, the present study was done on silica-supported Pt catalysts in a cell where adsorbed and gaseous species could be monitored by transmission infrared spectroscopy. Quantitative kinetic measurements could not be made in the infrared cell. Nevertheless, we demonstrate that the qualitative aspects of the kinetics of H_2CO oxidation on silica-supported Pt are identical to those on Pt wire. More importantly, this study provides direct spectroscopic observations of a CO(a) intermediate in H_2CO oxidation on Pt/SiO_2, thus supporting the dissociative reaction mechanism and demonstrating the important role of the strongly adsorbed CO intermediate in controlling the oxidation kinetics.

II. METHODS

The infrared spectra were obtained with a Digilab FTS-15/90 FTIR spectrometer. The stainless-steel cell that was used had a volume of about 80 cm^3 and was not well-mixed (*2*). The temperature-programmed desorption (TPD) experimental apparatus is discussed elsewhere (*3*).

The 0.7 wt% Pt/SiO_2 catalyst was prepared by ion exchange of $Pt(NH_3)_4Cl_2 \cdot H_2O$ with Davison 923 silica suspended in an excess of aqueous ammonium hydroxide. The synthesis followed closely the method of Uchijima *et al.* (*4*). The catalyst was then washed with distilled water, dried overnight at 373 K, calcined for 1 h at 393 K in air, and reduced at 573 K for 2 h in flowing 5% H_2/N_2. Chemisorption of H_2 at 308 K indicated a dispersion near 100% assuming a H : Pt stoichiometry of 1.

Gas phase H_2CO was generated by the decomposition of paraformaldehyde that was maintained at 353 K. Helium was the carrier gas and the H_2CO/He mixture was cooled to 195 K in a dry ice/acetone bath prior to entering the IR cell. The partial pressure of the H_2CO was estimated to be 27 Torr, assuming a saturated concentration of H_2CO in the He stream at 195 K.

The infrared experiments consisted of the following. After the catalyst was reduced in the cell at 633 K for 2 h under flowing H_2 at 1 atm, the cell was cooled to either 423 or 448 K in flowing H_2, evacuated, and filled with He. The H_2CO/He flow rate was started and maintained at 30–31

0021-9517/87 $3.00

cm^3/min over the catalyst at 1 atm. Spectra consisted of 100 scans (75 s, total duration) taken every 5 min up to 20 min at a resolution of 2 cm^{-1}. Oxygen was then mixed into the H_2CO/He stream at increasing O_2/He ratios while keeping the total O_2/H_2CO/He flow rate constant at 31 cm^3/min. Similar experiments were conducted over 100% Davison silica at 423 and 448 K.

In the TPD experiment, 0.204 g of Pt/SiO_2 was reduced at 573 K for 1 h in flowing H_2 at 1 atm, cooled to 301 K under flowing He, and subsequently ramped at 1.0 K/s to 673 K in a 30 cm^3/min H_2CO/He stream. Oxygen at 8 cm^3/min was added to the H_2CO/He stream while the catalyst was held at 673 K.

III. RESULTS

1. Silica at 423 and 448 K

The infrared spectra of silica following exposure to H_2CO/He were identical at 423 and 448 K, with absorbance peaks at 3000 to 2700, 1775, 1745, 1725, and 1502 cm^{-1}. No additional peaks were observed at an equivalence ratio of 0.10. The equivalence ratio, ϕ, is defined as the ratio of the stoichiometric O_2/H_2CO mole ratio to the feed O_2/H_2CO mole ratio. The ratio is based on the estimated partial pressure of 27 Torr for H_2CO in the He stream.

2. 0.7 wt% Pt/SiO_2 at 423 and 448 K

Figure 1a shows a progression of spectra at 448 K obtained after exposing the Pt/SiO_2 catalyst to O_2/H_2CO/He feeds containing constant H_2CO concentration but varying O_2 concentrations. The assignments of all the peaks are given in Table 1. Spectrum A was taken with only H_2CO/He flowing through the IR cell and shows an intense band at 2057 cm^{-1} which was not present in the silica spectra. Spectrum B shows that at a ϕ of 0.20 a doublet appeared in the region 2380 to 2300 cm^{-1} and a broad absorbance appeared at 1640 to 1600 cm^{-1}. At higher O_2 concentrations (lower ϕ), the

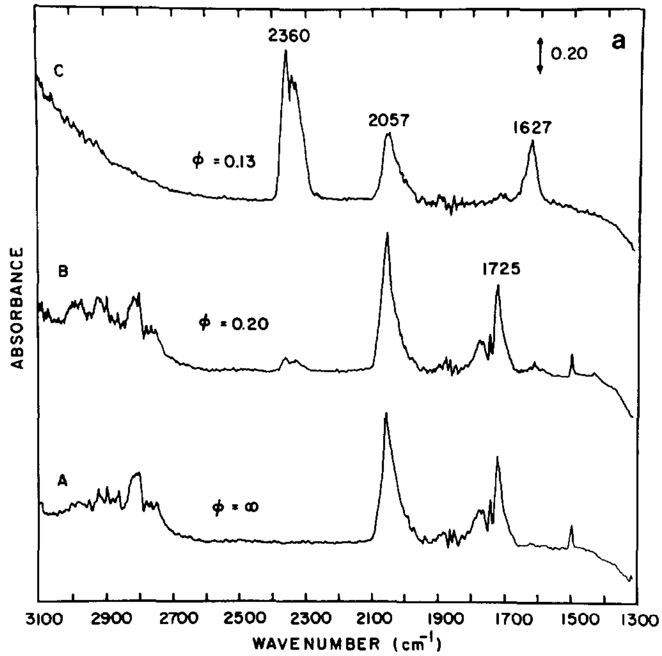

FIG. 1a. Infrared spectra of gas phase and adsorbed species for 0.7 wt% Pt/SiO_2 at 448 K. Spectrum A, after 11 min of flowing H_2CO/He at ϕ = ∞; B, after 10 min of flowing O_2/H_2CO/He at ϕ = 0.20; C, after 10 min of flowing O_2/H_2CO/He at ϕ = 0.13.

TABLE 1

Peak Assignments for Gas Phase and Adsorbed Species for 0.7 wt% Pt/SiO_2 at 423 and 448 K

Molecule	Band (cm^{-1})	Phase[a]	Vibration	Reference
H_2CO	2843	G	ν_{as} CH_2	*5*
	2766		ν_{sy} CH_2	*5*
	1745		ν CO	*5, 6*
	1502		δ_{sy} CH_2	*5, 6*
H_2CO	1725	A[b]	ν CO	—
CO	2057	A	ν C≡O	*7*
CO_2	2349	G	ν_{as} O=C=O	*6, 8*
H_2O	1627	A[c]	δ H—O—H	*9*

[a] A = adsorbed; G = gas phase; ν = stretch; δ = bend; as = asymmetric; sy = symmetric.

[b] Adsorbed on the silica support. This peak includes the P branch of the 1745 cm^{-1} ν CO fundamental of $H_2CO(g)$ (*6*). It was not possible in this study to determine if any H_2CO adsorbed onto the platinum.

[c] Adsorbed on the silica support.

peaks at 2380 to 2300 cm^{-1} grew and an intense peak at 1627 cm^{-1} developed while the peaks at 3000 to 2700, 2057, 1775, 1745, 1725, and 1502 cm^{-1} were attenuated. Spectrum C shows that of the original peaks, only the absorbance at 2057 cm^{-1} remained at a ϕ of 0.13. Figure 1b clearly shows that parallel increases in intensity can be seen in the pair 2360 cm^{-1} (CO_2), 1627 cm^{-1} (H_2O), and parallel decreases can be seen in the pair 2057 cm^{-1} (CO), 1725 cm^{-1} (H_2CO) between the ϕ's of 0.13 and 0.20.

The same peaks and the same types of parallel behavior were present at 423 K. However, sharp changes in the intensities of the pairs occurred at ϕ's between 0.10 and 0.13 at 423 K compared to ϕ's between 0.13 and 0.20 at 448 K.

3. *Effect of Evacuation*

In order to observe only the surface species, the gas phase was evacuated from the IR cell after the completion of the above experiments (a ϕ of ∞ was reestablished). The only difference between the Pt/SiO_2 and the 100% silica evacuated spectra was the existence of the very intense peak at 2057 cm^{-1}.

4. *Temperature-Programmed Desorption*

Formaldehyde was observed to desorb from the Pt/SiO_2 catalyst at 490 K and as the temperature was increased further, CO and H_2 desorbed. When O_2 was introduced at 673 K at a ϕ of 0.17, CO_2 and H_2O were formed. The same experiment performed

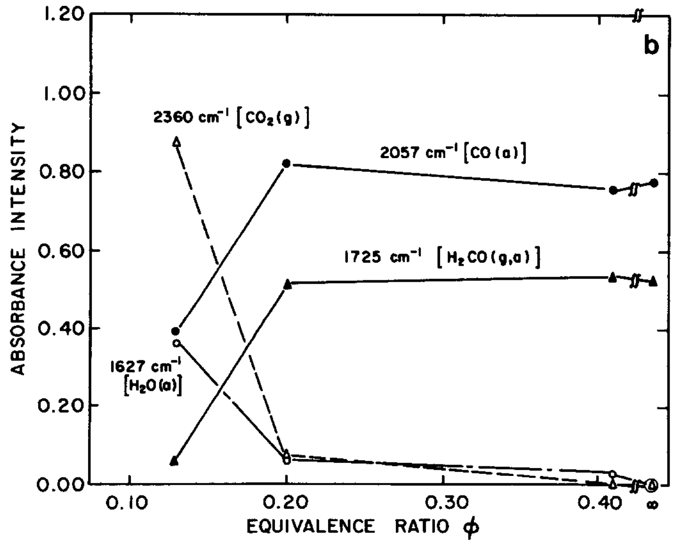

FIG. 1b. Absorbance intensity versus ϕ for IR spectra of 0.7 wt% Pt/SiO_2 at 448 K. The peak intensities were observed after 10–11 min of flow at each respective ϕ.

on the silica support showed only the desorption of H_2CO at 490 K.

IV. DISCUSSION

In the absence of O_2, the TPD results showed that CO and H_2 desorbed from the Pt/SiO_2 catalyst and the IR results showed that adsorbed CO existed on the Pt surface. These results support the following reaction scheme:

$$H_2CO(g) \rightleftharpoons H_2CO(a) \tag{1}$$

$$H_2CO(a) \rightarrow CO(a) + 2H(a). \tag{2}$$

These were the only significant reactions observed as long as ϕ was larger than 0.13 at 423 K and 0.20 at 448 K. At lower values of ϕ, CO_2 and H_2O were produced along with a concomitant decrease in the intensities of the IR bands for $H_2CO(g,a)$ and CO(a). Therefore, the oxidation reaction is proposed to proceed via steps (3) and (4) where the product H_2O is adsorbed on the silica (a*).

$$CO(a) + O(a) \rightarrow CO_2(g) \tag{3}$$

$$2H(a) + O(a) \rightarrow H_2O(a^*). \tag{4}$$

The requirement of a higher O_2 concentration (lower ϕ) at 423 K compared to 448 K for promoting reactions (3) and (4) is consistent with the data of MM for H_2CO oxidation on Pt wires. In that study, the oxidation of H_2CO occurred in two kinetic regimes, i.e., a low-temperature regime characterized by low rates that increased gradually with increasing temperature and a high-temperature regime where rates were high and largely independent of temperature. Significantly, the transition between kinetic regimes occurred over a narrow temperature range and the transition temperature decreased as ϕ was decreased (i.e., as the O_2/H_2CO ratio was increased). We note that the ϕ of 0.10 required to effect the transition between kinetic regimes at 423 K in the present study is close to the $\phi = 0.11$ condition of the MM study where the transition occured near 433 K. Also, in both studies, increasing ϕ (decreasing the O_2/H_2CO feed ratio) led to an increase in the transition temperature between kinetic regimes.

No gas phase CO was observed in the Pt/SiO_2 spectra, thus indicating that the desorption of CO appears to be negligible at temperatures of 423 and 448 K. The TPD results indicated that CO desorbed at temperatures greater than 490 K. This is consistent with the MM study where CO(g) was detected by mass spectrometry only at temperatures above 500 K and only for feeds with $\phi \geq 0.5$.

In the MM study, kinetic similarities between H_2CO and CO oxidation formed the basis for proposing the H_2CO oxidation mechanism given by reactions (1) to (4) above. The MM work suggested that the sharp transition between kinetic regimes observed with increasing temperature was associated with the changeover from a surface with high CO coverage to one with low CO coverage. The present study provides direct infrared spectroscopic evidence for such a transition. In this study, the transition was affected by changing ϕ at constant temperature, rather than temperature at constant ϕ as in the MM study. Together, the two studies provide consistent evidence for the dissociative mechanism of H_2CO oxidation involving CO(a) and H(a) intermediates. Furthermore, the infrared data do not support alternative mechanisms involving the addition of atomic oxygen to H_2CO or HCO species to produce formate or oxymethylene species which decompose to CO_2. Formate species have been observed by He and Ekerdt (*10*) on zirconia with absorbances at 2880, 1580, 1390, and 1360 cm^{-1}. No evidence for these bands was obtained in this study.

ACKNOWLEDGMENTS

The authors thank Michael J. D'Aniello, Jr., and Michael G. Zammit of the Physical Chemistry Department, General Motors Research Laboratories, for preparing the Pt/SiO_2 catalyst. This work was supported by the National Science Foundation under Grant CBT-8319494. The FTIR was funded by the Department of Defense Instrumentation Grant DAAG-29-83-G-0097.

REFERENCES

1. McCabe, R. W., and McCready, D. F., *Chem. Phys. Lett.* **111,** 89 (1984).
2. Campione, T. J., and Ekerdt, J. G., *J. Catal.* **102,** 64 (1986).
3. Jackson, N. B., and Ekerdt, J. G., *J. Catal.* **101,** 90 (1986).
4. Uchijima, T., Herrmann, J. M., Inoue, Y., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50,** 464 (1977).
5. Blau, H. H., Jr., and Nielsen, H. H., *J. Mol. Spectrosc.* **1,** 124 (1957).
6. Herzberg, G., "Infrared and Raman Spectra." Van Nostrand Reinhold, New York, 1945.
7. Sheppard, N., and Nguyen, T. T., "Advances in Infrared and Raman Spectroscopy," Vol. 5, p. 110. Heyden, London, 1978.
8. Cameron, D. M., and Nielsen, H. H., *Phys. Rev.* **53,** 246 (1938).
9. Benesi, H. A., and Jones, A. C., *J. Phys. Chem.* **63,** 179 (1959).
10. He, M-Y., and Ekerdt, J. G., *J. Catal.* **90,** 17 (1984).

MARK P. LAPINSKI
RONALD G. SILVER
JOHN G. EKERDT

Department of Chemical Engineering
University of Texas
Austin, Texas 78712

ROBERT W. MCCABE

Physical Chemistry Department
General Motors Research Laboratories
Warren, Michigan 48090-9055

Received May 28, 1986