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The Oxidation of CO and Hydrocarbons over Noble Metal Catalysts

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The oxidation of CO, C_3H_6, 1-hexene, and toluene under excess O_2 has been studied over precious metal (PM) catalysts, Pt, Pd, and Rh, in the form of unsupported wires or supported on γ-Al_2O_3 or CeO_2/Al_2O_3. The kinetics were affected by the state of the metal dispersion, the pretreatment temperature, the reaction conditions, and the presence of CeO_2. The existence of two types of surface sites each with its own reaction kinetics is postulated to explain the results; to wit: (1) Type I kinetics, exemplified by the PM wires, is first-order with respect to O_2 and negative first-order with respect to CO over all three metals. Over the same Pt or Pd catalysts, the olefin oxidation is strongly self-inhibited by HC and more than first-order in O_2, whereas the opposite was found for Rh. These sites are attributed to PM particles in low oxidation state. (2) Type II kinetics is positive order with respect to CO and nearly independent to oxygen partial pressure. The olefin oxidation is less self-inhibiting by HC (for Pt and Pd) and by O_2 (Rh) than type I. Generally, the activation energies are lower. This type of kinetics prevails over PM surface of higher dispersion and higher oxidation state. The presence of CeO_2 promotes the type II kinetics. The oxidation of 1-hexene and toluene is very similar to that of C_3H_6 and suggests that the adsorption of the hydrocarbon on the surface through the double bond is important.

INTRODUCTION

All of the catalysts presently used for purification of automotive exhaust contain the noble metals Pt, Pd, or Rh as active components. Because of the high cost and limited availability of these metals, it is important to use as low a noble metal concentration in these catalysts as feasible. This is accomplished by keeping the active metals at a high degree of dispersion. Two patents claimed that this can be achieved by adding a promoter such as CeO_2 (*1, 2*). It is important, however, to understand the ways in which efforts to reduce the noble metal content of the catalysts affect catalytic activity. It is well known, for example, that the degree of dispersion (*3–5*), the nature of the catalyst support (*6*), and the presence of the promoter (*7, 8*) affect the specific catalyst activity, the selectivity, and the kinetic parameters. Furthermore, catalysts are routinely exposed to high temperatures of 600°C and above for varying periods of time. This thermal aging can cause severe sintering and decreased dispersion. Thus the kinetics of the reaction over an aged catalyst may be different from those of a fresh catalyst. We have made a detailed study of the kinetic parameters of the total oxidation of CO and the model hydrocarbons as a function of the following variables: (1) nature and concentration of noble metal, Pt, Pd, and Rh; (2) bulk metal versus supported catalysts; (3) degree of dispersion; (4) thermal aging; (5) presence of the promoter, CeO_2; (6) effect of pretreatment; and (7) operating conditions, e.g., oxidizing or reducing. Results obtained for the oxidation of CO, C_3H_6, 1-hexene, and toluene are reported here. A similar study on a series of low-molecular-weight saturated hydrocarbons have been reported elsewhere (*9*).

EXPERIMENTAL METHODS

Catalyst preparation. Pt, Pd, or Rh wire, 99.99% pure and 0.25 mm diam. (purchased from Engelhard Mineral & Chemical Co.), was washed with dilute HNO_3 and rinsed

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with distilled water and acetone before use. A measured length of the wire, in single or tri-ply was encased tightly in a thin-walled quartz (for Pt or Rh) or Pyrex (for Pd) tube and then wound into a spiral of about 12 mm o.d. to facilitate good heat dissipation and to minimize gas bypassing the sample. The surface areas of the wires were assumed to be equal to their geometrical areas, which are in the range of 1.2 to 5 cm^2/sample.

The supported catalysts of PM/Al_2O_3 were prepared by the conventional impregnation method on γ-Al_2O_3 powder. Details of the preparation have been reported elsewhere (*9*). For the PM/CeO_2/Al_2O_3 catalysts, the CeO_2 was first coated on the γ-Al_2O_3 powder by impregnation and the resultant solid calcined at 800°C before impregnation with the noble metal salt solutions. The concentration of PM and CeO_2 were calculated from the amount and the concentration of the PM salt and $Ce(NO_3)_3$ solutions used. The surface area of the Al_2O_3 support was 80 m^2/g after 800°C calcination and 60–65 m^2/g after 1000°C calcination. The catalysts were heated in air at 600, 700, 800, and 900°C for 4 h or more before being used for the oxidation runs.

Reactants. Chemical pure or research grade gases from Matheson Gas Products Company were used without further purification. 1-Hexene and toluene were chromatoquality (+99% pure) from Matheson, Coleman and Bell Company.

Rate determination techniques. A flow reactor was constructed from thin-walled quartz or Pyrex U tubes of 4 mm o.d. Either the wire spiral (1.2–5 cm^2/sample) or the powdered supported sample (0.02–0.03 g) placed between two swabs of quartz wool was in the exit leg of the reactor with the inlet leg serving as the reacting gas preheater. Two type-K thermocouples (one to the controller and the other to the recorder) were secured to the outside wall of the reactor tube at the midpoint of the sample. The gas composition before and after the catalyst was monitored with an on-line CVC-612 Mass Spectrometer. The carrier gas, helium, was passed through the system continuously at atmospheric pressure. The flow rate over the wire sample was 25 ml/min. For the powdered catalyst, the space velocity, volume of gas flow/hour–volume of catalyst, was ~300 K h^{-1}.

The rate measurements were conducted in three modes. (1) For the evaluation of the kinetic parameters (partial reaction orders and activation energies), the reactor was operated isothermally and as close to differential reactor conditions as possible, that is, the conversion was limited to less than 20%, and oxidation rates were measured with the partial pressure of one reactant nearly constant while that of the other was varied. When the heat of reaction produced a temperature variation large enough to be detected by the thermocouples the data were excluded from the interpretation. (2) For the stoichiometric studies, data for higher conversions were utilized, particularly for the hydrocarbon oxidation. The amount of water produced was measured only for the wire samples. Over the supported catalysts, the large surface area of the Al_2O_3 support stored the water and hampered its quantitative determination. (3) With the inlet concentration unchanged, the percentage conversion of the reaction was followed by slowly increasing or decreasing the reaction temperature. Total conversion was included in this type of measurement. These curves of conversion versus temperature can serve as a convenient activity indicator for the practical application of these catalysts.

Prior to each series of measurements, the sample was heated to 500°C in a stream of He containing 1% O_2 to remove any combustible contaminants from the surface. The reaction temperature was in the range of 150 to 500°C. The actual temperature range for each case was much narrower, depending on the activity of the catalyst. The rate and stoichiometric measurements were made under oxygen-rich conditions in almost all cases, i.e., O_2/CO or O_2/hydro-

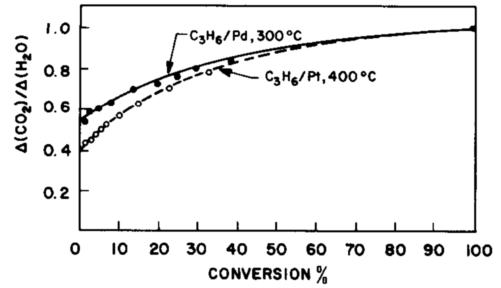

FIG. 1. Oxidation of C_3H_6 over (○) Pt-wire, (●) Pd-wire, 1% O_2, 0.2% C_3H_6.

carbon ratios were larger than their respective stoichiometric ratio.

CO chemisorption measurements. For the determination of the noble metal surface area of the supported catalyst by chemisorption of CO, the sample was first reduced with H_2 at 500°C followed by sweeping with H_2 at 500°C for 30 min. The amount of CO uptake at room temperature from a gas stream of He + 1% CO was determined from the mass spectrometer analysis of the exit gas and the known flow rate. The CO adsorption procedure was repeated after sweeping the sample with He for 30 min or more. The difference between the two runs was taken as the amount of CO irreversibly adsorbed on the surface.

RESULTS

Stoichiometry of the Oxidation Reactions

The following observations on the stoichiometry of the oxidation reactions of CO and hydrocarbons are common to the metal wires and the supported catalysts: (1) The CO reacted was accounted by the formation of CO_2 with stoichiometric consumption of O_2 in all cases. (2) The oxidation of C_3H_6, C_6H_{12}, and toluene were in most cases nonstoichiometric, with partial oxidation products being formed (CO, aldehydes etc.). Over the Pt and Pd wires, the amount of CO_2 formed from C_3H_6 oxidation was less than that of H_2O and the two coincide only near 100% conversion (Fig. 1). H_2O produced from the other two hydrocarbons was not measured. There was an increase in the *m/e* 28 peak during the hydrocarbon oxidation, which could only be assigned to CO formation. The degree of deviation from stoichiometry for oxidation to CO_2 decreased, as could be expected, with increasing O_2/HC ratio and increasing reaction temperature.

There were differences among the hydrocarbons and among the different noble metals. Qualitatively, the nonstoichiometry increases in the order of $C_3H_6 <$ toluene $< C_6H_{12}$. Among the three metals, Rh catalysts gives the highest and Pt the lowest degree of complete combustion to CO_2 and H_2O.

Dispersion of the Noble Metals (CO Chemisorbed/PM in Catalyst)

The metal surface areas of the PM/Al_2O_3 catalysts are shown in Table 1. These values are subject to the relatively large uncertainties inherent in the conventional method of using CO or H_2 chemisorption to determine the metal surface area of supported catalysts. The ratio of CO to surface PM atoms was assumed to be 1, which is probably too high for catalysts with low metal dispersion because of the bridging adsorption mode and too low for well-dispersed catalysts because of the doubly adsorbed mode (*10*). The data in Table 1 should be viewed with this assumption in mind. The metal atom density was assumed to be 1.25×10^{19} PM/m^2. The results of the metal surface area determination, or more precisely, the proportion of the metal available for CO chemisorption, show that the dispersion of Pd on Al_2O_3 remains almost the same with increasing calcination temperature (in air) from 600 to 900°C whereas that of Pt and Rh decreases sharply under similar calcination conditions. The dispersion of Pt decreases faster with increasing PM concentration than Pd and Rh.

For the PM/CeO_2/Al_2O_3 catalysts, a very complex pattern of H_2 reduction and CO chemisorption involving both the PM and the CeO_2 was observed. The PM promotes

TABLE 1

PM Dispersion on PM/Al_2O_3 Catalysts

Catalyst	Pretreatment T(°C)	Dispersion	Catalyst	Pretreatment T(°C)	Dispersion
Pd(0.038%)	600	0.41	Pt(0.023%)	600	0.87
Pd(0.038%)	800	0.55	Pt(0.023%)	800	0.36
Pd(0.038%)	900	0.64	Pt(0.023%)	900	0.13
Pd(0.155%)	600	0.51	Pt(0.22%)	600	0.19
Pd(0.155%)	800	0.67	Pt(0.22%)	800	0.07
Pd(0.155%)	900	0.66	Pt(0.22%)	900	0.06
			Pt(0.12%)	900	0.04
Rh(0.03%)	600	0.69			
Rh(0.153%)	600	0.57			
Rh(0.153%)	800	0.07			

Note. Dispersion = mole CO chemisorbed/mole of PM in catalyst; Pretreatment = calcination in air 4–16 h.

the redox reaction of the ceria itself from the Ce^{4+} to Ce^{3+}, has been reported previously (*11*). Therefore, the dispersion of PM on the CeO_2/Al_2O_3-supported catalysts cannot be determined by conventional CO chemisorption methods.

Kinetic Parameters of the Oxidation Reactions

The activity of the wires and the supported catalysts for total oxidation of CO and hydrocarbons is expressed as the rate of CO_2 production. Over the wires and Al_2O_3-supported catalysts of which the metal surface areas were measured, the specific reaction rates are given in milliliters (STP) of CO_2 produced/minute-square meter of PM. For the other supported catalysts of which the metal surface area could not be determined, the rates are in milliliters (STP) CO_2 produced/minute-milligram of PM. The average value of the inlet and exit partial pressure of each reactant was taken as its partial pressure over the entire catalyst bed. For the kinetic parameter determinations, data for low conversion and under isothermal conditions were used, as described above.

The rates, as a function of the partial pressure of the reactants (partial reaction order), were derived using the simple empirical power law:

$$\text{Rate of } CO_2 \text{ formation} = k(P_{O_2})^m(P_{\text{CO or HC}})^n$$

The m and n values are obtained from log–log plots of rates versus partial pressure of one of the reactants keeping that of the other reactant constant. The rates obtained at various temperatures normalized to a set of aribtrarily chosen conditions, e.g., 0.5% O_2 + 0.5% CO and 1% O_2 + 0.1% HC for most cases, were plotted according to the Arrhenius equation to evaluate the apparent activation energy, ΔE.

It has been found by previous workers (*12–14*) and in this investigation as well, that the kinetic parameters, m, n, and ΔE for each set of reaction/catalyst could vary with the reaction conditions such as O_2/CO or O_2/hydrocarbon ratio, the temperature of reaction, and sometimes the sequence of variation of reaction conditions. To minimize the extent of partial oxidation of the hydrocarbons and the possible change of reaction kinetics associated with exposing the catalyst to reducing atmosphere (as it will be shown later), only those data obtained under predominantly oxidizing con-

TABLE 2

CO Oxidation

PM(%)/CeO$_2$(%)[a]	T (°C)[b]	m	n	ΔE (kcal/mol)	R_t[c] (°C)	R_s[d] (°C)	Predominant type of sites
Pt-wire		1	−1	30	—	100 (300)	I
Pt(0.023)/0	(600)	1	−0.8	22	4.9 (300)	23 (300)	I
Pt(0.023)/0	(800)	1	−0.9	26	2.75 (300)	31 (300)	I
Pt(0.023)/0	(900)	1	−0.6	26	0.64 (300)	20 (300)	I
Pt(0.12)/0	(900)	0.7	−0.6	25	0.56 (300)	51 (300)	I
Pt(0.22)/0	(700)	1	−0.9	30	1.9 (300)	40 (300)	I
Pt(0.22)/0	(800)	0.9	−0.8	27	0.97 (300)	57 (300)	I
Pt(0.22)/0	(900)	0.8	−1	25	0.94 (300)	62 (300)	I
Pt(0.05)/23	(900)	0	1	12	1.4 (300)	—	II
Pt(0.05)/23	(900)[e]	0.3	0.3	19	76 (250)	—	
Pt(0.23)/20	(700)	~0.5	0–0.6	20	0.8 (300)	—	I + II
Pt(0.23)/20	(700)[e]	0.9	−0.5	20	14 (300)	—	
Pt(0.3)/23	(900)	0.6	0.4	16	1.5 (300)	—	I + II
Pt(0.3)/23	(900)[e]	0.2	0.4	28	65 (250)	—	
Pd-wire		1	−1	30	—	137 (250)	I
Pd(0.038)/0	(600)	1	−0.9	32	16.2 (250)	87 (250)	I
Pd(0.038)/0	(800)	0.8	−1	32	24 (250)	96 (250)	I
Pd(0.038)/0	(900)	0	1	13	10 (250)	34 (250)	II
Pd(0.155)/0	(800)	0.9	−0.9	30	7.9 (250)	27 (250)	I
Pd(0.155)/0	(900)	0.9	−0.8	26	15 (250)	50 (250)	I
Pd(0.037)/23	(900)	0	1	9	14 (250)	—	II
Pd(0.037)/23	(900)[e]	0.5	0	20	33 (250)	—	
Pd(0.1)/20	(900)	0	1	12	11 (250)	—	II
Pd(0.154)/20)	(800)	0.6	0.7	11(≤225°C)	2.2 (200)	—	I + II
				15(≥225°C)	21 (250)		
Pd(0.2)/8.9	(900)	0.2	0.3	10(≤225°C)	2 (200)	—	I + II
				(≥225°C)	15 (250)	—	
Rh-wire		1	−1	28	—	300 (250)	I
Rh(0.03)/0	(600)	1	−0.7	22	17 (250)	55 (250)	I
Rh(0.03)/0	(800)	1	−0.7	27	1.3 (300)	—	I
Rh(0.03)/0	(900)	0	0.4	23	0.04 (300)	—	II
Rh(0.153)/0	(600)	1	−1	27	3.2 (250)	12 (250)	I
Rh(0.153)/0	(900)	0.8	−0.5	23	0.44 (300)	—	I + II
Rh(0.03)/20	(600)	0.4	0.5	22	31 (225)	—	II
Rh(0.03)/20	(800)	0.2	0	23	3.5 (225)	—	II
Rh(0.155)/20	(600)	0	0.2	25	63 (225)	—	II
Rh(0.155)/20	(900)	0.2	0	18	1.1 (225)	—	II

[a] Balance Al_2O_3.

[b] Pretreatment = calcination in air at T(°C) for ≥ 4 h.

[c] R_t in ml (STP) CO_2 produced/min − mg of PM, 0.5% O_2 and 0.5% CO at T(°C).

[d] R_s in ml (STP) CO_2 produced/min − m^2 of PM, 0.5% O_2, 0.5% CO at T(°C).

[e] Reduced at ≥300°C with ~1% CO for a few minutes.

ditions are included in Tables 2–4. The specific criterion for the data selection is validity over at least 80% of the ranges of O_2/CO or O_2/HC ratio of 0.8- to 5-fold of their stoichiometric ratio for oxidation to CO_2. The reaction temperatures were mostly above 200°C to avoid possible interference by CO_2 adsorption. The rate of CO_2 formation instead of hydrocarbon or CO consumption was used for the kinetic eval-

TABLE 3

C_3H_6 Oxidation

Catalyst PM(%)/CeO_2(%)[a]	T(°C)[b]	m	n	ΔE (kcal/mol)	R_t[c] (°C)	R_s[d] (°C)	Predominant type of sites
Pt-wire		1.8	−0.8	22	—	190 (300)	I
Pt(0.023)/0	(600)	2.2	−1	17	5.2 (300)	24 (300)	I
Pt(0.023)/0	(800)	2.0	−1.1	16	0.4 (300)	4.5 (300)	I
Pt(0.023)/0	(900)	2.0	−1	20	0.24 (300)	7.4 (300)	I
Pt(0.12)/0	(900)	2.2	−1.2	18	0.07 (300)	6.4 (300)	I
Pt(0.22)/0	(800)	2.0	−0.9	18	0.3 (300)	17 (300)	I
Pt(0.05)/23	(900)	0.8	0.1	19	1.3 (300)	—	II
Pt(0.23)/20	(700)	1.2	−0.3	18	0.3 (300)	—	I + II
Pt(0.3)/23	(900)	1.5	−0.6	19	0.8 (300)	—	I + II
Pd-wire		1.5	−0.6	30	—	50 (250)	I
Pd(0.038)/0	(600)	1.0	−0.7	22	1.7 (250)	9.2 (250)	I
Pd(0.038)/0	(800)	1.6	−0.7	25	2.2 (250)	8.9 (250)	I
Pd(0.038)/0	(900)	1	−0.3	14	1.9 (250)	6.6 (250)	II
Pd(0.155)/0	(800)	1	−0.7	28	1.1 (250)	3.7 (250)	I
Pd(0.155)/0	(900)	0.9	−0.8	30	1.2 (250)	4.1 (250)	I
Pd(0.021)/20	(600)	0.2	0.4	13	0.4 (250)	—	II
Pd(0.037)/23	(900)	0.6	−0.2	19	0.31 (250)	—	II
Pd(0.1)/20	(900)	0.7	−0.3	15	0.47 (250)	—	II
Pd(0.154)/20	(800)	1	−0.4	27	0.5 (250)	—	I + II
Rh-wire		−1.3	1.3	23	—	580 (300)	I
Rh(0.03)/0	(600)	−0.6	0.8	22	5.5 (300)	17.7 (300)	I
Rh(0.03)/0	(800)	−0.9	1.1	22	0.1 (300)	—	I
Rh(0.03)/0	(900)	0.6	0.7	22	0.01 (400)	—	II
Rh(0.153)/0	(900)	−1	1	16	0.25 (400)	7.9 (400)	I
Rh(0.131)/0	(600)	0.2	0.6	25	3.7 (300)	—	I + II
Rh(0.031)/20	(800)	0	0.3	17	0.4 (300)	—	II
Rh(0.155)/20	(600)	0	0.5	22	2.8 (300)	—	II
Rh(0.155)/20	(900)	0.2	0.3	24	0.3 (300)	—	II

[a] Balance Al_2O_3.

[b] Pretreatment = calcination in air at T(°C) for ≥ 4 h.

[c] CO_2 ml (STP) produced/min − mg PM, at T(°C), 1% O_2, 0.1% hydrocarbon.

[d] CO_2 ml (STP) produced/min − m^2 PM at T(°C), 1% O_2, 0.1% hydrocarbon.

uation thus excluding the partial oxidation portion of the reaction.

Conversion vs Temperature Results

To examine the complete range of oxidation from 0 to 100% conversion, the rate of CO_2 production with constant inlet composition was monitored by slowly increasing and then decreasing temperatures. Some typical results are shown in Figs. 2–4. In these experiments, the total gas flow rate/weight of the catalyst samples were held constant to give the standard space velocity, 300 K h^{-1}. For some of the catalysts, changes of reaction kinetics could occur when the catalysts were reduced briefly with 1% CO in He. This was done by interrupting the O_2 supply during the O_2 + CO run at the top temperature of a-curves in Figs. 2–4. The oxidation was then resumed in the decreasing temperature mode to give the b-curves, followed again by the increasing temperature mode to test the stability of the reduced state. Interruption of the O_2 supply during oxidation of olefins was not attempted because of the possible accumu-

TABLE 4

Toluene Oxidation

Catalyst PM(%)/CeO$_2$(%)^a	T(°C)^b	m	n	ΔE (kcal/mol)	$R_t{}^c$ (°C)	$R_s{}^d$ (°C)	Predominant type of sites
Pt-wire		2.1	−2	28	—	664 (350)	I
Pt(0.023)/0	(600)	2.5	−1.9	29	7.58 (350)	350 (350)	I
Pt(0.023)/0	(900)	2.2	−1.2	21	3.86 (350)	119 (350)	I
Pt(0.05)/23	(900)	0.7	0.2	22	3.49 (350)	—	II
Pd-wire		1.3	−1.2	24	—	332 (300)	I
Pd(0.038)/0	(900)	0.8	−1.0	21	13.6 (300)	45.3 (300)	II
Pd(0.154)/20	(900)	1.0	−1.3	24	5.0 (300)	17.0 (300)	I + II
Pd(0.037)/23	(900)	0.6	−0.3	18	1.3 (300)	—	II
Pd(0.1)/20	(900)	1.1	−0.1	17	2.1 (300)	—	II

[a] Balance Al$_2$O$_3$.
[b] Pretreatment = calcined in air at T(°C) for ≥ 4 h.
[c] CO$_2$ ml (STP) produced/min − mg PM at T(°C), 2% O$_2$, 0.1% hydrocarbon.
[d] CO$_2$ ml (STP) produced/min − m^2 PM at T(°C), 2% O$_2$, 0.1% hydrocarbon.

lation of partial oxidation products or carbon residual on the catalyst surface. In a few cases, the C$_3$H$_6$ oxidation was carried out on the catalyst surface after being reduced with CO. In general, the difference between the oxidized and reduced surfaces is greater for CO oxidation than for C$_3$H$_6$ oxidation.

DISCUSSION

Pt, Pd, and Rh Wire Catalysts

CO oxidation over Pt, Pd, and Rh wire is stoichiometric and first-order with respect to O$_2$ and negative first-order with respect to CO. The activation energies are in the range of 28–30 kcal/mol. These results are in agreement with those reported by previous workers (*15, 16*). The favored mechanism in the literature is the interaction between adsorbed O$_2$ and CO (Langmuir–Hinshelwood mechanism) with the latter strongly adsorbed on the surface causing self-inhibition. Because of the similarity in the kinetic parameters for CO oxidation among the three metals, the results

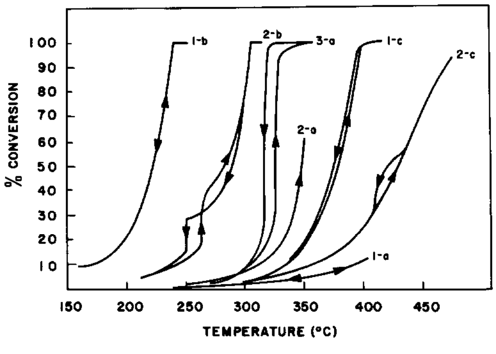

FIG. 2. Conversion of CO and C$_3$H$_6$ to CO$_2$ over Pt catalysts. (1) Pt/CeO$_2$/Al$_2$O$_3$ (0.05/23%, 900°C), (2) Pt/CeO$_2$/Al$_2$O$_3$ (0.22/20%, 700°C), (3) Pt/Al$_2$O$_3$ (0.22%, 700°C). (a) Oxidized surface, inlet 0.6% O$_2$, 0.6% CO; (b) reduced surface, inlet 0.6% O$_2$, 0.6% CO; (c) oxidized surface, inlet 1% O$_2$, 0.1% C$_3$H$_6$.

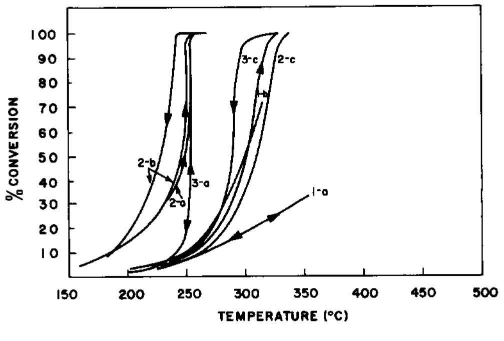

FIG. 3. Conversion of CO and C$_3$H$_6$ to CO$_2$ over Pd catalysts. (1) Pd/CeO$_2$/Al$_2$O$_3$ (0.021/12%, 800°C), (2) Pd/CeO$_2$/Al$_2$O$_3$ (0.155/20%, 800°C), (3) Pd/Al$_2$O$_3$ (0.153%, 800°C). (a) Oxidized surface, inlet 0.5%, O$_2$, 0.5% CO; (b) reduced surface, inlet 0.5% O$_2$, 0.5% CO; (c) oxidized surface, inlet 1% O$_2$, 0.1% C$_3$H$_6$.

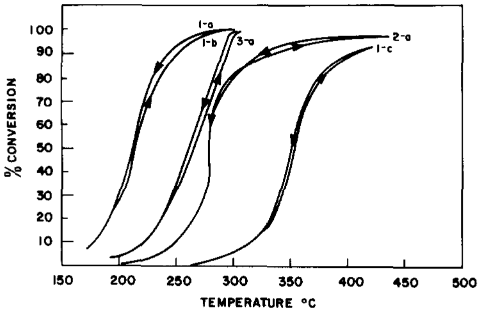

FIG. 4. Conversion of CO and C_3H_6 to CO_2 over Rh catalysts. (1) $Rh/CeO_2/Al_2O_3$ (0.155/20%, 600°C), (2) Rh/Al_2O_3 (0.153%, 600°C), (3) $Rh/CeO_2/Al_2O_3$ (0.03%/20%, 600°C). (a) Oxidized surface, inlet 0.6% O_2, 0.6% CO; (b) reduced surface, inlet 0.6% O_2, 0.6% CO; (c) oxidized surface, inlet 1.0% O_2, 0.15% C_3H_6.

indicate that the specific activity for CO oxidation as Rh ≥ Pd > Pt.

Oxidation of the olefins and toluene over all three metals involves partial oxidation to a varying degree, dependent on the reaction conditions and the nature of the hydrocarbons. Over Pd and Pt, the rates of complete oxidation to CO_2 are strongly dependent on the O_2 partial pressure, orders of 1.3 to 2, and inhibited by hydrocarbons, orders of −0.6 to −2. The negative order of the reaction suggests that the situation is similar to that with CO, involving strong adsorption of the unsaturated hydrocarbon on the Pt and Pd surface through the π-bonds. Because of the nonstoichiometry of the reaction, one can attribute part of the apparent positive order in O_2 and the apparent negative order in hydrocarbon to the adsorption and removal of the partially oxidized products. The oxidation rate at large olefin/O_2 ratio or low temperature, where the nonstoichiometry is large, is further suppressed by the strong adsorption of the partial oxidation products. At smaller olefin/O_2 ratios or higher temperature, the rate is enhanced by the removal of the products from the surface sites by O_2. The similarity between the kinetics for C_3H_6 and 1-hexene and their sharp contrast to those found for the alkanes over the same catalysts (*9*) indicates that the double bond plays a primary role in the oxidation reaction with a minor effect of the chain length.

The oxidation C_3H_6 over Rh wire is negative order with respect to O_2 and positive order with respect to C_3H_6, just opposite compared to Pt and Pd. Similar kinetic parameters were reported by Cant and Hall for C_3H_6 oxidation over the Pt, Pd, and Rh catalysts supported on SiO_2 (*17*). The simplest qualitative rationalization of the differences in partial reaction orders is that Rh is not as "noble," i.e., it has a lower ionization potential, than the other two precious metals. The surface of Rh is probably in the state of Rh_2O_3 under the oxidizing reaction conditions (*18*), this is equivalent to a strong adsorption of oxygen to the exclusion, or weakening, of the adsorption of the olefins. If the Langmuir–Hinshelwood mechanism indeed prevails, as it was proposed for the CO oxidation, the outcome could be a negative order in oxygen, i.e., O_2 self-poisoning. Furthermore, C_3H_6 was stoichiometrically converted into CO_2 over the Rh surface. Therefore, the contribution from the partial oxidation products and their retention–removal from the Pt or Pd surface to the kinetic parameters discussed above is absent for the Rh catalyst.

Supported Catalysts

The results for CO and olefin oxidation over the supported catalysts with or without CeO_2 are complex. The kinetic parameters shown in Tables 2–5 and the conversion curves in Figs. 2–4 suggest that there is more than one type of catalytic sites, each having a different set of kinetic parameters.

For convenience, we call the kinetic behavior that closely resembles that obtained over the wire samples as type I kinetics. The conversion curves for this type of kinetics generally show the light-off phenomenon, a sharp rise in conversion from 20 to 100% within a very narrow range of temperature.

The kinetics of CO and olefins oxidation over many low PM concentration catalysts,

TABLE 5

1-Hexene Oxidation

Catalyst PM(%)/CeO_2(%)[a]	T(°C)[b]	m	n	ΔE (kcal/mol)	R^c (°C)	R^d (°C)	Predominant type of sites
Pt-wire		1.7	−1.2	16.3	—	33.5 (300)	I
Pt(0.023)/0	(600)	0.7	−0.3	12	0.61 (300)	2.9 (300)	I
Pt(0.023)/0	(900)	1.5	−0.3	17.4	0.20 (300)	6.22 (300)	I
Pt(0.05)/23	(900)	0.5	0.22	22	1.39 (300)	—	II
Pd-wire		2	−1	24	—	100 (300)	I
Pd(0.038)/0	(900)	1.2	−0.4	18	6.2 (300)	20.7 (300)	II
Pd(0.155)/0	(900)	1.5	−1	21	2.5 (300)	9.05 (300)	I
Pd(0.037)/23	(900)	2	0.2	18	4.8 (300)	—	II
Pd(0.1)/20	(900)	0.8	0.2	17	3.5 (300)	—	II

[a] Balance Al_2O_3.

[b] Pretreatment = calcined in air at T(°C) for ≥ 4 h.

[c] CO_2 ml (STP) produced/min − mg PM at T(°C), 2% O_2, 0.1% hydrocarbon.

[d] CO_2 ml (STP) produced/min − m^2 PM at T(°C), 2% O_2, 0.1% hydrocarbon.

particularly those containing CeO_2, differ sharply from those of the wires. In general, they are less inhibited by CO or hydrocarbon (over Pt or Pd) or by O_2 (over Rh) and show a smaller partial reaction order with respect to the other reactant. The activation energies for CO oxidation are also much lower. This type of kinetics is designated as type II in Tables 2–5.

In any supported catalyst, pure type I or type II behavior is not expected and the parameters deviate from the two limits. If the kinetic parameters did not markedly deviate from the behavior of the wire catalyst, a type I classification is given. Similarly, catalysts with parameters close to the other extremes are designated as type II. The catalysts with parameters fall in between are considered as composed of both types, type I + II. It is of interest to note that the assignment of kinetic types based on CO oxidation (Table 2) can be carried over to the olefins (Tables 3–5) without exception.

Figures 2–4 show the conversion curves as a function of reaction temperature with the inlet condition remaining constant. For each metal, three catalysts, representing the type I, type II, and type I + II were used. For the type I catalysts, the typical light-off curves for CO oxidation were obtained. Interruption of O_2 supply, intended for reduction by CO, has no effect. Over the Pt or Pd catalysts exhibiting type II or type I + II kinetics, a large increase in CO oxidation activity was observed after the O_2 stoppage (reduction). The conversion curve also changed from the gradual rise with temperature to approach that of the type I. The stability or life of the reduced type II, II-R, state is dependent on the nature of the precious metal, the order being Pt > Pd > Rh. It is favored by high reduction temperature and low O_2/CO. For Pt catalysts, the reduced state II-R was stable enough to allow the evaluation of the kinetic parameters. Some results are shown in Table 2. Comparison of these results with those before reduction for the same catalysts show that after reduction the reaction kinetics has changed from predominantly type II to predominantly type I. Over the Rh catalysts with type II kinetics, the reduced state reverted back to the oxidized state so fast that only a momentary increase in activity was observed after the stoppage of O_2.

Several publications from this laboratory (*19*) and others have shown that the state of metal or metal oxide on a support can generally be characterized as two states. At low concentration, the metals or metal oxides are in isolated or two-dimensionally dispersed state, so-called δ-phase. As the concentration increases, three-dimensional particles with bulk properties, β-phase, starts to form and coexist with the δ-phase. Because the type I kinetics in this work is defined as that observed over the metal wires, one might intuitively assign the type I kinetics to the β-phase, or particles. Similarly, the type II kinetics was found over catalysts of low PM concentration and thus may be possibly associated with the δ-phase. We must note however, that the type II kinetics for CO oxidation changes to type I kinetics after a brief exposure to 1% CO in He at 300°C (or even lower) and is reversed under oxidizing atmosphere while a significant change of dispersion is not expected to accompany this change in reactivity. This suggests that the type II sites are in a higher oxidation state than the type I sites under reaction conditions in an oxidizing atmosphere. In essence, the active type II sites present as cations would be surrounded by oxygen either as ions or as adsorbed oxygen species. The adsorption of CO on the PM cations, in the presence of high oxygen surface concentration would be less competitive. Thus the reaction is near zero-order in O_2 and positive order with respect to CO as observed for the type II kinetics. The metal cations in the dispersed phase are, as a rule, more resistant to reduction (a manifestation of support interaction) and in this sense it may be expected that type II sites assume a higher oxidation state. The difference in the stability of the type II-R sites for the three metals follows the same reasoning. Pt with its higher ionization potential than Pd and Rh would show a higher tendency to be in the metallic or zero-valent state. Pt on Al_2O_3, even at very low concentration and high dispersion, is predominantly type I. On the other hand, Pd and Rh by virtue of their lower ionization potentials, would tend to be in a higher oxidation state.

The results (Tables 2–4) show that CeO_2 generally promotes the type II kinetics. The interaction between ceria and PM is complex. We have reported that PM can promote the reduction of Ce^{4+} to Ce^{3+} (*11*). Thus the presence of Ce next to PM on the catalyst surface may facilitate a charge transfer from PM to Ce resulting in higher oxidation state in the PM and again favoring type II kinetics. It has also been proposed that CeO_2 can promote the catalytic activity of PM by stabilizing the PM dispersion (*1, 2*). However, the PM surface areas on the ceria-containing supported catalysts have not been actually measured. Indirectly, one can compare the specific activities for CO oxidation over the PM/γ-Al_2O_3 and PM/CeO_2/Al_2O_3 catalyst exhibiting predominantly type II kinetics. For the Pd catalysts with type II kinetics, the presence of CeO_2 did not affect significantly their specific activity (per mg of Pd). Perhaps, the high dispersion of Pd on γ-Al_2O_3 (Table 1) would mask the ceria effect. On the other hand, the addition of ceria to supported Rh catalysts enhanced the CO oxidation by an order of magnitude. The loss of Rh surface area after heating to 700°C has been attributed to the diffusion of Rh into the Al_2O_3 support (*20*). The presence of ceria in this case appears to stabilize the Rh on the surface.

Comparison of the catalytic activity of the various catalysts can only be made among catalysts with approximately the same kinetic parameters. Among the PM/Al_2O_3 catalysts exhibiting predominantly type I kinetics and for which the approximate surface areas are known, the rate of CO oxidation per unit PM surface areas varies within 0.2 to 0.6 of the value found for the respective wire. In view of the fact that the areas of the wires are underestimated (the geometrical area without correction for the roughness was used) and the large range of metal dispersions covered in the results, the specific rate of CO oxidation can be considered to be independent of the presence of the Al_2O_3 support. The specific oxidation rates of C_3H_6 over the type I sites of the PM/Al_2O_3 catalysts are at least one order of magnitude lower than those over the PM wire. This may be rationalized by the size effect, i.e., C_3H_6 is a larger molecule than CO and may require several adjacent sites for adsorption, thus not all the surface metal sites are usable for C_3H_6 oxidation.

The quantitative determination of the rates of oxidation for 1-hexene and toluene is hampered by the lower instrumental sensitivity for these molecules and the complexity of the nonstoichiometry of the reaction. Qualitatively, one can see that the characterization and assignment of the two type of sites for the 1-hexene and toluene oxidation are the same as that for CO and C_3H_6. The resemblance to C_3H_6 and contrast to the behavior of saturated hydrocarbons (*9*) supports the idea that double-bond adsorption and breaking is rate controlling.

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REFERENCES

1. Sergey, F. J., Masellei, J. M., and Ernest, M. V., W. R. Grace Co. U.S. Patent 3,903,020 (1974).
2. Hindin, S. G., Engelhard Mineral and Chemical Co., U.S. Patent 3,870,455 (1973).
3. Boudardt, M., "Advances in Catalysis," Vol. 20, p. 153. Academic Press, New York/London, 1969.
4. Carballo, L. M., and Wolf, E. E., *J. Catal.* **53,** 366 (1978).
5. Hanson, F. V., and Boudardt, M., *J. Catal.* **53,** 56 (1978).
6. Bodrikov, I., Khulbe, K. C., and Mann, R. S., *J. Catal.* **43,** 339 (1976).
7. Zanevskaya, O. S., Vol'fson, V. Va, and Chugaeva, O. T., *Kinet. Catal.* (*USSR*) (*Engl. Transl.*) **18,** 777 (1977).
8. Bond, G. C., Fuller, M. J., and Molloy, L. R., "Proceedings, 6th International Congress on Catalysis (London)," Paper No. A-26 (1976).
9. Yu Yao, Y. F., *I&EC Prod. Res. Dev.* **19,** 293 (1980).
10. Yao, H. C., and Rothschild, W. G., *J. Chem. Phys.* **68,** 4774 (1978); **74,** 4186 (1981).
11. Yao, H. C., and Yu Yao, Y. F., *J. Catal.* **86,** 254 (1984).
12. Morooka, Y., and Ozaki, A., *J. Catal.* **5,** 116 (1966).
13. Gerberich, H. R., Cant, N. W., and Hall, W. K., *J. Catal.* **16,** 204 (1970).
14. Patterson, W. R., and Kemball, C., *J. Catal.* **2,** 465 (1963); *Proc. Roy. Soc. London, Ser. A* **207,** 219 (1962).
15. Baddour, R. F., Modell, M., and Heusser, U. K., *J. Phys. Chem.* **72,** 3621 (1968) and references quoted in the paper.
16. Langmuir, I., *Trans. Faraday Soc.* **17,** 621 (1922).
17. Cant, N. W., and Hall, W. K., *J. Catal.* **16,** 220 (1970); **22,** 310 (1971).
18. Wang, T., and Schmidt, L. P., *J. Catal.* **70,** 187 (1981).
19. Yao, H. C., Gandhi, H. S., and Shelef, M., "Metal-Support and Metal-Additive Effects in Catalysis" (B. Imelik *et al.* Eds.), p. 159. Elsevier, Amsterdam, 1982.
20. Yao, H. C., Japar, S., and Shelef, M., *J. Catal.* **50,** 407 (1977).