

Influence of Diluent Gases on CO Oxidation over a Platinum-Alumina Catalyst

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A study was made of the influence of inert, diluent gases (He, Ar, N₂, SF₆, and to a limited extent, C₄F₈) on the rate of oxidation of CO over a platinum-alumina catalyst. Temperatures ranged between 523 and 558 K, and total pressures were between 102 and 145 kPa. The diluent gas was usually a minimum of 80 mol% of the total reaction gas mixture. In the region where no rate hysteresis occurs (lower branch), the rate decreases in order of diluents: SF₆ > N₂ > Ar > He. Furthermore, the influence of diluents is greatest at the lower values of the feed CO/O₂ ratio; only at the lowest ratios is there a measurable difference in rates between He and Ar diluents. The occurrence of hysteresis is influenced by the diluent gas. Ar promotes hysteresis while He prevents it; thus, an enormous diluent gas effect exists in the hysteresis regime. The diluent effect on hysteresis cannot be explained entirely by the alteration of transport rates. For the first time, evidence is presented to suggest that the diluent gas changes the adsorption equilibrium for the individual reactants adsorbed on the surface. This explanation is compatible with hysteresis observations. It also suggests why the same diluent may enhance the reaction rate on one catalyst while reducing it on another.

INTRODUCTION

The influence of diluent gases on reaction rates has been studied for many years in our laboratory (1-5). Our purpose has been to discover the causes of the unexpected influence of the noble gases and other non-reacting gases on the rates of catalytic reactions. This study was designed to complete the matrix given in Table 1, employing two oxidation reactions, SO₂ and CO, over the two quite different catalysts: V₂O₅/silica and Pt/alumina. Our object in the group of studies was to discover whether the diluent gas effect (DGE) is a general phenomenon or one simply associated with particular catalysts or a certain mechanism.

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EXPERIMENTAL

The flow diagram of the experimental apparatus is shown in Fig. 1. The feed gases, dried by silica-gel and molecular sieve drying columns and then metered, were mixed in a manifold, and passed through a preheater to the reactor. Both preheater and reactor were located in a constant-temperature fluidized sand bath. The reactor consisted of a 9.93-mm-o.d., 7.62-cm-long 316 stainless tube. Two chromel-alumel thermocouples, one at the reactor inlet and the other at the outlet, were used to monitor the temperature. A temperature controller maintained the sand bath temperature to within about $\pm 1^\circ\text{C}$.

The catalyst was 0.1% Pt on γ -Al₂O₃. Its catalog number is T-309 and the sample was obtained from United Catalysts who report mean Pt crystallite size as 5 nm. Mean pore

TABLE I
Studies of Reactions over Similar Catalysts in the Presence of Inert, Diluent Gases

Catalyst	Reaction	
	SO ₂ oxidation	CO oxidation
V ₂ O ₅ /Silica (kieselguhr)	Yeremian <i>et al.</i> (1)	Silva <i>et al.</i> (5)
	Rungta <i>et al.</i> (2)	
	Rhodey <i>et al.</i> (3)	
Pt/Alumina	Silva <i>et al.</i> (4)	Present study

diameter from CCl₄ uptake and BET surface area was 5 nm. Catalyst pellets were crushed and sieved to 40/50 mesh size. Catalyst of this mean size was diluted in a 1 : 2 ratio with crushed quartz of a similar mesh size for use in the reactor. Dilution insured the absence of radial and axial temperature gradients in the catalyst bed.

A Beckman Acculab 2 infrared (ir) spectrophotometer was used to analyze the outlet gas mixture for CO and O₂. Conversion was calculated from the CO₂ analysis only.

The gases used had the following minimum purities. O₂, 99.99%; CO, 99.99%; Ar, 99.99%; N₂, 99.9%; SF₆, 99.8%; C₄F₈, 99.99%. Hydrocarbon content was less than 15 ppm. The maximum amount of moisture was also 15 ppm.

Rates were measured in the region of differential conversions (i.e., less than 10% of the entering CO) except in an initial study of the influence of CO/O₂ ratio on rate. All measurements were made at steady state. This was verified by multiple readings over a 30- to 60-min period. A blank run with the reactor filled with quartz particles was made at 567 K. No activity was observed. The catalyst was found to be very stable. Its activity was periodically checked at 583 K, using a p_{CO}/p_{O_2} ratio of 0.40 with an argon diluent. No disproportionation reaction ($2CO \rightarrow C + CO_2$) was evident even when O₂ was not present in the feed gas, in contrast to results with a V₂O₅ catalyst used earlier (5).

A material balance on CO indicated agreement of measurements to within 4%.

Precautions were taken to obtain data free from disguise by transport phenomena.

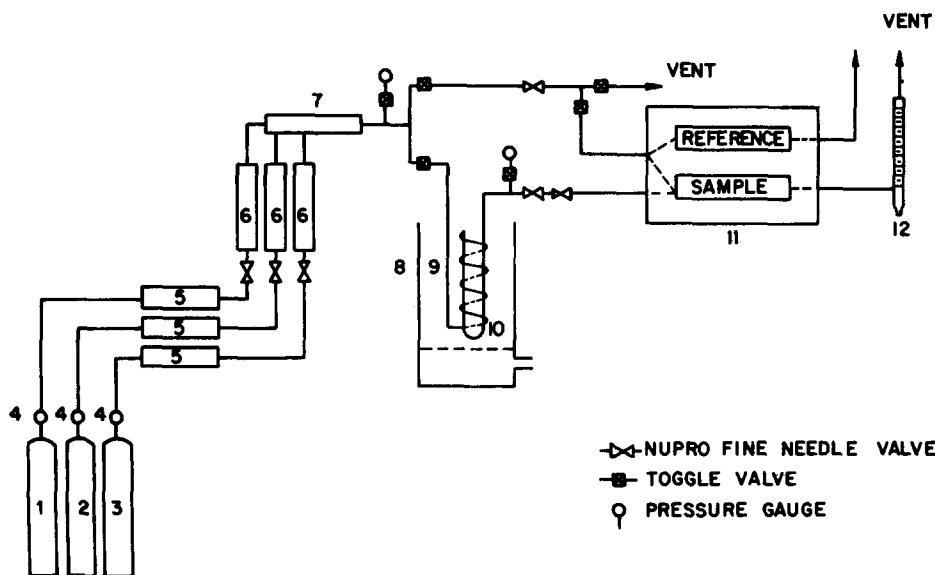


FIG. 1. Schematic of apparatus. 1, CO cylinder; 2, O₂ cylinder; 3, inert diluent cylinder; 4, pressure regulator; 5, drying tubes; 6, rotameters; 7, manifold; 8, fluidized sand bath; 9, preheater coil; 10, reactor tube; 11, ir spectrometer; 12, bubble flowmeter.

Isothermality of the reactor was assured by diluting the catalyst with inert quartz particles and by keeping the conversion less than 10%. The catalyst particles were 40/50 mesh (average diameter of 0.36 mm) to prevent intraparticle concentration or temperature gradients. At low CO/O₂ ratios, conversions approached 100%, and CO concentration gradients existed inside the catalyst particles despite their small size.

To check for interphase gradients, the flow rate of the reactants was varied 10-fold with He and N₂ diluents, 8-fold with Ar, and 6-fold with SF₆. The results are shown in Fig. 2. The sudden increase in the rate of reaction at the lowest flow rate has been observed previously (6, 12) and is explained by the coupling of mass transfer of CO to the particle surface and CO inhibition of the rate of oxidation. For this reason, all runs were carried out in the flat region of Fig. 2 at flow rates of about 19 (10⁻⁶) m³ (STP)/s through the catalyst bed.

Three types of experiments were undertaken. The first involved measuring the rates of CO oxidation in the presence of different diluents: He, Ar, N₂, and SF₆. In the second, the effect of diluents was exam-

ined on the hysteresis in CO oxidation as the CO/O₂ ratio was changed.

A third experiment, dynamic adsorption, was performed to try to explain the DGE observed in this work. In this, the surface coverages of CO and O₂ were measured separately, under the influence of different diluents by initially exposing the catalyst to a stream containing diluent and CO, and after saturation was reached, abruptly switching to a stream containing the diluent plus O₂. The CO₂ produced was a measure of the adsorbed CO on the catalyst under that partial pressure of CO and that diluent. Oxygen adsorbed was measured by reversing the procedure.

Inhibition of CO oxidation on Pt-alumina catalysts by CO is well established in the literature (8, 9). This leads to a maximum in the rate of oxidation at low values of the CO/O₂ ratio, and is also associated with isothermal multiplicity for this reaction system (9, 10). To see whether our system exhibited a rate maximum, an experiment was performed at a constant partial pressure of oxygen, a constant temperature, and a constant total flow rate, whereby the inlet ratio of CO/O₂ was decreased stepwise from 0.4 (2.53% CO) to 0.017. For each step the conversion to CO₂ was measured after steady state was attained. The conversion (and thus the rate) exhibited a maximum corresponding to a CO/O₂ mole ratio of about 0.1.

The effect of diluents on reaction rates was explored by varying the inlet CO/O₂ ratio in the presence of different diluents at three different temperatures: 523, 548, and 558 K. In these experiments, the oxygen partial pressure was held constant at 10.5 kPa. The measurement procedure was the same as that described above and results obtained are shown in Figs. 3a-c.

The second set of data were taken at a constant total pressure of 132.4 kPa, at the same three temperatures. Measurements were made at relatively low values of the inlet CO/O₂ ratios, where oxidation rates change rapidly with this variable, and at

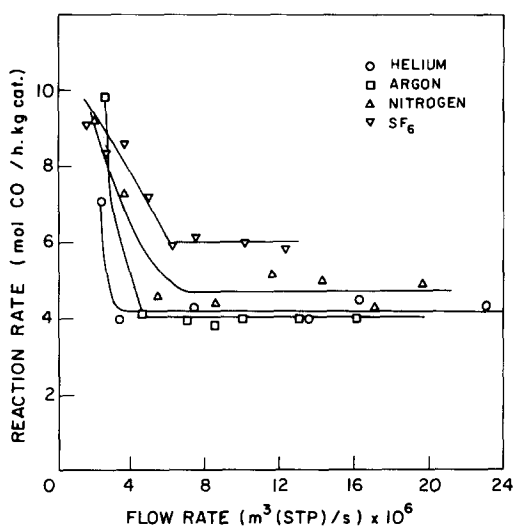


FIG. 2. Tests for presence of external diffusion control of reaction: 558 K and 132 kPa total pressure; inlet CO/O₂ mole ratio = 0.40.

larger ratios where the ratio has only a small effect on rate. Results for the different diluents are shown in Table 2. The final column in the table compares the rate measured with a specific diluent to that measured in helium.

All rates in Table 2 are means of three observations. An error analysis of the reaction rate (11, 12) shows a possible maximum error $\pm 7.8\%$ in the rates reported. However, replicate measurements indicate that the standard deviation is less than 1%. Thus, rate differences greater than 16% between two diluents are certainly significant.

Rate hysteresis was investigated for six diluents—He, Ar, Kr, N₂, SF₆, and C₄F₈—at the three temperatures used in other parts of this study. Figure 4 presents results at 523 K for He and Ar diluents. Observations for other diluents and at different tem-

peratures are shown in Table 3. This table shows that for the four diluents tested, argon permits hysteresis and SF₆ suppresses hysteresis at all temperatures. Temperature dictates whether or not hysteresis exists for the other two diluents.

TABLE 2

Influence of Diluent Gases on Reaction Rates (Total Pressure = 132 kPa)

Inlet CO/O ₂ ratio	Diluent	Reaction rate (mol CO ₂ /h · kg cat.)	(Rate)/(rate) _{He}
Temperature: 523 K			
0.12	He	1.76	1.00
	Ar	2.51	1.43
	N ₂	3.76	2.14
	SF ₆	4.43	2.52
Temperature: 548 K			
0.40	He	3.13	1.00
	Ar	3.16	1.01
	N ₂	3.62	1.16
	SF ₆	4.44	1.42
0.21	He	4.37	1.00
	Ar	4.52	1.03
	N ₂	5.38	1.23
	SF ₆	6.19	1.42
Temperature: 558 K			
0.57	He	3.76	1.00
	Ar	3.71	0.99
	N ₂	4.32	1.15
	SF ₆	4.75	1.26
0.40	He	4.48	1.00
	Ar	5.04	1.13
	N ₂	5.02	1.12
	SF ₆	5.77	1.29
0.21	He	6.62	1.00
	Ar	7.48	1.13
	N ₂	8.10	1.22
	SF ₆	9.18	1.39

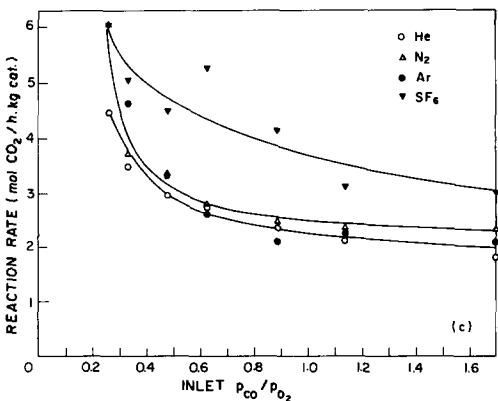
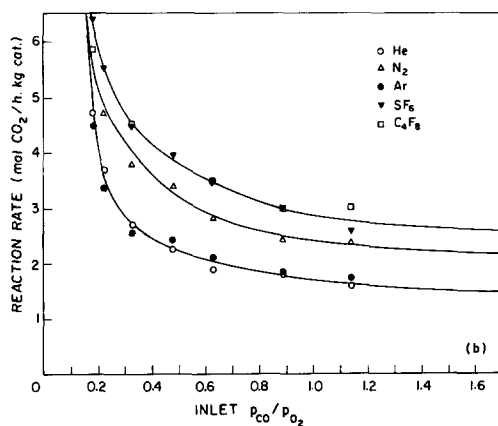
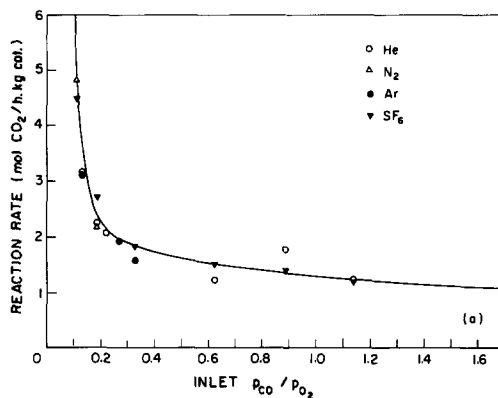


FIG. 3. CO oxidation rate as a function of inlet CO/O₂ mole ratio: 102 kPa total pressure; $P_{C_4F_8}$, $P_{SF_6} \sim 145$ kPa; $P_{O_2} = 10.5$ kPa. (a) 523 K; (b) 548 K; (c) 558 K.

Two additional diluents, perfluorocyclobutane (C_4F_8) and krypton (Kr), were tested at 548 K. C_4F_8 suppresses hysteresis, while krypton permits it.

Figures 5 and 6 show the results of experiments in which one reactant was first preadsorbed to saturation from a stream of that reactant with diluent, and was then flushed with the other reactant in the same diluent. The resulting CO_2 production measures approximately the preadsorbed reactant (in micromoles of CO_2 formed). The values are plotted on the vertical axes in the figures. Even though there is some contribution to the CO_2 peak resulting from the mixing of O_2 and CO both before and during displacement of the one stream by the other, minimizing the dead volume will reduce this interference significantly. Nonetheless, the measurements are inexact and it is the relative amounts of CO and O_2 adsorption that occur in the presence of different diluents that will be considered.

The measurements of adsorption were fairly reproducible. Each point plotted in Figs. 5 and 6 is the mean of from one to three trials, with most being two. The standard deviation in CO_2 produced is less than 10%.

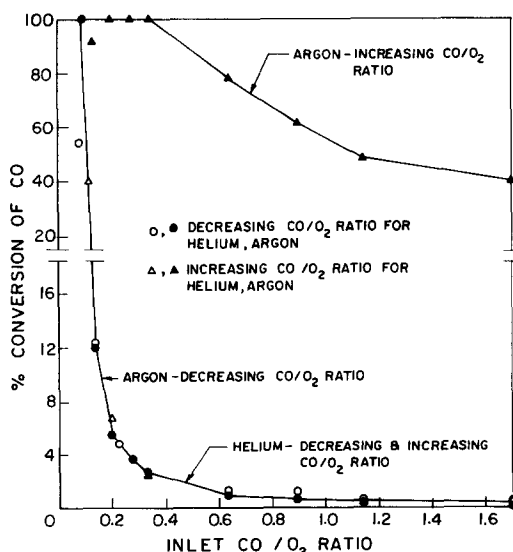


FIG. 4. Influence of diluent gas on hysteresis: 523 K; 102 kPa total pressure, 9.8 kPa p_{O_2} .

TABLE 3

Summary of Hysteresis Measurements for Different Diluents

Temperature	Diluent	Existence of an upper branch (hysteresis effect)
523	Helium	Absent
	Nitrogen	Only at very low CO/O_2 ratios
	Argon	Present
548	SF_6^a	Absent
	Helium	Absent
	Nitrogen	Present
	Argon	Present
	SF_6^a	Absent
	Krypton ^a	Present
558	$C_4F_8^a$	Absent
	Helium	Present
	Nitrogen	Present
	Argon	Present
	SF_6^b	Absent

^a System pressure about 50% higher.

^b System pressure about 40% higher.

The inlet ratio of p_{CO}/p_{O_2} on the axes in Figs. 5 and 6 is therefore not to be interpreted as reactants occurring simultaneously in the same stream, but rather in successive streams. In Fig. 5, the interpretation is that CO was preadsorbed and reacted with O_2 following; in Fig. 6, the order is reversed. Runs at identical temperatures were performed at essentially the same partial pressures of the diluents, which represented from 70 to 90% of the gas flowing through the reactor.

DISCUSSION

a. Comparison of Oxidation Rates with Different Diluents at Low Conversions

The most extensive data were collected at 548 K. (Fig. 3b). These show a significant DGE for CO oxidation over the entire range of inlet CO/O_2 ratios examined. Nitrogen, perfluorocyclobutane (C_4F_8), and sulfur hexafluoride (SF_6) markedly accelerate oxidation. Measurements for SF_6 and C_4F_8

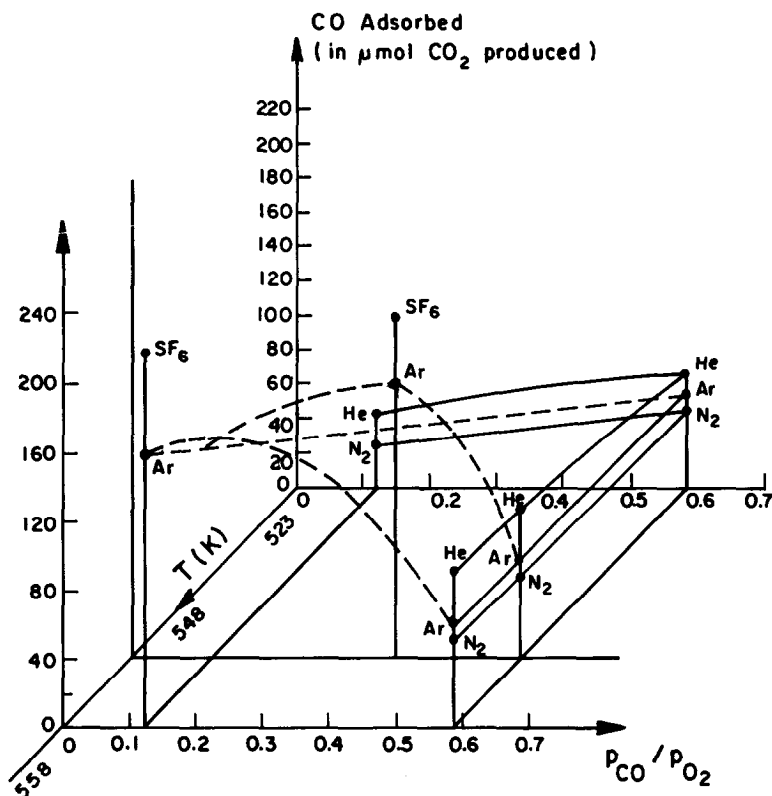


FIG. 5. CO adsorbed as a function of $p_{\text{CO}}/p_{\text{O}_2}$, temperature, and diluent gas. Solid contours are used where data seem more plentiful; broken contours where data are sparse.

were made at a higher total pressure, 150 kPa rather than 102 kPa used with the other diluents. Since the total pressure has a small effect on rate, no correction for this pressure difference has been made. A single curve has been drawn for both SF_6 and C_4F_8 although the data at $\text{CO}/\text{O}_2 = 1.4$ and 1.7 suggest that rates are higher for C_4F_8 . No rate differences appear for the noble gas diluents He and Ar at this temperature.

At 558 K, the data set is less extensive, but a trend similar to that at the lower temperature can still be seen. Substituting SF_6 for a He diluent increases the rate by greater than 50% for most of the composition range studied. Unlike the lower temperature data, the rates with the N_2 diluent are only slightly larger than those measured with He. For most of the CO/O_2 range, rate

measurements with Ar and He are essentially identical; only at inlet ratios below 0.46 do the rates with Ar begin to increase over those with He.

For the lowest temperature used in this study, 523 K (Fig. 3a), no diluent effects seem to appear.

The data of Table 2 confirm the observations in Fig. 3. The reaction rates in different diluents decrease at each of the three temperatures as $\text{SF}_6 > \text{N}_2 > \text{Ar} > \text{He}$. It is further evident that the DGE is largest at the lower values of the inlet CO/O_2 ratio where the oxidation rate begins to climb rapidly as the CO/O_2 ratio decreases. At 548 K there is no significant difference between oxidation rates with the noble gas diluents. This is also true at the higher inlet CO/O_2 ratio at 558 K. Both of these results

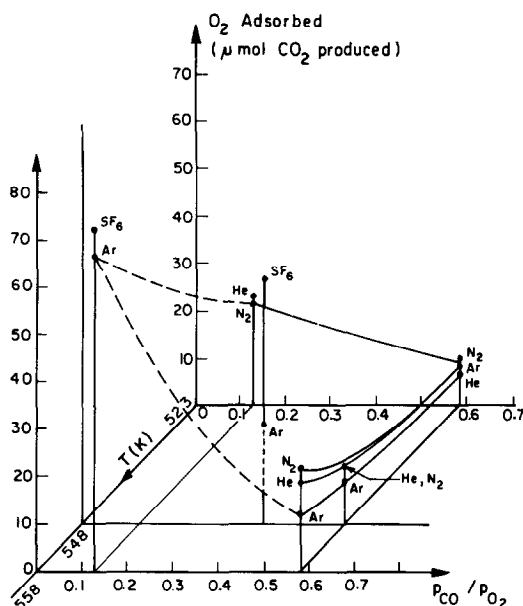


FIG. 6. Oxygen adsorbed as a function of p_{CO}/p_{O_2} , temperature, and diluent gas. Solid and broken contours as in Fig. 5.

agree well with the data shown in Fig. 3, taken at a different pressure and using a different procedure. However, in Table 2 at 558 K, a difference between He and Ar appears at inlet CO/O_2 ratios <0.4 .

b. Diluent Effect on Oxidation Rate Hysteresis

Hysteresis arises as a consequence of more than one stable operating state at a given inlet feed composition, temperature, and space velocity. The observations above suggest that hysteresis could be influenced by the choice of diluent.

Figure 4 shows results obtained with Ar and He diluents. Hysteresis occurs with argon but not with helium.

The lower branch of the hysteresis diagram shows virtually no rate difference between measurements made with the two diluents (also shown in Fig. 3a). The absence of an upper branch for helium indicates an enormous DGE for these two noble gases. Argon promotes the oxidation rate over helium to an astonishing extent.

Although hysteresis is present with krypton, oxidation rates in the upper branch are significantly lower than those observed with the other diluents which show hysteresis at 548 K. Whereas with the N_2 and Ar diluents conversions of 100% are observed when the CO/O_2 ratio increases stepwise from 0.12 to 0.48, conversion with a Kr diluent was only 82% at the lower ratios and dropped to 52% for a CO/O_2 ratio of 0.4. Although this result suggests a DGE in the upper branch of the hysteresis curve, it is opposite in the sense of normal boiling point of the diluent to that mentioned above with respect to He and Ar. This suggests that the difference between Ar and Kr may reflect transport interferences as these are quite likely to arise for the high oxidation rates observed in the upper branch. An alternate explanation is that the Kr experiments were carried out at pressures which were 50% higher than experiments with the other diluents, resulting in much different partial pressures of the reactants and rendering a comparison of conversion inappropriate.

Explanation of the existence or absence of hysteresis through changes in the transport properties of the diluents can be dismissed for a number of reasons, even though the interaction of transport processes with surface rate processes may be the source of isothermal multiplicity (6, 9). First of all, experiments discussed in the last paragraphs were carried out at essentially identical conditions except for the presence of different diluents. Key transport properties of the pure diluents at 548 K and 102 kPa are tabulated along with the hysteresis observations in Table 4. It is evident from this table that transport properties do not correlate with the presence of oxidation rate hysteresis. He and SF_6 both suppress hysteresis, yet their transport properties are quite different. Furthermore, the area mean pore radius for the catalyst is 5 nm (12). At atmospheric pressure, Knudsen diffusion of CO will dominate, so the effective diffusivity within the particle will

be virtually independent of the diluent. It can be readily shown (12) that the catalyst particle is isothermal and no more than 1°C hotter than the gas phase at rates corresponding to 100% conversion at low CO/O₂ ratios. Evidently, the diluents exert their effect on hysteresis by affecting the surface rate steps rather than the transport properties.

A further argument favoring an adsorption explanation for our hysteresis observations is that when 2 vol% of SF₆ is mixed with the argon diluent system hysteresis was found. However, increasing the percentage SF₆ to greater than 3.3% suppressed hysteresis (12). Yet there is no significant change in transport properties of the gas as its SF₆ content increases from 2 to 3.3%.

It is known that the rate hysteresis can be suppressed by adsorbing inerts (10). The SF₆ results mentioned in the previous paragraph indicate a similar explanation of our observations. SF₆ adsorption on the catalyst at 548 K and 102 kPa is measurable by conventional BET techniques (11). These results suggest that the DGE on rate hysteresis arises from the influence of the diluents on the amounts of reactants adsorbed, their partial distribution, or their activity on the surface.

c. Comparison With Previous DGE Studies

In Table 5, the results obtained in this study are compared with studies on other catalytic systems introduced in Table 1. The data show the effect on rate of different diluents arranged by the oxidation reaction in the two right-hand columns and by the catalysts for the rows. Identical catalysts were used for both oxidation reactions. The vanadia catalyst was a Cyanamid Aero SA catalyst (9.1 wt% V₂O₅, 10.1% K₂O, 0.45% Fe on kieselguhr). Details of this catalyst are given by Rungta *et al.* (2) and by Tamura *et al.* (13). For example, in the right-most column, Ar > He means that the rate of reaction in the presence of argon is significantly larger than the rate in the presence of helium. The symbol ≈ indicates similar rates.

Examination of the data indicates that the most significant variable is the ratio of reductant (either CO or SO₂) to oxygen in the mixture fed to this reactor. Therefore, the results are shown for different values of this ratio. The diluent concentrations in most of the ratios was greater than 80% by volume; only at the highest value of the ratios shown in this table and for a few of the ratios used with the vanadia catalyst did the

TABLE 4
Comparison of Diluent Transport Properties and Hysteresis Observations at 548 K and Operating Pressures

	He	Ar	Kr	N ₂	SF ₆
Diluent viscosity (μPa · s)	29	36	42	28	26
Diluent thermal conductivity (mW/m · K)	230	28	16	42	25
Binary diffusivity D _{CO-diluent} × 10 ⁵ (m ² /s)	19	5.6	2.9	5.6	1.9
Heat capacity (kJ/mol · K)	0.021	0.021	0.021	0.031	0.1
Prandtl number	0.67	0.67	0.67	0.75	0.93
Hysteresis	Absent	Present	Present	Present	Absent

TABLE 5
Summary of Diluent Gas Studies^a: Order of Rates with Different Diluents

	Carbon monoxide			Sulfur dioxide		
	Feed CO/O ₂	T (K)	Order	Feed SO ₂ /O ₂	T (K)	Order
0.1 wt% Pt/γ-Al ₂ O ₃	0.12	523	N ₂ > Ar > He			—
	0.21	548	SF ₆ > N ₂ > Ar ≈ He			—
	0.4	548	SF ₆ > N ₂ > Ar ≈ He	0.4	653-703	Ar > He ⁽⁴⁾
	1.7	548	SF ₆ > N ₂ > Ar ≈ He	1.8 ^c	653-703	Ar ≈ He ⁽⁶⁾
V ₂ O ₅ /K ₂ O/SiO ₂ (kieselguhr)	0.12	653-703	Ar > He ⁽⁵⁾	0.2	678	Ar > He ⁽³⁾
	0.4	693	Ar > He ⁽⁵⁾	0.4	678-723	CO ₂ > N ₂ > Ar > He ^(1,3,13)
	0.6	693	Ar ≈ He > Kr > SF ₆ ⁽⁵⁾	0.4	823	N ₂ ≈ He ⁽¹³⁾
				0.6	653-703	C ₂ F ₆ > Kr > Ar > SF ₆ > C ₂ F ₆ > CF ₄ > He ⁽²⁾
	2.4 ^c	693	Ar ≈ He > Kr > SF ₆ ⁽⁵⁾	4	678	Ar ≈ He ⁽³⁾

^a Total pressure 100 to 150 kPa; diluent greater than 80% of feed.

^b Diluent ca. 70% of feed.

^c Diluent between 50 and 60% of feed.

diluent account for just 50% by volume. In general, the DGE appears to be largest at low values of the inlet reductant/oxygen ratio. At the higher values, differences in rates measured in the presence of either helium or argon disappear.

Results of this work appear in the first row, middle column, of Table 5. Only observations for the lower branch of the rate hysteresis curve are considered. We noted in the previous section that the DGE is pronounced in the upper branch.

For CO oxidation, Table 5 indicates that the DGE on the two catalysts is totally different. With 0.1% Pt/ γ -alumina catalyst, the lowest oxidation rates were observed with the noble gases argon and helium, whereas with the Aero V₂O₅ catalyst, measurements with these gases exhibited the highest oxidation rate. Of course, there is a substantial temperature difference between the two experiments (>100 K), but this seems not to account for the difference. Measurements made with the vanadia catalyst covered a 50 K range and the only temperature trends observed were to diminish the differences in rates measured with the argon and helium diluents, as may be seen in the results at CO/O₂ = 0.4. We previously explained (5) the differences between the DGE for CO and SO₂ oxidation on the Aero vanadia catalyst in terms of the rate controlling step. This explanation no longer seems tenable in the light of the next section.

The results for the two catalysts exhibit the same trend with the inlet CO/O₂ ratio. Diluent effects are more pronounced at low values of this ratio. As the ratio increases above 0.2 for the platinum catalyst and above 0.4 for the vanadia catalyst, the differences in rates between argon and helium begin to disappear, although rate differences persist for diluents with higher normal boiling points than for He and Ar. The interpretation of the inlet ratio effect for the CO oxidation system is that virtually complete coverage of the active surface by adsorbed CO at higher values of the ratio re-

duces the surface concentration of oxygen to the point where each oxygen adatom is screened completely by CO or the mechanism switches to Eley-Rideal. For either of these situations the diluent effect decreases or even ceases.

A comparison of the two oxidation reactions on the Pt/ γ -Al₂O₃ catalyst shows that both seem to behave alike. Although just fragmentary data are available for SO₂ oxidation, rates in the presence of Ar are higher than those measured in He. The inlet feed ratio is critical. The difference between helium and argon disappears when the CO/O₂ ratio is greater than 0.21 for CO oxidation. For SO₂ oxidation, Table 5 indicates the same behavior but at a much higher ratio of SO₂/O₂. There seems to be very little temperature effect on the DGE for the SO₂ system, at least in the 50 K range examined. Results for the two catalysts were obtained at quite different temperatures, reflecting different activity of the catalyst for these two reactions.

For SO₂ oxidation, Table 5 illustrates that diluents with higher normal boiling points promote the oxidation reaction. Although not shown in the table, Yeramian *et al.* (1) observed that the DGE tends to disappear at higher temperatures. This was observed by Baron *et al.* (14) in the earliest work on the DGE phenomenon. For the vanadia catalyst, the effect also disappears as the SO₂/O₂ ratio approaches 2 (3).

d. Influence of Diluents on Adsorption

Results discussed in (b) above suggest that the curious DGE on CO oxidation rate and the presence of rate hysteresis may arise from sorption changes accompanying a change in diluent. Measurement of diluent adsorption under experimental temperature and partial pressure was attempted using a conventional volumetric BET unit (12). Only adsorption of SF₆ and C₄F₈ could be detected. The measurement showed that for a gas mixture of 88.4% SF₆ in He (percentage SF₆ similar to that used in multiplicity studies), 0.36 (10⁻⁶) STP m³ of SF₆

were adsorbed on the catalyst surface at 130 kPa and 548 K. This value is well outside the $\pm 2\hat{\sigma}$ error limits of ± 0.18 (10^{-6}) STP m^3 for the measurement. Our equipment did not permit the simultaneous measurement of CO or O_2 and the diluents. As a substitute for BET measurements, the dynamic adsorption experiments described under "Experimental" were undertaken.

It can easily be seen by comparing Figs. 5 and 6 that much more CO_2 was produced from the CO preadsorption runs than was produced from the oxygen preadsorption runs. This indicates that CO was adsorbed to a much greater degree than oxygen. Thus, on the catalyst surface, the ratio of CO/O_2 was considerably above the stoichiometric value of 2, even though the opposite was true for the gas phase.

Unfortunately, data on CO adsorption and oxygen adsorption are still rather limited. The effect on adsorption has not been determined for a large number of diluents under a variety of conditions. Nonetheless, a pattern does emerge between the two figures showing that considerable differences can arise between the amounts of CO and oxygen adsorbed under different temperatures, partial pressure ratios of CO and O_2 , and different diluent gases. It appears that the CO/O_2 adsorption ratio at similar temperatures and $p_{\text{CO}}/p_{\text{O}_2}$ feed ratios is changed about fourfold by the choice of diluent.

Although adsorption has been thought to be affected by the diluents used, this study is the first in which some correlation has been established between a change in the abundance of the reactant species adsorbed and the diluent gas. Further study will be needed to establish the nature of this relationship.

Despite the limited data, examining CO and O_2 adsorbed in the presence of helium and nitrogen suggest what is occurring. At $p_{\text{CO}}/p_{\text{O}_2} = 0.6$ at all three temperatures and at 0.12 for 523 K, substituting N_2 for He suppresses adsorption of CO (Fig. 5), but exerts very little effect on the adsorption of O_2 (Fig. 6). The diluent, therefore, changes

the ratio of CO and oxygen adatoms on the surface. Nitrogen decreases this ratio. Figure 3 shows lower CO/O_2 feed ratios increase the reaction rate. Thus, the effect of switching to N_2 is an increase in the oxidation rate. Figures 5 and 6 also explain the lack of an effect when Ar is substitute for He. Argon suppresses both O_2 and CO adsorption. Sulfur hexafluoride promotes both CO and O_2 adsorption with respect to that found with a He diluent. Unfortunately the measurements are too limited to explain the DGE observations.

The absence or presence of rate hysteresis may also be explained by these figures. Other workers (9, 10) explain the hysteresis in terms of blanketing of the active surface by CO at high feed CO/O_2 ratios so that CO inhibits the rate. If high CO/O_2 ratios are approached from very low CO/O_2 ratios where reaction is rapid, the blanketing cannot occur and the reaction proceeds at a very high rate. The surface CO and oxygen adatom ratio seems critical. Consider the situation at $p_{\text{CO}}/p_{\text{O}_2} = 0.6$ in Figs. 5 and 6. As the temperature increases from 523 to 558 K with a He diluent, the adatom ratio decreases sharply. If this temperature effect persists at $p_{\text{CO}}/p_{\text{O}_2} = 0.12$ where hysteresis occurs we can then explain the existence of hysteresis at 558 K and its absence at 523 K in the presence of helium. An identical argument can be made for nitrogen on the basis of the two figures. Unfortunately, the adsorption measurements were not made for these diluents at $p_{\text{CO}}/p_{\text{O}_2} = 0.12$. Examination of the argon envelope in Figs. 5 and 6 suggests the CO and oxygen adatom ratios on the surface are much lower for Ar than for He at all temperatures. This agrees well with the observation of hysteresis at all temperatures with the Ar diluent.

Because of equipment difficulties with direct measurement of SO_3 , we did not attempt to investigate this explanation of the results for Pt/ γ - Al_2O_3 and CO oxidation on the other systems shown in Tables 1 and 5.

If the adsorption equilibrium of the reactant for both the V_2O_5 and Pt catalysts is

altered by the choice of diluent gas, we can explain why we have observed different effects of the diluents on CO oxidation over the two catalysts as shown in Table 6. Evidently, the equilibrium sorbate concentrations must be enhanced or reduced by the diluents depending on the catalyst used.

Dialer *et al.* (16), and earlier Force and Bell (17-19), investigating the partial oxidation of ethylene to ethylene oxide on a supported silver catalyst, demonstrate the existence of strong interactions among adsorbates on the catalyst surface (17). Dialer *et al.* use the Force and Bell observation to suggest adatom concentration changes on the surface. Their view is similar to ours except that we suggest the diluent affects surface concentrations.

CONCLUSIONS

From this study and those which preceded it, we conclude:

(1) The diluent gas effect is not specific to certain oxidation reactions or certain catalysts. It seems to be a general phenomenon whose existence depends on the catalyst environment.

(2) Since the diluent gas can both promote and suppress rates, we cannot predict in advance from any simple criterion the outcome of using a specific diluent on the rate of oxidation.

(3) Most reaction rates, i.e., SO₂ oxidation on both catalysts, and CO oxidation on Pt/Al₂O₃, tend to increase with exposure to the diluents exhibiting higher normal boiling points; CO oxidation over V₂O₅ shows the opposite trend.

(4) The ratio of SO₂/O₂ and CO/O₂ in the inlet (and presumably on the surface) seems to be critical in establishing the extent of a DGE. Higher ratios appear to kill the effect. This seems to be indirect evidence for the notion that the surface ratio of reactants may be altered by the diluent gas.

Specifically for this study, we have found:

(1) The choice of diluent influences the adsorption equilibrium on the surface.

(2) Various diluents alter the ratio of reactants adsorbed and these in turn influence the reaction rates.

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