JOURNAL OF CATALYSIS **161,** 517–523 (1996)
ARTICLE NO. 0213

The Influence of Support on the Low-Temperature Activity of Pd in the Reaction of CO Oxidation

3. Kinetics and Mechanism of the Reaction

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Received September 21, 1994; revised October 27, 1995; accepted January 24, 1996

The unsteady and steady-state kinetics of low-temperature CO oxidation over Pd supported on TiO_2, SiO_2, and Al_2O_3 were investigated by using pulse/flow microcatalytic installation. *In situ* Fourier-transformed IR spectroscopy was used to monitor Pd surface under reaction conditions. The kinetic parameters were found to differ considerably from those typical for the high-temperature region. Room-temperature CO oxidation was demonstrated to be structure-sensitive and to proceed via interaction between weakly bound CO and oxygen located at defect centers. Analysis by a semiempirical interacting bonds method showed weakly bound forms of CO to appear due to cooperative Pd–Pd bond rearrangement induced by CO adsorption/desorption processes, while oxygen incorporation into the subsurface layer hinders this reconstruction, thus strengthening Pd–CO bond. In the range of 298–373 K, transition to a mechanism of the usual Langmuir–Hinshelwood type occurs, affecting observed kinetic features of the reaction.

INTRODUCTION

In the preceding parts of this series of papers (1, 2) we demonstrated weakly bound forms of CO adsorbed on supported Pd to be highly reactive, easily interacting with gas-phase oxygen at room temperature. EXAFS, TEM, and IR data suggested that these forms appear to be due to surface disordering or its decoration by support fragments.

To elucidate the role of these weakly bound forms in the low-temperature catalytic CO oxidation, dynamics of the steady-state attainment and the stationary kinetic parameters should be analyzed. Besides, supposed steps of the reaction scheme have to be verified by pulsing mixtures of either oxygen or CO in He onto the steady-state surface and measuring the rate of the reaction product—CO_2 evolution.

Interrelation between support-induced structure sensitivity of the low-temperature reaction and abundance/energetics of the weakly bound forms of carbon monoxide deserves special attention. The possible impact of flexibility of the open-type Pd faces easily rearranging both in vacuum and under the effect of reacting gases (3) is also worth considering. To choose the most probable types of defect surface centers, a semiempirical interacting bonds method (IBM) earlier successfully used for oxides (4) and supported Pt (5) seems to be also helpful here.

EXPERIMENTAL

The details of samples preparation (2.3% Pd/TiO_2, 2.6% Pd/Al_2O_3, 2.47% Pd/SiO_2) and some their characteristics are given in (1). In all experiments, pulse/flow microcatalytic installation and vibrofluidized bed microreactor were employed, helium being used as a carrier gas; other details of the experimental techniques are given in (2). *In situ* IR spectroscopy experiments were carried out using a flow cell and a IFS-113v Fourier Bruker spectrometer with a MCT detector at 4 cm^{-1} resolution.

RESULTS

Kinetic Data

Catalytic activity relaxations. As a typical example, Fig. 1 shows the temperature dependencies of the initial (in the first pulse of reaction mixture feeded on the fresh catalyst surface) and steady-state activities for Pd/TiO_2. The highest activity is obtained in the first pulse, the quasistationary activity in the pulse regime is considerably lower, while in the stream of reaction mixture a further fall in activity is well manifested. Therefore, interaction with the reaction media decreases the low-temperature catalytic activity. According to (6, 7), a rapid variation of activity during the first pulses (~10–30 s) is primarily determined by attainment of the steady-state CO surface coverages, thus blocking sites for oxygen adsorption. The difference between the rates in the pulse and flow regimes (Fig. 1) is in part explained by desorption of a weakly bound carbon monoxide, thus leaving centers accessible for oxygen adsorption.

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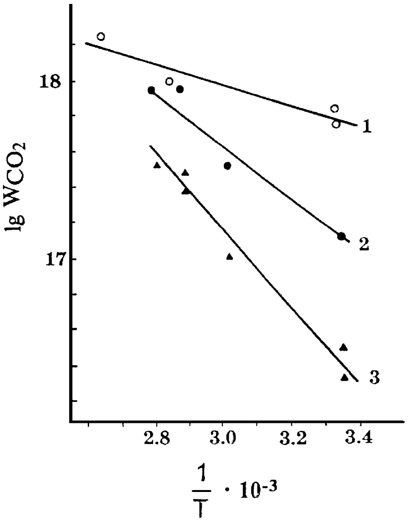

FIG. 1. Arrhenius plots of the CO formation rate for Pd/TiO_2 during CO catalytic oxidation. 1% CO + 1% O_2 in He. 1, First pulse after standart pretreatment; 2, quasistationary level of activity achieved after 10–15 pulses of reaction mixture; 3, steady-state activity in flow regime.

A dynamics of the steady-state activity attainment was found to depend upon the support nature (Fig. 2). For Pd/SiO_2 a monotonous decrease of the gas-phase CO consumption rate (i.e., a sum of the rates of CO adsorption and oxidation) is accompanied by extreme dependence of the rate of CO_2 evolution that is typical for the surface reaction of a Langmuir–Hinshelwood (L–H) type between the adsorbed CO and oxygen (6, 7). Domination of a moderately bound (and thus capable of reacting with adsorbed oxygen at ambient temperatures) form of adsorbed CO (2) seems to explain this type of relaxation. On the contrary, for Pd/TiO_2 and Pd/Al_2O_3 a monotonous decrease of the rates of CO_2 evolution (as well as CO conversion) is observed (Fig. 2). Such dependence seems to indicate that CO_2 production rate is mainly determined by interaction of a weakly bound carbon monoxide with gaseous or adsorbed oxygen. In the case of Pd/Al_2O_3, the reaction rate falls abruptly due to a rapid attainment of a nearly monolayer coverage of the surface by a strongly bound carbon monoxide. For Pd/TiO_2 the activity decline is relatively small due to a lower steady-state CO coverage (2). Hence, dynamics of the unsteady-state catalytic reaction appears to be affected by the peculiarities of CO bonding with the surface of supported Pd. A slow rate decline observed at $t > 10$–30 s is probably due to oxygen incorporation into the subsurface layer, thus strengthening the Pd–CO bond (2).

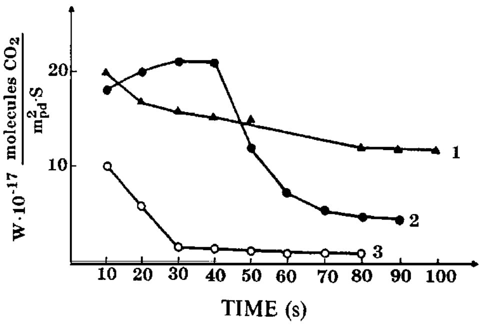

FIG. 2. Dynamics of CO_2 evolution in the pulses of 1% CO + 19% O_2 in He at 293 K. 1, Pd/TiO_2; 2, Pd/SiO_2, 3, Pd/Al_2O_3.

Steady-state catalytic parameters. The temperature dependencies of the stationary CO catalytic oxidation rates in the pulses of 1% CO + 19% O_2 in He mixture are shown in Fig. 3a (Pd/TiO_2) and Fig. 3b (Pd/SiO_2). Table 1 compares the steady-state kinetic parameters found here and the literature data (8–11). In the low-temperature region, structural sensitivity of Pd-catalyzed CO oxidation reaction is quite obvious: at the same composition of reaction mixture specific rates vary broadly. Further, activation energies and reaction orders differ considerably from those typical for high-temperature structure-insensitive reaction (13). Hence, some other mechanism not of a L–H type operates in the low-temperature region. This conclusion is supported by the observed difference in temperature dependencies of the steady-state rates of catalytic reaction and that of the maximum rate (2) of the surface reaction $CO_{ads} + O_{ads}$ (Fig. 3).

Rate-determining step. To elucidate this mechanism or at least to clarify the rate-determining step, the rate of the catalytic reaction should be compared with those of the proposed steps. To do so, after attainment of a low-temperature steady-state activity in the stream of the reaction mixture (1% CO + 19% O_2) and purging the reactor by He at the same temperature, the rates of CO_2 evolution in the first pulses of various mixtures ($W(CO + O_2)$, a pulse of the reaction mixture; $W^1(CO)$, pulse of 1% CO in He; and $W^1(O_2)$, a pulse of 1% O_2 in He) were measured (Table 2).

According to step-wise desorption data (2), in pulse conditions the coverage of the Pd surface by CO is lower than that under the stream of a reaction mixture. Hence, the catalyst surface is less blocked by adsorbed CO that explains higher activities in the former case. So the rates of the catalytic reaction and those of the supposed steps were compared at θ_{CO} values as close to each other as possible, namely, in the pulse mode.

For various reaction schemes, relation between these rates is expected to be quite different. If the rate of catalytic reaction is determined by interaction between a weakly bound CO and oxygen strongly chemisorbed at steps, kinks, etc. (13), the rate of CO_2 evolution in the CO pulse should be equal to that in the pulse of a reaction mixture provided that θ_O is not changed appreciably under the pulse action. In our experiments an amount of oxygen removed from the Pd surface by a CO pulse was usually quite low—less than

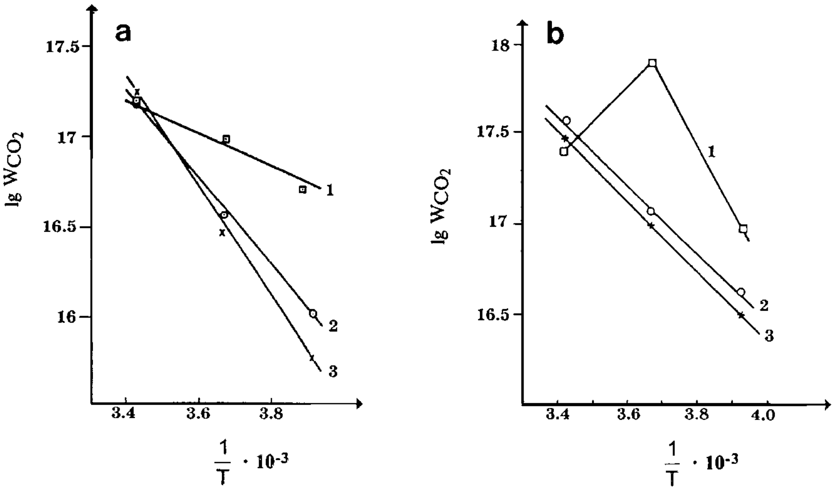

FIG. 3. Arrhenius plots of CO_2 formation rates for Pd/TiO_2 (a) and Pd/SiO_2 (b). 1, Rate of CO catalytic oxidation in the mixture of 1% CO + 19% O_2 in He, pulse regime; 2 and 3, the maximum rate of CO_2 formation during titration of CO adsorbed on Pd surface precovered by oxygen (2) and on the steady-state surface (3).

1% of monolayer. In all cases (Table 2), $W^1(CO)$, the rates of the $(CO_{gas} + O_{ads})$ stage were found to be considerably less than the rate of catalysis, $W(CO + O_2)$. It suggests that step $O_{ads} + CO_{gas}$ is not rate-determining.

If the interaction between CO and a weakly bound (or gas phase) oxygen is a rate-determining step, $W^1(O_2)$ and $W(CO + O_2)$ are expected to be equal. Some underestimation of the rate of this stage is expected if weakly bound CO easily desorbing into the He stream also participates in the reaction. On the contrary, overestimation of this rate ($W^1(O_2)/W(CO + O_2) > 1$) may be caused by a considerable change of θ_{CO} under the oxygen pulse, thus increasing a number of surface centers accessible to oxygen adsorption. Indeed, for our steady-state samples, curves of adsorbed CO titration by gas-phase oxygen were found to go through the pronounced maximum at $\theta_O \sim \theta_{CO} \sim 0.5$ (2). To minimize this effect, we have used here a rather dilute oxidizing mixture (1% O_2 in He). Due to such difference between the oxygen concentrations in the reaction mixture (19%) and the oxidizing pulse (1%), and taking into account a positive reaction rate order of oxygen (~0.5, Table 1), one would expect $W(CO + O_2)/W^1(O_2) \sim 2–3$ even if stage $CO_{ads} + O_{2gas}$ is rate-determining. With all this in mind, we can conclude that data of Table 2 favor the step $CO_{ads} + O_{2gas}$ to be rate-determining. For Pd/Al_2O_3, an apparent overestimation of the rate of this stage at 293 K clearly correlates with the highest ability of this sample to be oxidized, revealed by EXAFS (1). In such a way, under the oxygen pulse action

TABLE 1

Kinetic Parameters of the Catalytic CO Oxidation on Pd-Containing Catalysts

Catalyst	Temperature range (K)	Activation energy (kJ/mol)	n_{CO}	n_{O_2}	Reaction rate at 313 K[a, b]	Reference
Pd(foil)	473–673	−8.84	~1	0	3×10^9	8
	<450	47.8	−0.5	1		
Pd (foil)	323–373	27.5	1	−0.14	1×10^{14}	9
5% Pd/SiO_2	>400	103	−0.8	1	1.7×10^{14}	10
	<373	50	0.2	0.57		
2% Pd/SiO_2	>400	83	−1	1	—	11
2% Pd/SnO_2	>400	46	0	0.4–0.6	—	11
2.3% Pd/TiO_2	293–400	38	0	0.2–0.5	2.8×10^{17}	This work
2.6% Pd/Al_2O_3	293–333	42	0	—	1.8×10^{16}	This work
2.47% Pd/SiO_2	293–333	0	—	0.4	3.5×10^{16}	This work

[a] Reaction rate in molecules CO_2/m^2 Pd s^{-1}.

[b] Rate value at 313 K and reaction mixture composition 1% CO + 1% O_2 in He was calculated using kinetic parameters given in the Refs. (8–10).

TABLE 2

Rates of Carbon Dioxide Evolution in Catalytic and Titration Reactions

	293 K				273 K		
Catalyst	$W(CO+O_2)$	$W_{fl.}$	$W^1(O_2)$	$W^1(CO)$	$W(CO+O_2)$	$W_{fl.}$	$W^1(O_2)$
Pd/TiO_2	20	12	11	0.5	12	2	1.4
Pd/Al_2O_3	10	0.79	20	—	8	0.5	1.85
Pd/SiO_2	24.5	1.5	6.2	1.7	80	11	8

Note. All rates in units of 10^{16} molecules CO_2/m^2 Pd s^{-1}. $W(CO+O_2)$, rate in the first pulse of the reaction mixture after switching from the flow to pulse regime. $W_{fl.}$, rate in the flow regime. W^1, rate in the first pulse of CO or O_2 given after switching from the flow to pulse regime. Reaction mixture, 1% CO + 19% O_2 in He; oxidizing mixture, 1% O_2 in He; reducing mixture, 1% CO in He.

a pronounced change of θ_{CO} occurs, thus enhancing W^1. For all samples, the increase of a discrepancy between the $W(CO+O_2)$ and the $W^1(O_2)$ as temperature decreases suggests increasing participation of a weakly bound CO form in the overall catalysis rate. This factor could not be taken properly into account when measuring the rate of CO_2 evolution under the action of a CO-free oxidizing pulse (*vide supra*). The observed reaction orders (Table 1) are not in contradiction with the proposed scheme.

From the point of view of a suggested mechanism, high activity of Pd/SiO_2 at 273 K is determined by the low-temperature form of CO specific for this catalyst (2). The catalytic rate decrease in the temperature range from 273 to 293 K (Fig. 3b) and apparent zero activation energy for this catalyst above 293 K (Table 1) could be assigned to desorption of this form earlier proved to be reactive in titration experiments (2). At 313–370 K the most active catalyst is Pd/TiO_2 due to a moderate coverage of its surface by the form of CO desorbing in this range of temperatures (2). Since in steady-state conditions the amount of CO adsorbed on this catalyst is lower than for other samples (θ_{CO} at high oxygen pressure being below 0.5) (2), the catalytic reaction at temperatures higher 293 K seems to proceed primarily via interaction of the adsorbed CO and adsorbed oxygen. Indeed, direct evidence for this statement is provided by the coincidence of the steady-state catalytic rate measured here and maximum rate of the surface reaction $CO_{ads} + O_{ads}$ ($\theta_{CO} \sim 0.5$) (Fig. 3). As a result, for Pd/TiO_2 transition to a high-temperature state of the surface mainly covered by oxygen proceeds continuously (14). In contrary, a steep fall in CO coverage and corresponding jump in activity occur for Pd/Al_2O_3 and Pd/SiO_2 around 380–400 K (14).

IR Spectroscopy

Figure 4 shows that in steady-state conditions even in mixtures with an oxygen excess Pd is not oxidized to any detectable extent into Pd^{2+}/Pd^{+} states (typical absorption bands at $\sim$2160 and 2120 cm^{-1} are absent). Similar results were earlier obtained for Pd/SiO_2 and Pd/Al_2O_3 at higher temperatures (above 353 K) (6, 7). As follows from these data, oxygen adsorption on the surface of Pd/TiO_2 or its incorporation into the subsurface layer of Pd clusters on Al_2O_3 and SiO_2 (1, 2) leads only to some charging of Pd detectable by a slight shift of the absorption bands to higher frequencies. A similar conclusion about Pd-on-titania clusters charging when mixed CO–oxygen adlayer is formed was earlier derived from the EXAFS data analysis (1).

Substantial differences in the kinetic behavior of Pd/TiO_2 and Pd/Al_2O_3 are mirrored also in the steady-state coverages of Pd surface by reactive species. As is clearly seen from Fig. 4, for the former both linear and bridged forms are greatly depleted by oxygen added into the reaction mixture, while for the latter only a small fraction of the linear form is reactive. This conclusion is in good agreement with the IR data of the previous article obtained in a static cell (2).

Note also enhanced relative intensity of the linear carbonyls band for the steady-state Pd/TiO_2 (Fig. 4). Namely, such phenomenon is expected when a mixed CO–O adlayer is formed (hence, number of neighboring pairs of Pd atoms falls), thus supporting our earlier conclusion based upon indirect STD data (2).

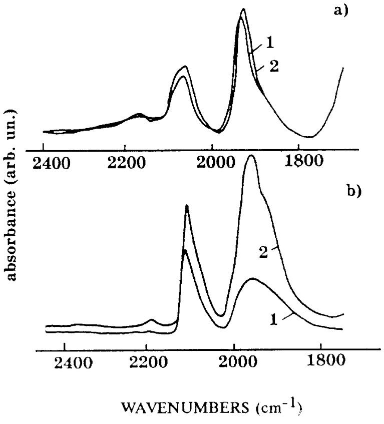

FIG. 4. IR spectra of CO adsorbed on 2.6% Pd/Al_2O_3 (a) and 2.3% Pd/TiO_2 (b). Flow cell, 293 K. 1, 1% CO in air; 2, 5% CO in N_2.

DISCUSSION

The Structure of Pd Clusters and the Enthalpies of CO and Oxygen Adsorption

Our results have demonstrated that at low temperatures high reactivity of weakly bound CO forms determine catalytic properties of supported Pd both in the unsteady-state and under stationary conditions. As judged from the IR-data, such forms can be linear or bridge-bonded dependent upon the support nature. To discriminate possible models of the surface centers capable of stabilizing these weakly bound forms, a semiempirical IBM was used to estimate enthalpies of CO adsorption.

According to (15, 16), initial enthalpies of CO adsorption on various faces of Pd single crystals as well as on foils differ only slightly, being in the range of 142–165 kJ/mol. The increase of coverages was found to decrease a heat of adsorption mainly due to intermolecular repulsion. An amount of the weakly bound CO increases as Pd cluster size decreases (17, 19). Thus, the decrease of the size of Pd cluster supported on α-Al_2O_3 from 50 to 15 Å was accompanied by a nine-fold increase in the amount of low-temperature CO form (q_{des}, ca. 95 kJ/mol) (17).

Some ideas about the structure of supported Pd clusters and its variation induced by chemisorption based upon the EXAFS data are given in the first article of this series (1). The main point is that open faces of the (100) and (110) type easily undergo reconstruction into more dense corrugated layers with a local hexagonal arrangement of atoms (3). The most developed (110) faces of anatase and γ-Al_2O_3, have square or rectangular arrangement of atoms thus favoring the preferential development of the (100) and (110) faces for Pd clusters on these supports. As far as SiO_2 support is concerned, IR spectroscopy of adsorbed CO data assume the increase of the (100) face exposition for highly dispersed Pd particles (18).

Due to corrugation, a part of Pd atoms is situated in the hollows formed by four atoms of the second layer, and a part is bound with only one atom; the others occupy intermediate positions. We expect atoms with the weakest bonding to be squeezed from the surface layer.

In routine IBM procedure (5), Me–L bond energy is considered as a parameter evaluated from the thermochemical data for corresponding bulk compounds. However, up to now such data for Pd carbonyls are absent. As a first approximation, E_{Pd-C} was proposed to be equal to that of the Pt–C bond (446 kJ/mol) (5). However, this assumption overestimates heats of CO adsorption on Pd, while for Pt calculated values were found to be in a good agreement with the experimental ones (5). For correction, we have used a slightly reduced E_{Pd-C} parameter equal to 400 kJ/mol. Some adjustment was also applied to parameter K determining variation of the C–O bond energy (E_{co}) as a function of CO coordination (5): instead of 75 kJ for Pt–CO we used 84 kJ for Pd–CO. The heats of adsorption calculated by using these parameters could not be considered as absolute values, but effect of the local structure of adsorption center and CO coordination on these enthalpies were hoped to be reproduced correctly.

According to our calculations, CO adsorption heats on the regular centers of Pd (100) face are equal to 84 kJ/mol for linear CO and 112 kJ/mol for bridge-bonded CO. As an example of the "squeezed" atom, we have considered Pd atom bound only with four atoms of the first layer. In this case heat of CO adsorption considerably increases, reaching 119 kJ/mol for linear and 132 kJ/mol for bridge-bonded forms, respectively. If after CO desorption an upper Pd atom forms an additional bond with Pd atom of the second (subsurface) layer, heats of CO desorption decrease to 85 and 99 kJ/mol for linear and bridge-bonded forms, respectively.

For quasi-hexagonal reconstructed layer on the Pd (100) face, the heats of CO adsorption in linear and bridge-bonded forms are equal to 67 and 87 kJ/mol, respectively, provided that adsorption is not accompanied by rupture of the Pd–Pd bonds ("rigid surface"). If adsorption causes local reconstruction of a part of the hexagonal network into square one with rupture of two surface Pd–Pd bonds, these values decrease to 39 and 29 kJ/mol, respectively.

The results obtained explain the appearance of a considerable amount of weakly bound CO for Pd on all supports. The highest coverage of the surface of Pd/TiO_2 by this form seems to correlate with the most pronounced shape anisotropy of Pd clusters (*vide supra*) and the highest degree of Pd disordering after CO adsorption revealed by EXAFS (1). Hence, flexibility of the structure of Pd open-type faces is one of the main factors affecting adsorbed CO bonding strength. Some additional effect of Pd decoration by SiO_x species appears to be of importance for Pd/SiO_2, decreasing further heat of CO adsorption. The range of the calculated values of q_{CO} is in a good agreement with the experimental one (17, 20). Note that exposed defect centers possess lower as well as higher heats of CO adsorption in comparison with Pd atoms on closely packed planes; that explains our TPD results (2).

The calculated heats of molecular oxygen adsorption on Pd were found to vary between 46 and 32 kJ/mol for regular and low-coordinated centers, respectively. These values are close to experimental heats of adsorption reported by Popova *et al.* (21).

The Influence of the Subsurface Oxygen

Another important feature of the low-temperature CO oxidation on supported Pd found here is the increase of CO bonding strength and q_{CO} due to incorporation of oxygen into the subsurface layer. This phenomenon is the most pronounced at high CO coverages and appears to be the main reason of a slow activity decline in the reaction media (*vide* *supra*). Quite recently, for the (110) face of Pd a fall in adsorbed CO reactivity due to dissolved oxygen has also been well documented (22). So some models considering such a phenomenon are worth attention. We suppose that in one way or another dissolved oxygen can hinder Pd–Pd bond rearrangement in the course of CO adsorption/desorption that affects heats of adsorption (*vide supra*). To be reversible at ambient temperatures, such rearrangement implies rather low activation barriers. Indeed, the comparatively easy transition between the reconstructed and unreconstructed open face structures of Pt, Ir, Au, and Pd (23) suggests their nearly equal surface energies, while for Pd a "hexagonal" reconstructed layer appears to be somewhat more stable. The relative stability of these layers could be reversed by chemisorption as well as by dissolved admixtures including subsurface oxygen. One of the possible mechanism of the influence of this oxygen is as follows.

Atoms of the subsurface oxygen located in an orderly or a disordered manner along the surface may decrease the sizes of the undisturbed surface regions (patches) of the metal, destabilizing first of all the hexagonal structure. This statement could be easily demonstrated in the framework of a simple model of a pair-wise interaction, though it also will be true for more complex models. The stability of the metal surface layer is mainly determined by Pd–Pd interactions both within this layer and with atoms of the first subsurface layer. For a "square" layer, interaction with the second layer is a linear function of the number of atoms in the patches being equal to four bonds per atom. For a hexagonal layer this function is only approximately linear due to the fact that various atoms in the patches have different numbers of bonds varying from 4 to 1, on the average higher than 3. This uncertainty is caused by the fact that the effective range of interaction is not strictly defined here. Within the layers, the interaction varies linearly only in the case of a great number of atoms in the patches, which gives two bonds per atom for square and three bonds for hexagonal structures. Number of bonds rapidly decreases as patch size falls. Thus, for a limiting case of 1 or 2 atoms, the number of bonds is equal to 0 and 1/2, respectively. This decline is more pronounced for the hexagonal layer, which is simple to demonstrate by calculating the number of bonds. For example, at $n = 36$ the number of bonds is equal to 204 for a square structure and 167 for a hexagonal one (difference, ~20%), while at $n = 164$ the number of bonds is equal to 988 and 969, respectively (difference, ~5%).

Therefore, one of the possible reasons for the decrease of adsorbed CO reactivity due to subsurface oxygen might be some restrictions on the flexibility of Pd open face structures.

Mechanism of the Low-Temperature CO Oxidation

The results obtained in this work have demonstrated that the reaction of low-temperature CO oxidation proceeds via interaction of weakly bound forms of CO and oxygen, specific activity varying rather broadly. It is explained by the fact that a number of surface defect centers which can stabilize weakly bound CO and oxygen changes considerably depending upon the sizes of Pd clusters and the character of their interaction with support as well as with components of the reaction mixture. These defect centers consist primarily of low-coordinated Pd atoms emerged on the reconstructed faces of the (100) and (110) type. Due to comparable heats of CO and molecular oxygen adsorption on these centers, they are not blocked by CO, thus enabling them to maintain a catalytic cycle at ambient or lower temperatures. This type of mechanism can operate only in the low-temperature region since weakly bound CO and oxygen desorb completely at temperatures around 373 K. Due to this phenomenon, such mechanism was not found earlier while studying this reaction at temperatures higher than 400 K (12, 17). In fact, Boudart conclusion about the structure insensitivity of CO oxidation catalyzed by Pd (12) is in a good agreement with our results (2), demonstrating stage $CO_{ads} + O_{ads}$ to be structure-independent at $\theta_{CO} \sim \theta_O$. Indeed, it is this stage that determines catalytic activity of supported as well as bulk Pd at elevated temperatures. Despite of the difference in activation energies of this step for supported and bulk Pd on ca. 24 kJ/mol (and, therefore, two orders of magnitude higher rate constant for supported Pd at 293 K) (2), at temperatures ~400 K the rate constants practically coincide. In this case flexibility of the Pd face structure appears primarily to be caused by disordering due to adsorbed/incorporated oxygen effect (2), thus eliminating all initial structure specificity (3).

Our experiments have not revealed any dependence of the Pd catalytic activity on the types of hydroxyls on various supports (2). Hence, contrary to the proposed earlier scheme (24), low-temperature mechanism hardly involves any surface carboxylates. Note that at temperatures lower than 273 K the most active is Pd on SiO_2 where carbonates are not stabilized at all. It suggests that carbonates could not be active species as well. Our IR data (2) directly prove this point. As far as the participation of molecular oxygen is concerned, a hypothesis of (24–26) seems to be quite plausible. Reaction orders determined in this work are in agreement with this scheme. Moreover, earlier obtained ESR data for Pd/TiO_2 (27) are indeed in favor of the presence of highly reactive O^- species on the reduced sample surface.

CONCLUSION

The unsteady and steady-state kinetic data obtained in this work show that low-temperature CO oxidation over supported Pd proceeds via interaction of the weakly bound CO and oxygen forms. A specific activity of Pd supported on SiO_2, TiO_2, and Al_2O_3 varies over a rather broad range. This is explained by the fact that a number of surface defect centers capable of stabilizing weakly bound CO and oxygen changes considerably, depending upon the Pd cluster morphology and character of their interaction with support as well as with components of the reaction mixture. Possible models of these centers in both "rigid" and "flexible" approximation are considered and heats of CO and oxygen adsorption are estimated using a semiemperical interacting bonds method. Due to rather low and comparable heats of CO and molecular oxygen adsorption on these centers, they are not blocked by adsorbed CO, thus enabling them to maintain a catalytic cycle at ambient or lower temperatures. This type of mechanism can operate only in the low-temperature region since weakly bound CO and oxygen desorb completely at temperatures around 373 K.

ACKNOWLEDGMENT

The authors are grateful to Savchenko V. I. for valuable discussions.

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