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SYNERGISM AND KINETICS IN CO OXIDATION OVER PALLADIUM-RHODIUM BIMETALLIC CATALYSTS

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Abstract – The activity and kinetics of CO oxidation over alumina-supported Pd-Rh bimetallic catalysts were investigated. One bimetallic catalyst, Pd-Rh(2), was prepared by two-step impregnation and another, Pd-Rh(1), by simultaneous impregnation. Monometallic catalysts as well as a physical mixture of them were also prepared. The catalysts were characterized by selective chemisorption of both H_2 and CO, and an attempt was made to determine the surface compositions of the bimetallic catalysts. The bimetallic catalysts showed different kinetic behavior, such as higher turnover frequencies (TOFs), lower apparent activation energies and/or negative reaction orders for CO which were smaller in the absolute value, from that of the monometallic catalysts as well as a physical mixture of them. It is suggested that this Pd-Rh synergism is due to an interaction on the catalyst surface, such that adsorbed CO or oxygen on one metal migrates to the other metal site so that the reaction rate is facilitated and also that the particles of Pd and Rh are located close enough to each other for the interaction to occur. On the surface of Pd-Rh (2) most of the Pd and Rh particles existed as separate entities, while a great portion of the particles on Pd-Rh(1) exhibited the surface enrichment of Pd. This explains the higher TOF and the negative reaction orders for CO over Pd-Rh(2) which were smaller in the absolute value than those over Pd-Rh(1).

Key words: *CO Oxidation, Kinetics, Palladium-rhodium, Surface Composition, Synergism*

INTRODUCTION

The modern automotive catalysts for the emission control primarily use platinum (Pt) and rhodium (Rh) as the precious metal components. Currently, however, an interest in the use of palladium (Pd) as a replacement for Pt and/or Rh continues to grow because Pd is relatively abundant and considerably less expensive than either [Williamson et al., 1984; Fisher et al., 1992; Heck and Farrauto, 1995], and a Pd-Rh catalyst has been put into certain commercial automotive tests [Lui and Dettling, 1993]. The CO oxidation over noble metals has been extensively studied because of its practical importance in the control of emissions and also because of its complex kinetic behavior [Taylor, 1984; Ioannides et al., 1995]. Pd has long been recognized as an effective catalyst for the oxidation of CO and hydrocarbons (HC), and Rh is known to be the most effective metal in reducing NO [Fisher et al., 1992]. Rh is, on the other hand, known to be favorably compared with Pt and Pd as the catalyst for CO oxidation [Taylor, 1976; Yao, 1984; Fisher et al., 1992]. Although the CO oxidation has been extensively studied over each of Pt, Pd and Rh and over the Pt-Rh bimetallic catalyst, relatively few studies on the CO oxidation over Pd-Rh catalysts have been reported.

Supported bimetallic catalysts often exhibit certain desirable properties, such as improved activity, selectivity or thermal stability, which are absent in each of the individual metals. While no synergistic effect was observed in CO oxidation over Pd-Rh alloy films [Moss and Whalley, 1972], activity increase was reported over supported Rh catalysts to which Pt or Pd was added [Schlatter and Taylor, 1977] and over supported Pt to which Pd or Rh was added [Fisher et al., 1992]. For these supported catalysts, however, the active metal surface areas and the surface compositions were not reported, and furthermore the method of catalyst preparation was obscurely described. Hence, it is not clear that the activity increase is due to a synergistic effect. Park et al. [1992] have observed that an alumina-supported Pt-Pd catalyst prepared by simultaneous impregnation of the metal-chloride precursors did not show any appreciable activity increase compared with the monometallic catalysts. Meanwhile, Oh and Carpenter [1986] have reported that a Pt-Rh bimetallic catalyst exhibited synergistic enhancement of the CO oxidation activity when compared with a physical mixture of Pt and Rh monometallic catalysts; they also reported that this synergistic effect was observed over the bimetallic catalyst prepared by two-step metal impregnation, but not over the one prepared by simultaneous impregnation. Lui and Dettling [1993] have reported that a Pd-Rh catalyst prepared with an engineered washcoat to minimize alloying of Pd and Rh can exceed the performances of a current Pt-Rh commercial catalyst and conventional Pd-Rh catalysts, but the details of the catalyst preparation procedure have not been disclosed in the proprietary development work.

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In this work, the kinetics of CO oxidation over alumina-supported Pd-Rh bimetallic catalysts was investigated. The Pd-Rh bimetallic catalysts were prepared by two different impregnation procedures, i.e., two-step and simultaneous impregnation, and the effects of the impregnation procedure were examined. Pd and Rh monometallic catalysts, as well as a physical mixture of them, were also investigated in order to see if any synergistic effects would be observed. The catalysts were characterized by selective chemisorption of both H_2 and CO, and an attempt was made to determine the surface compositions of the bimetallic catalysts.

EXPERIMENTAL

1. Catalyst Preparation

$PdCl_2$ (Inuisho Precious Metals Co.) and $RhCl_3 \cdot xH_2O$ (BDH Chemicals Co., 40 % Rh) were used as the precursors of the noble metals. The support used was a γ-alumina (Harshaw Al-3996R, surface area of 188 m^2/g, pore volume of 0.53 cm^3/g), which was crushed to −70/+100 mesh particles. The catalysts were prepared from aqueous solutions of the metal chlorides and the support dried before use by employing the incipient wetness method. All the impregnated samples were subsequently dried at 393 K for 12 h and calcined at 573 K for 2 h in air. The metal content for each monometallic catalyst was 1 wt%. The Pd-Rh bimetallic catalysts, having the content of 0.5 wt% for each metal (1 wt% total), were prepared by two different procedures. One was by simultaneous impregnation, in which a mixed solution of the two precursors was used. The other was by two-step impregnation, in which Pd was impregnated first and then Rh secondly; after the first (before the second) impregnation the sample was dried and calcined by the same procedure as described above. The catalysts in this work were designated as 1 % Pd and 1 % Rh for the monometallic catalysts, Pd-Rh(1) for the bimetallic catalyst prepared by the simultaneous impregnation, and Pd-Rh(2) for the one prepared by the two-step impregnation. A physical mixture of the monometallic catalysts with the weight ratio of 1 to 1 was also prepared, and it was designated as (Pd+Rh).

2. Selective Chemisorption

CO and H_2 chemisorption measurements were carried out in a conventional volumetric adsorption apparatus by following the procedure given elsewhere [Knor, 1968; Anderson and Pratt, 1985]. The CO (Takachiho Chemicals Co., 99.95 %) and H_2 (Dong-A Gas Co., 99.95 %) gases were further purified with an Oxytrap and a 5A molecular sieve trap. The catalyst samples were reduced under flowing hydrogen of 50 cm^3/min at 373 K for 30 min and then at 473 K for 30 min. After evacuation of the reduced samples at 673 K for several hours, the H_2 adsorption experiments were performed. For the Pd-containing catalysts, in order to avoid formation of the β hydride of Pd which normally occurs at room temperature, the H_2 adsorption experiment was performed at 373 K [Benson et al., 1973], but it was performed only at room temperature for 1 % Rh. After the H_2 adsorption experiment and subsequent evacuation at 673 K for each sample, the CO adsorption experiment was performed at room temperature by employing a dual isotherm method, and the amount of chemisorbed CO was determined by the difference between the first isotherm and the second isotherm [Emmett and Brunauer, 1937; Jung et al., 1982; Yoon and Kim, 1995].

3. Activity Testing

The activity was measured by using a conventional tubular reactor system operating under ambient pressure. The reactor was made of 1/4-inch stainless steel tubing. The catalyst was packed above glass wool at the lower part of the tubing, and the feed gas flowed downward. The catalyst loading was about 0.15 g. The reaction temperature was controlled by an electric heater surrounding the tube, a thermocouple which was directly contacting with the catalyst particles, and a temperature programmer (REX Instrument Co., REX-P100). The catalyst was activated by the same procedure described above and then the reaction experiments were carried out. The feed gases, used as received, were a mixed gas of 10.1 % O_2 in N_2, a mixed gas of 5.03 % CO in N_2 and a pure N_2 gas (Dong-A Gas Co., 99.9 %), and their flow rates were controlled by flowmeters (KOFLOC Co.). The ranges of the reactant feed compositions were from 0.5 to 3.2 % for CO and from 0.5 to 4.0 % for O_2. The total flow rate ranged from 80 to 280 cm^3/min, and the reaction temperature ranged from 433 to 473 K. The effluent gas from the reactor was analyzed by a gas chromatograph (GC) using a 3 m × 1/8 inch Carbosieve S-II column (Supelco Inc.), helium as the carrier gas and TCD as the detector. The oven temperature ranged from 313 to 493 K.

RESULTS AND DISCUSSION

1. Chemisorption Results

The chemisorption results are shown in Table 1. It is generally admitted that the chemisorption stoichiometry of hydrogen on Group 8-10 metals, i.e. H_{ad}/M_s, is 1, where H_{ad} is the amount of dissociatively adsorbed hydrogen atoms and M_s is the amount of surface metal atoms. From the H_2 chemisorption, the number of surface metal atoms or the percentage exposed of metals can be determined. The percentage exposed is defined as the ratio of M_s/M_t, or usually as H_{ad}/M_t for Group 8-10 metals, where M_t is the total amount of the metal(s), and it is given in Table 1. The percentage exposed of Rh in 1 % Rh, 55 %, was relatively high when compared with the percentages exposed in the other catalysts which were around 20 %. The different procedures of impregnation of the two metals did not appear to affect the percentage exposed.

The chemisorption stoichiometry of CO on Group 8-10 metals, CO_{ad}/M_s, has been reported to vary depending on the

Table 1. Results of H_2 and CO chemisorption

Catalyst	Chemisorption [μmol/g-cat]		% exposed, $(H_{ad}/M_t)\times 100$	Surface composition	
	$H_{2,ad}$	CO_{ad}		Pd_s/M_s	Rh_s/M_s
1 % Pd	10.0	12.5	21	1	-
1 % Rh	27.0	90.0	55	-	1
Pd-Rh(1)	9.5	17.8	20	0.70	0.30
Pd-Rh(2)	9.1	20.8	19	0.50	0.50

metal, support and other factors, because several possible forms of adsorbed CO may coexist. The stoichiometries have been reported to range from 0.5 to 1 for Pd due to the presence of both linear and bridged CO, and to range from 1 to 2 for Rh due to the presence of linear and subcarbonyl (or gem-dicarbonyl) CO as the major species especially on highly-dispersed Rh, as summarized in some review articles [Eischens and Pliskin, 1958; Moss, 1976; Somorjai, 1981; Vannice, 1982; Foger, 1984]. For example, from the IR study of CO adsorbed on Carbosil-supported Pd, Eischens and Pliskin [1958] observed that most of the CO was in the bridged form at low surface coverages and the portion of linear CO was about 1/10 at the surface coverage of 100%. From the IR study of CO adsorbed on alumina-supported Rh, Yang and Garland [1957] reported that almost all of the CO adsorbed on a 2% Rh sample is the subcarbonyl form, and that on the samples with higher Rh loadings three species of adsorbed CO, i.e. subcarbonyl, linear and bridged CO, were present with the first species being dominant and the third species being considerably small; thus, the CO_{ad}/Rh_s ratio in any of these samples has been estimated to be 1.5-2.0 [Vannice, 1982]. The results in Table 1 are in agreement with those of the earlier works. The chemisorption stoichiometries of CO, or CO_{ad}/H_{ad}, were found to be 0.625 on 1 % Pd and 1.67 on 1 % Rh. From these ratios and by using the CO_{ad} and M_s balances, the ratio of the bridged to linear CO on 1% Pd was calculated to be 0.60/0.40, and the ratio of the subcarbonyl to linear CO on 1% Rh to be 0.80/0.20 [i.e., for 1% Pd (2)(0.60)(12.5) + (0.40)(12.5)=20.0=2 $H_{2,ad}$=Pd_s; for 1% Rh (1/2)(0.80)(90.0) + (0.20)(90.0)=54.0=Rh_s]. In other words, the fraction of surface Pd atoms covered with the bridged CO was 0.75 and the fraction of surface Rh atoms covered with the subcarbonyl CO was 0.66.

By utilizing the different chemisorption stoichiometries of an adsorbate between different metals, an attempt was made to estimate the surface compositions of the bimetallic catalysts, as has been applied in earlier works [Foger, 1984; Kaminsky et al., 1985; Kim and Yoon, 1996]. One premise on this attempt is to assume that the stoichiometry on each metal in the bimetallic catalyst is the same as that in the monometallic catalyst, although this has been found to be severely violated in some cases. Since this violation occurs especially in the case that the bulk or surface composition of one metal is much higher than that of the other [Kaminsky et al., 1985; Kim and Yoon, 1996], the extent of violation may not be significant for the catalysts in this work. Under the above premise and by using again the CO_{ad} and M_s balances, the surface compositions of Pd and Rh in Pd-Rh(1) were estimated to be 0.70 and 0.30, respectively, and those in Pd-Rh(2) were estimated to be 0.50 and 0.50, respectively. This means that the surface of Pd-Rh(1) is certainly enriched by Pd, in spite of some uncertainty in the premise.

The surface enrichment of one metal in bimetallic alloys and clusters is a well-known phenomenon, and Pd is expected to be enriched in Pd-Rh alloys [Sachtler, 1976; Foger, 1984]. Furthermore, for the binary alloy of Pd and Rh in the bulk composition range of 30-80% Rh, it has been reported that phase separation occurs and it has also been proposed that the crystallites consisting of a Rh-rich phase will be surrounded by other phases having poorer Rh [Moss and Whalley, 1972]. Therefore, the result of the surface composition estimated for Pd-Rh(1) suggests that a large part of the metal particles in this catalyst may be biphasic, consisting of a kernel of a Rh-rich phase surrounded by a Pd-rich phase, and another part may consist of separate particles of Pd and Rh. On the contrary, most of the particles in Pd-Rh(2) may be considered to consist of separate particles of Pd and Rh (in other words, the surface consists of a statistical mixture of Pd and Rh sites as separate entities [Oh and Carpenter, 1986]). This is one effect of the different procedures of impregnation, similar to the observation for Pt-Rh by Oh and Carpenter [1986], which may be explained as follows. After the Pd impregnation and subsequent calcination in air in the course of the two-step impregnation procedure, the catalyst surface is expected to be populated primarily by palladium oxide, and then the majority of the Rh precursors would be deposited onto the alumina surface rather than on top of the palladium oxide particles because the fraction of the support surface area covered by the palladium oxide particles is estimated to be quite small and also because the Rh precursor would display similar affinity for both alumina and palladium oxide [Oh and Carpenter, 1986]. In the course of the simultaneous impregnation procedure, however, the formation of bimetallic (and biphasic in this case) particles would be more probable, since it is considered that the affinity between the two metal-chloride precursors may be greater than that between a metal precursor and the oxide support.

2. Reaction Orders

The reaction orders for CO and O_2 were determined by plotting the averaged reaction rate against the average partial pressure of one reactant, while the partial pressure of the other reactant at the reactor inlet was kept constant at a given set of experiments. Typical sets of the data are shown in Figs. 1

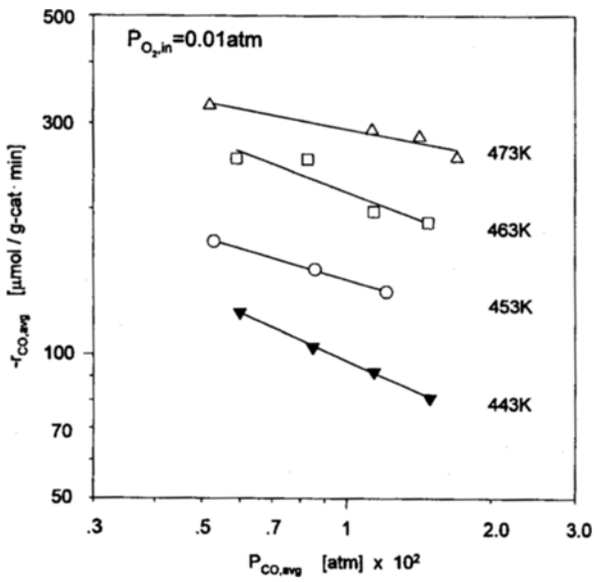

Fig. 1. Dependence of the reaction rate on the partial pressure of CO over Pd-Rh(2) at different reaction temperatures.

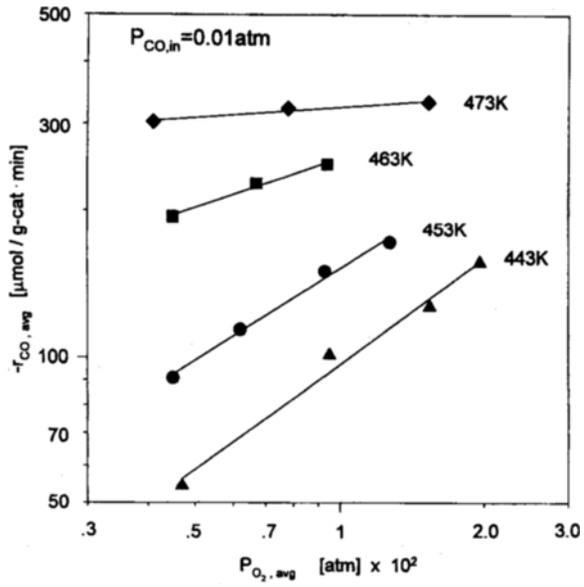

Fig. 2. Dependence of the reaction rate on the partial pressure of O_2 over Pd-Rh(2) at different reaction temperatures.

and 2 for Pd-Rh(2), and the reaction orders over all the catalysts at different temperatures are given in Table 2. One thing to state here is that the chosen rate equation took the power-law form and the mechanistic study was not attempted in this work.

The reaction orders for CO, X's, were all negative, and most of them lay around from −0.6 to −0.8. The reaction orders for O_2, Y's, were all positive, and most of them lay around from 0.6 to 0.8. No pronounced differences or trends were observed depending on the catalyst and temperature, except the X's over Pd-Rh(2). The X's over Pd-Rh(2) exhibited considerably lower absolute values compared with those over the monometallic catalysts and Pd-Rh(1), and this will be discussed later in Subsection 5.

Table 2. Reaction orders and rate constants

Catalyst	T [K]	X (for CO)	Y (for O_2)	$k \times 10^6$
1 % Pd	443	−1.47	0.60	0.38
	453	−0.65	0.71	0.72
	463	−0.73	0.61	1.53
	473	(−0.07)[a]	0.60	3.08
1 % Rh	433	−0.55	0.67	0.78
	453	−0.70	0.70	2.62
	473	(−0.07)[a]	(0.30)[a]	6.84
(Pd+Rh)	443	−0.58	1.27	0.82
	453	−0.79	0.67	1.39
	463	−0.80	0.81	2.74
	473	−0.61	0.53	3.88
Pd-Rh(1)	433	−0.69	0.74	0.64
	443	−0.83	0.60	1.09
	453	−0.55	0.66	1.41
	463	(−0.08)[a]	(0.46)[a]	2.74
Pd-Rh(2)	443	−0.42	0.75	1.55
	453	−0.29	0.67	2.43
	463	−0.37	(0.25)[a]	3.64
	473	−0.20	(0.07)[a]	4.79

[a]less reliable due to high conversions or possible falsification of the kinetics (see text).

The reaction orders over the monometallic catalysts are in agreement with those reported in the literature over Pd [Matsushima et al., 1975; Engel and Ertl, 1979; Yao, 1984; Berlowitz et al., 1988; Landry et al., 1990; Choi and Vannice, 1991; Logan and Paffett, 1992] and over Rh [Yao, 1984; Goodman and Penden, 1986; Oh et al., 1986; Ioannides et al., 1995], in which X's were near −1 and Y's were near 1 under the similar reaction conditions to those in this study; as the partial pressures of both reactants became higher, both X's and Y's changed more or less toward zero. The negative reaction order for CO indicates that, under the reaction conditions in this study, CO occupies most of the metal surface and thus inhibits the adsorption of oxygen because CO adsorbs more strongly than oxygen. Therefore, the reaction rate will be limited by the adsorption rate of oxygen or the desorption rate of CO [Engel and Ertl, 1979; Oh et al., 1986; Berlowitz et al., 1988; Choi and Vannice, 1991; Logan and Paffett, 1992; Ioannides et al., 1995].

Some of X's and Y's, especially at high temperatures, appeared to be considerably lower in absolute values (closer to zero) than the others at lower temperatures over the same catalyst. One reason for this is considered due to high conversions of the reactants because the reaction rates are high at high temperatures, which violate the assumption of a differential reactor employed as a requirement for estimation of reaction orders. At lower temperatures the conversions were in most cases lower than 20 or 30 %, but at the higher temperatures those were in many cases higher than 50 %. Usually a conversion of 20 or 30 % may be too high for the reactor system to be called differential, but in this case of CO oxidation this may be considered to be acceptable because the apparent overall reaction order, X+Y, is near zero and high conversions of that much would not significantly distort the determined values of the reaction orders. Another possible reason may be the so-called falsification of the kinetics, which is caused by mass and heat transfer limitations between the bulk gas phase and the catalyst particles due to the high reaction rate [Satterfield, 1980]. In this case, the both reasons are considered to be simultaneously applicable. Consequently, the confidence in those reaction orders may be low, and those values are put in parentheses in Table 2. Nevertheless, these values were used in the following analyses of the data.

3. Rate Constants

Although the conversions were low in most cases, they were high in some cases. Hence, the rate constants were estimated by using the performance equation for the integral reactor rather than that for the differential reactor, and they were given also in Table 2. Actually, we had estimated the rate constants by using the performance equation for the differential reactor, and found that the differences between the two values estimated by the different methods were sufficiently small even at high conversions, say, being smaller than 10 % at most. Thus, the assumption of the differential reactor may be considered to be valid in most cases in the estima-

tion of the kinetic parameters in this study. A rate constant in Table 2 at a given temperature is the average value of several values obtained under different partial pressures of the reactants; the largest deviation from the average value were about 10 %, but such cases were only a few.

The rate constant in this study has the unit of $10^{2(X+Y)}\times$ mol·atm$^{-(X+Y)}$/(g-cat·s). The main reason for affixing '$10^{2(X+Y)}$' is simply for the sake of convenience, that is, to easily calculate the reaction rate because the reaction orders are not integers and the partial pressures are 10^{-2} atm of the orders of magnitude.

4. Turnover Frequencies and Apparent Activation Energies

A few of the requirements in estimating the activation energy from the conventional ln(k)- or ln(rate)-1/T relationship are the same reaction orders as well as the same partial pressures of reactants or low conversions with respect to temperaure in a set of experiments. However, these were not satisfactorily met in this reaction system. Hence, the apparent activation energies (E_{app}'s) in this study were estimated by using the turnover frequencies (TOFs) at different temperatures calculated from the rate equations obtained above with the same partial pressures of the reactants. Plots showing the relationships between ln(TOF) and 1/T are given in Fig. 3, and the data show good linear relationships. The obtained E_{app}'s are listed in Table 3, and it is noted that the E_{app}'s for the bimetallic catalysts are lower than those for the monometallic catalysts and the physically mixed catalyst. This is considered due to interactions of Pd and Rh, and will also be discussed later. The E_{app}'s for the monometallic catalysts in this work lie in the range of those previously reported, most of which range from about 90 to 140 kJ/mol at above 400 K [Yao, 1984; Goodman and Penden, 1986; Berlowitz et al., 1988; Wong and McCabe, 1989; Choi and Vannice, 1991; Oh and Eickel, 1991; Logan and Paffett, 1992; Ioannides et al., 1995].

Fig. 3 shows that the TOFs for 1 % Pd, 1 % Rh and (Pd+Rh) in the temperature range studied are about the same to each other but those for the bimetallic catalysts are higher than these. This is considered due to a synergistic effect of the two metals. Discussion about this will also be made later in the next section.

From the reported data available in the literature under similar reaction conditions to those in this study, the TOFs under the same conditions were estimated and listed in Table 4 for comparison. Over Pd and Rh catalysts, it has been shown that the reported TOF values may vary by factors of greater than 5 to more than 10, even for the same catalyst system studied by the same investigators [Yao, 1984; Choi and Vannice, 1991], and it was again noted that the TOF values over the monometallic catalysts in this work were somewhat lower than some reported values or considerably lower than others. One reason for the relatively low TOFs

Table 3. Apparent activation energies estimated from TOF ($P_{CO}=P_{O2}=0.01$ atm)

Catalyst	1 % Pd	1 % Rh	(Pd+Rh)	Pd-Rh(1)	Pd-Rh(2)
E_{app} [kJ/mol]	121	92.9	93.3	78.2	66.1

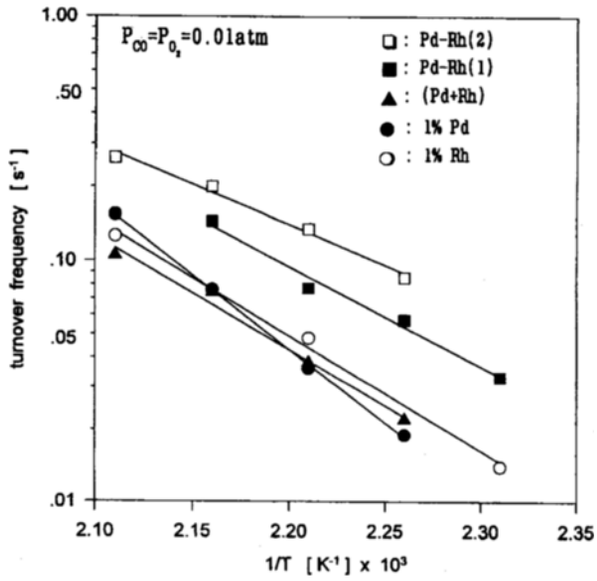

Fig. 3. Arrhenius plots: log(TOF) vs. 1/T.

Table 4. Reported TOF's for CO oxidation (T=453 K, $P_{CO}=P_{O2}=0.01$ atm)

Catalyst	TOF [s^{-1}]	Ref.[a]
1 % Pd	0.038	This work
Pd(110)	0.06	[1]
4.88 % Pd/Al_2O_3	0.09	[2]
2.19 % Pd/δ-Al_2O_3	~0.2	[3]
1% Rh	0.048	This work
Rh(100), Rh(110)	~0.2	[4]
0.01 % Rh/θ-Al_2O_3	0.32[b]	[5]
0.5 % Rh/γ-Al_2O_3	0.11	[6]
0.03 % Rh/θ-Al_2O_3	~0.08	[7]
0.5 % Rh/α-Al_2O_3	0.25	[7]
0.5 % Rh/γ-Al_2O_3	~0.16	[8]
(Pd+Rh)	0.038	This work
Pd-Rh(1)	0.075	This work
Pd-Rh(2)	0.132	This work

[a]Ref.: [1] Berlowitz et al., 1988; [2] Landry et al., 1990; [3] Choi and Vannice, 1991; [4] Goodman and Penden, 1986; [5] Oh et al., 1986; [6] Wong and McCabe, 1989; [7] Oh and Eickel, 1991; [8] Ioannides et al., 1995.

[b]Based on CO chemisorption on the catalyst used for about 1 year.

in this study might be due to the relatively low temperatures of catalyst calcination and reduction, compared with the usual temperatures of 573-773 K in other studies [for example, Yao, 1984; Landry et al., 1990; Choi and Vannice, 1991; Ioannides et al., 1995], which result in insufficient reduction to some degree. In Fact, it has been reported that different calcination and/or reduction temperatures may result in different TOF values [Yao, 1984; Wong and McCabe, 1989], although the CO oxidation over noble metals is more widely regarded as a structure-insensitive reaction [Boudart and Djéga-Mariadassou, 1984; Oh and Eickel, 1991; Ioannides, 1995].

5. Discussion on Synergism

The Pd-Rh bimetallic catalysts in this work exhibited dif-

ferent kinetic behavior from that of the monometallic catalysts and a physical mixture of them, such as negative reaction orders for CO which were smaller in the absolute value, lower activation energies and/or higher TOFs. The reason for the absence of synergism in the physical mixture of the monometallic catalysts is considered due to the distance between the particles of Pd and Rh which is not close enough for the interaction to occur; in other words, a short-range surface interaction is needed for the synergism, as has also observed and suggested by Oh and Carpenter [1986]. However, the mechanism of synergism or what kind is the surface interaction is not still well understood.

As mentioned in Subsection 2, it has been proposed from the kinetic model that the reaction rate is limited by the adsorption rate of oxygen or the desorption rate of CO and thus the apparent activation energy is almost equal to the heat of desorption of CO when the surface is dominantly covered with CO [Engel and Ertl, 1979; Oh et al., 1986; Berlowitz et al., 1988; Choi and Vannice, 1991; Logan and Paffett, 1992; Ioannides et al., 1995]. The apparent activation energy over 1 % Rh is considerably lower than that over 1 % Pd. This may be explained by the lower heat of desorption of CO or by the relatively lower surface coverage of CO or higher surface converage of O_2 on Rh compared with that on Pd. The adsorption of O_2 on Rh may be easier than on Pd, if considering that rhodium oxides are reported to be easily formed especially on supported Rh [Kim et al., 1980; Oh and Carpenter, 1983] or that desorption of the CO on Rh, most of which is not likely in the bridged form as described in Subsection 1, may be easier than that of the bridged form on Pd. This does not mean that the heat of desorption (or adsorption) of CO or the surface coverage of CO is lower than that of O_2 on the Rh surface. On the contrary, the Rh surface can still be covered dominantly with CO, but probably to a less extent compared with the Pd surface. The similar reaction orders over both Rh and Pd are not necessarily in contradictory to the above explanation as long as the surfaces are occupied much more with CO than with O_2, since the reaction orders can be affected by some other factors such as relative rates of adsorption and desorption or relative heats of adsorption and desorption of O_2 and CO on the same metal (in other words, relative values of the adsorption terms in the Langmuir-Hinshelwood kinetic model) under given temperatures.

If there occurrs migration of the adsorbed oxygen or CO from Rh to Pd or vice versa while maintaining its excited state, the synergism of the bimetallic catalysts may be explained as follows. Migration of adsorbed species on the metal surface, through the support surface or through the space (hopping) has often been suggested to explain an enhanced reaction rate, although there is no direct evidence for that and it is not well understood [Smith, 1981; Boudart and Djéga-Mariadassou, 1984]. If this were to occur, readsorption of the migrated species or its surface reaction with the other species at the different metal site will proceed more rapidly. Migration of CO from Rh to Pd or migration of oxygen from Pd to Rh would be more plausible than the other cases. A similar suggestion has been given by Oh and Carpenter [1986] in the CO oxidation over the Pt-Rh catalyst, in which it is required that the particles of different metals are located close enough. Then, the higher TOF for Pd-Rh(2) than for Pd-Rh(1) can be explained by the more balanced numbers of separate particles of Rh and Pd in Pd-Rh(2) than in Pd-Rh(1). The negative reaction orders for CO over Pd-Rh (2), being smaller in the absolute value than those over the other catalysts, could be explained by the same token, because a negative reaction order which is greater in the absolute value for a reactant indicates that removal of that reactant from the surface is more difficult.

Oh and Carpenter [1986] has suggested as another possible interpretation of the synergism in CO oxidation that the palladium (or platinum) enhances the activity of the rhodium by promoting and stabilizing a reduced condition of Rh because of Pd (or Pt) being oxidized less easily, if taking into account the observation that rhodium metal is more active than its oxide [Kim et al., 1980; Oh and Carpenter, 1983]. However, this is a matter of speculation without direct evidence and it is questionable whether this could be applicable to the case of this work under the net oxidizing environment.

CONCLUSIONS

The supported Pd-Rh bimetallic catalysts showed different kinetic behavior, such as higher TOFs, lower apparent activation energies and/or negative reaction orders for CO which were smaller in the absolute value, from that of the monometallic catalysts as well as a physical mixture of them. It is suggested that this Pd-Rh synergism is due to an interaction on the catalyst surface, such that adsorbed CO or oxygen on one metal migrates to the other metal site so that the reaction rate is facilitated and also that the particles of Pd and Rh are located close enough to each other for the interaction to occur. The surface compositions of the bimetallic catalysts were estimated from both H_2 and CO chemisorption. On the surface of the bimetallic catalyst prepared by two-step impregnation, Pd-Rh(2), most of the Pd and Rh particles can be considered to exist as separate entities, while a significant portion of the particles on the surface of the catalyst prepared by simultaneous impregnation, Pd-Rh(1), can be considered to consist of bimetallic particles and exhibit the surface enrichment of Pd. This explains the higher TOF and the negative reaction orders for CO over Pd-Rh(2) which were smaller in the absolute value than those over Pd-Rh(1).

NOMENCLATURE

CO_{ad} : amount of adsorbed CO [μmol/g-cat]
E_{app} : apparent activation energy [kJ/mol of CO]
$H_{2,ad}$: amount of adsorbed hydrogen molecules [μmol/g-cat]
H_{ad} : amount of adsorbed hydrogen atoms [μmol/g-cat]
k : reaction rate constant $[\text{mol}\cdot\text{atm}^{-(X+Y)}/(\text{g-cat}\cdot\text{s})\times 10^{2(X+Y)}]$
M_s : amount of (total) surface metal atoms [μmol/g-cat]
M_t : amount of total metal atoms [μmol/g-cat]
P_{CO} : partial pressure of CO [atm]
$P_{CO,avg}$: average partial pressure of CO between reactor inlet and outlet [atm]

$P_{CO,in}$: partial pressure of CO at reactor inlet [atm]
P_{O_2} : partial pressure of O_2 [atm]
$P_{O2,avg}$: average partial pressure of O_2 between reactor inlet and outlet [atm]
$P_{O2,in}$: partial pressure of O_2 at reactor inlet [atm]
Pd_s : amount of surface Pd atoms [μmol/g-cat]
$-r_{CO,avg}$: reaction rate of CO consumption to CO_2 [μmol/(g-cat·min)]
Rh_s : amount of surface Rh atoms [μmol/g-cat]
T : absolute temperature [K]
TOF : turnover frequency calculated by using H_2 chemisorption [s^{-1}]
X : reaction order for CO [-]
X_{CO} : conversion of CO [- or %]
Y : reaction order for O_2 [-]

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