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Effects of Altervalent Cation Doping of TiO_2 on Kinetic Parameters of CO Hydrogenation and CO Oxidation on Supported Rh

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The reactions of CO hydrogenation and CO oxidation over Rh are used to determine the influence of altervalent cation doping of a TiO_2 support on kinetic parameters. Rh crystallites are dispersed on TiO_2 doped with W^{6+} cations at concentration levels up to 0.67 at%. It is shown that turnover frequencies of CO hydrogenation increase monotonically with increasing dopant content in the TiO_2 matrix, apparent activation energy is reduced, and selectivity shifts towards smaller-chain saturated hydrocarbons. Turnover frequencies of CO oxidation at low CO/O_2 ratios are shown to pass through a maximum with increasing W^{6+} dopant content of TiO_2. A small activity enhancement is observed at higher CO pressures. The apparent activation energy is found to vary with W^{6+} content. It is proposed that charge transferred from the doped semiconducting carrier to the metal crystallites alters the chemical potential of the crystallites and, therefore, the work function of surface metal atoms, while a strong electrostatic field is caused by the dipole developed at the metal–semiconductor interface. As a result, the mode of H_2 and CO adsorption is altered, as well as the intrinsic kinetic parameters of the reactions investigated. © 1994 Academic Press, Inc.

INTRODUCTION

The effects of altervalent cation doping of TiO_2 on chemisorptive and catalytic properties of supported Pt and Rh crystallites have been discussed in previous publications (1, and references therein). In a preceding paper (1), the influence of W^{6+}-doping of TiO_2 on the mode of H_2 and CO adsorption on Rh crystallites dispersed on doped carriers was presented. In the present communication, the effects on kinetic parameters are presented, employing CO hydrogenation and CO oxidation as probe reactions, and the same family of catalysts, namely 0.5% Rh/TiO_2 ($x\%$ W^{6+}), where x represents the dopant content in TiO_2, in atom%. The same probe reactions have also been used to study the influence of altervalent cation doping on kinetic parameters over Pt dispersed on higher or lower valence doped TiO_2.

Carbon monoxide hydrogenation over Group VIII metals can lead to a large number of products, depending on the particular metal employed and the reaction conditions. CH_4 and higher hydrocarbons can be obtained over Rh, as well as oxygenated molecules, depending on the carrier used to disperse the metal and on process conditions (2). The state of the catalyst under reaction conditions was recently investigated by Efstathiou and Bennett (3), who showed that a large fraction of the metallic surface is occupied by CO, while smaller fractions are occupied by active and inactive carbon. The fraction of the surface occupied by hydrogen is very small. Erdöhelyi and Solymosi (4) report that the dissociation of CO is affected by the carrier and is reduced in the order $Rh/TiO_2 > Al_2O_3 > SiO_2 > MgO$, while surface carbon reacts more easily with H_2 on Rh/TiO_2. This observation is supported by the work of Mori *et al.* (5), who showed that the rate constant of CO decomposition and the rate constant of hydrogenation of CH_x species is reduced in the order $TiO_2 > Al_2O_3 > SiO_2$. It has also been shown (5, 6) that the rate constants are affected by the degree of dispersion of Rh, decreasing with increasing dispersion. Rh/TiO_2 catalysts have also been investigated under SMSI conditions (7, 8). However, contradictory results concerning the influence of SMSI on activity have been reported. Various other parameters influencing activity and selectivity, such as the metal precursor compound (9), promoters (10, 11), support (12, 13), and the oxidation state of Rh (14), have been investigated. Solymosi *et al.* (15) studied the behavior of Rh dispersed on TiO_2 doped with WO_3. A significant enhancement of the activity in the CO/H_2 and CO_2/H_2 reactions was observed. The increased activity was attributed to a higher dissociation rate of CO on W^{6+}-doped catalysts. It was found that larger quantities of carbon were formed on doped catalysts after exposure to CO/H_2 or CO/He mixtures for 60 min at 573 K.

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The CO oxidation reaction over Rh as well as other Group VIII metals has been studied extensively due to inherent complexities of the kinetics of this reaction, such as multiple steady states and periodic or aperiodic oscillations in the CO_2 production rate. The reaction is generally considered to be structure insensitive, since the rate does not depend on the crystallographic orientation of the surface or on the dispersion of the metal (16). The kinetics of the CO/O_2 reaction over Rh can be described by a simple Langmuir–Hinshelwood model with rate controlling step the surface reaction betwen adsorbed CO and adsorbed atomic oxygen (17). The most important characteristics of the kinetics over Rh under UHV conditions are as follows. The rate exhibits a maximum in the temperature range of 130–300°C, depending on the CO partial pressure. The reaction order with respect to CO is -1 (16, 17), while it is positive at very low CO pressures (17). The reaction order with respect to O_2 is $+1$ and assumes negative values when the O_2/CO ratio exceeds a certain value (16–18). The reduction of activity under strongly oxidizing conditions was attributed to oxidation of the Rh surface towards Rh_2O_3.

Kellogg (19) reports surface oxide formation at 500 K for O_2/CO ratios larger than 40. The oxide produced can be reduced with CO at temperatures higher than 420 K. Martens *et al.* (20) report that the oxide formation in Rh/Al_2O_3 catalysts commences at temperatures as low as 100 K in an oxidizing atmosphere, while at 300 K the largest fraction of the surface has been transformed to Rh_2O_3. Concerning the mechanism of the reaction, Cho and Stock (21) have found that the rate of CO decomposition is significant under reaction conditions, approaching 50% of the rate of oxidation at 300°C. Amongst the three modes of CO adsorbed on Rh/SiO_2, the most reactive has been found to be the carbonylic form and the bridged form the least reactive (22).

The aim of the present study was to investigate the influence of altervalent cation doping of TiO_2 on kinetic parameters in the CO hydrogenation and CO oxidation reactions over Rh catalysts. The influence of W^{6+}-dopant concentration in the TiO_2 matrix on kinetic parameters was also investigated.

EXPERIMENTAL

The preparation of W^{6+}-doped TiO_2 carriers and Rh/TiO_2 (D) catalysts has been described in detail in a previous publication (1). The characterization of the catalysts in terms of their electrical conductivity, activation energy of electronic conduction, exposed metallic surface area, and metal dispersion has also been described in the same publication. Similarly, details of the experimental setup and procedures related to temperature-programmed desorption and temperature-programmed surface reaction, have been reported (23).

The amount of surface carbon formed on the catalysts in the presence of $CO/H_2/He$ (8% CO, 24% H_2, 68% He) or CO/He (8% CO, 92% He) mixtures was measured in the same apparatus used for the TPD and TPSR experiments by the following procedure. After reducing the catalyst sample (~0.5 g) in H_2 flow at 250°C for 60 min and purging with He, the catalyst was exposed to the CO/H_2 or CO/He mixture (at a flow of 30 cm^3/min) for 60 min at the temperature of 210 or 250°C. After this treatment, the catalyst was cooled under He and temperature programming (heating rate ~20°C/min) was initiated under He flow, up to 450°C. During TPD, the mass numbers 15(CH_4), 28(CO), and 44(CO_2) were monitored in the mass spectrometer. After cooling again under He, the flow was switched to 10% O_2/He and temperature-programmed oxidation (TPO) of surface carbon was performed. The amount of CO_2 produced during TPO was used to determine the amount of surface carbon formed on the catalysts during the CO/H_2 or CO exposure.

The apparatus employed for CO hydrogenation and CO oxidation rate measurements has been described in detail in a previous publication (23). In all cases, the reactor was operated in the differential mode, with conversions, in most cases, less than 5% and generally less than 10%. The CO/H_2 reaction was investigated in the temperature range of 170 to 250°C. The feed (50–300 cm^3 STP/min) consisted of 24% H_2, 8% CO, and 68% N_2 ($H_2/CO = 3$), on a molar basis. Rate measurements were obtained after the system had reached steady state, which normally required two to three hours. After each set of measurements under a particular set of conditions the catalyst was exposed to H_2 flow for 30 min at 250°C.

The CO/O_2 reaction was investigated in the temperature range 90–150°C. The feed (50–350 cm^3 STP/min) consisted of 0.05 to 5% CO and 0.5 to 18% O_2, balance N_2. The catalyst bed was diluted with γ-Al_2O_3 particles of the same size as the catalyst at a ratio of 5 parts Al_2O_3 to 1 part catalyst. This dilution was found necessary in order to obtain isothermal conditions along the length of the catalyst bed. It was determined that γ-Al_2O_3 was not catalytically active in this temperature range. After each set of measurements the catalyst was exposed to air followed by H_2 flow for 30 min at 200°C to clean the surface from any contamination.

RESULTS

The effects of altervalent cation doping on kinetic parameters were investigated over the Rh/TiO_2 (x% W^{6+}) catalysts, employing CO hydrogenation and CO oxidation as probe reactions. An inherent difficulty with the doped catalysts is the fact that turnover frequencies cannot be directly estimated due to their abnormal hydrogen adsorption capacity, which is used to estimate metal dispersion. It has been shown (1) that the H_2 adsorption capacity of

TABLE 1

Influence of Carrier Doping (D = W^{6+}, Zn^{2+}, or Mg^{2+}) on Specific Activity of Rh in CO Hydrogenation at 210°C

0.5% Rh/ $TiO_2(x\%D)$	H/Rh	N_{CH_4} (s^{-1}) × 10^3		N_{CO_2} (s^{-1}) × 10^3		N_{CO} (s^{-1}) × 10^3		$\frac{(N_{CH_4})_d}{(N_{CH_4})_u}$	$\frac{(N_{CO})_d}{(N_{CO})_u}$
		(a)	(b)	(a)	(b)	(a)	(b)	(b)	(b)
0	0.10	1.5	1.5	—	—	2.5	2.5	1	1
0.11% W^{6+}	0.13	4.0	5.2	0.8	1.0	7.9	10.4	3.5	4.2
0.22% W^{6+}	0.62	3.6	22.8	0.3	1.9	6.6	41.5	15.2	16.6
0.45% W^{6+}	0.81	3.0	24.5	0.3	2.1	5.3	43.0	16.3	17.2
0.67% W^{6+}	0.99	2.9	28.5	0.2	2.2	4.8	48.1	19.0	19.2
0.66% Zn^{2+}	0.03	0.12	0.04	0.11	0.04	0.29	0.10	0.03	0.04
0.66% Mg^{+2}	0.02	1.3	0.34	0.90	0.24	2.6	0.69	0.23	0.28

Note. (a) Based on the H/Rh ratio of each catalyst; (b) based on the H/Rh ratio of the undoped catalyst.

Rh/TiO_2 ($x\%$ W^{6+}) catalysts is a strong function of the dopant content of the carrier. However, the dispersion of doped catalysts is not significantly different from that of the corresponding undoped ones. This conclusion is supported by TEM analysis of doped and undoped catalysts, equilibrium CO adsorption results, and TPD results of CO (1). On the basis of these findings, turnover frequencies of doped catalysts are estimated assuming metal dispersion to be equal to that of the corresponding undoped catalysts. Turnover frequencies are also estimated using the H/Rh ratio observed over each of the doped catalysts. For the reasons stated above, these turnover frequencies are not considered to express the activity of the catalysts in any accurate way.

(*a*) *CO Hydrogenation*

Turnover frequencies of CO hydrogenation, based on CO consumption, as well as on CH_4 and CO_2 formation, obtained over Rh dispersed on TiO_2 doped with W^{6+} cations at 210°C are reported in Table 1. Values shown in column (a) are estimated employing the H/Rh ratio obtained for each catalyst, while values shown in column (b) are estimated on the basis of the H/Rh ratio (dispersion) of the undoped catalyst. It is apparent that, regardless of the way of estimation of turnover frequency, the hydrogenation activity of doped catalysts is higher than that of the undoped one. The true enhancement of activity is between the limits of columns (a) and (b). However, on the basis of the discussion concerning the dispersion of the doped catalysts, the true enhancement of activity is strongly believed to be very close to that reflected by column (b). For this reason, the activity enhancement is quantified by the ratio of turnover frequencies of doped catalysts (results of column (b)) over the turnover frequency of the undoped catalyst, and this is also shown in Table 1. It is apparent that the activity of Rh for CO hydrogenation is significantly enhanced when it is dispersed on W^{6+}-doped TiO_2 carriers. The enhancement is a function of concentration of the dopant, especially at low concentrations.

Higher stability or no deactivation at all for a period of 3 h on-stream was observed on W^{6+}-doped catalysts. A similar result has been obtained by Solymosi *et al.* (15) for Rh catalysts with high W^{6+}-dopant content.

Rh was also dispersed on lower-valence (Zn^{2+}, Mg^{2+}) doped TiO_2 carriers and the influence of these dopants on its hydrogenation activity is also shown in Table 1. A reduction in catalytic activity is observed in this case, especially when TiO_2 is doped with Zn^{2+} cations.

The temperature sensitivity of the CO hydrogenation reaction was investigated within the temperature range 170–250°C. The apparent activation energies, which were observed over the various higher-valence and lower-valence doped catalysts, are shown in Table 2. A reduc-

TABLE 2

Apparent Activation Energies of CO Hydrogenation over 0.5% $Rh/TiO_2(x\%D)$ Catalysts

Dopant *D*	Dopant content (atom%)	E_{CH_4} ($kJ \cdot mol^{-1}$)	E_{CO} ($kJ \cdot mol^{-1}$)
—	—	128	131
W^{6+}	0.11%	127	108
W^{6+}	0.22%	108	104
W^{6+}	0.45%	103	100
W^{6+}	0.67%	108	107
Zn^{2+}	0.66%	51	—
Mg^{2+}	0.66%	66	—

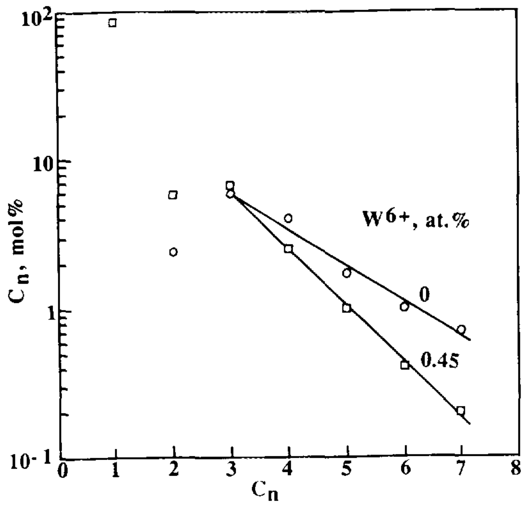

FIG. 1. Schulz–Flory–Anderson distribution of hydrocarbon chains formed over 0.5% Rh/TiO_2 and 0.5% Rh/TiO_2 (0.45% W^{6+}) catalysts.

tion of the apparent activation energy by approximately 20 kJ · mol^{-1} is observed when Rh is dispersed on W^{6+}-doped TiO_2. The reduction in apparent activation energy does not seem to depend on dopant concentration. A larger drop in apparent activation energy is observed when Rh is dispersed on lower-valence (Mg^{2+}, Zn^{2+}) doped TiO_2 carriers. In this case, the apparent activation energy of methanation is reduced by more than 60 kJ · mol^{-1}.

Doping of the carrier with W^{6+} cations was also found to influence the distribution of the hydrocarbons formed. The fraction of saturated C_2 and C_3 hydrocarbons was larger when the reaction was carried out over doped catalysts, at the expense of the corresponding unsaturated ones. Thus, the ratio C_2H_6/C_2H_4 over the undoped catalyst was approximately 0.5, while over the doped catalysts it varied between 4 and 16. Similarly, the ratio C_3H_8/C_3H_6 increased from approximately 0.07 on the undoped catalyst to 0.3–2.1 over the doped catalysts. Furthermore, selectivity towards higher hydrocarbons (C_{4+}) was found to decrease when the reaction was carried out over W^{6+}-doped catalysts.

The hydrocarbons produced followed the Schulz–Flory or Anderson distribution, which is described by relationship (24)

$$\log(\text{mol\%}C_n) = k + C_n \log \alpha, \qquad [1]$$

where C_n is the number of carbon atoms, k is a constant, and α the probability of development of carbon chains. The distributions obtained over the 0.5% Rh/TiO_2 and 0.5% Rh/TiO_2(0.45% W^{6+}) catalysts are shown in Fig. 1. It is apparent that the Schulz–Flory distribution is satisfied for $C_n \geq 3$, while a significant deviation is observed for $C_n = 2$. The same deviation has been observed by other investigators (24) and has been attributed to rapid incorporation of ethylene into other carbon chains. The probability of development of carbon chains, which describes the ability of the catalyst to form higher hydrocarbons, is obtained from the slopes of the linear relationships of Fig. 1. This parameter was found to vary between 0.28 over the undoped catalyst and 0.17 over the 0.67 at% W^{6+}-doped catalyst. It is obvious that, as a result of doping of the TiO_2 carrier with W^{6+} cations, the probability of development of carbon chains is reduced, which is reflected in reduced selectivity of these catalysts for formation of higher hydrocarbons.

(*b*) *CO Oxidation*

The influence of W^{6+}-doping of the TiO_2 support on kinetic parameters was also investigated under CO oxidation conditions in the temperature range of 90 to 150°C. Specific reaction rates at the temperature of 120°C and oxygen partial pressure of 0.06 bar are shown in Fig. 2 as a function of CO partial pressure for catalysts with variable dopant concentration. These experiments were conducted starting with the highest CO partial pressure and gradually progressing towards the lowest. A hysteresis effect was observed when the opposite direction was followed, in which case lower rates were observed. Doping of the carrier with W^{6+} cations does not seem to influence the position of maximum rate, which in all cases appears at a CO partial pressure of approximately 1×10^{-3} bar. However, the dopant concentration does influence the maximum rate, but not in a monotonic fashion.

The influence of W^{6+} concentration in the TiO_2 matrix

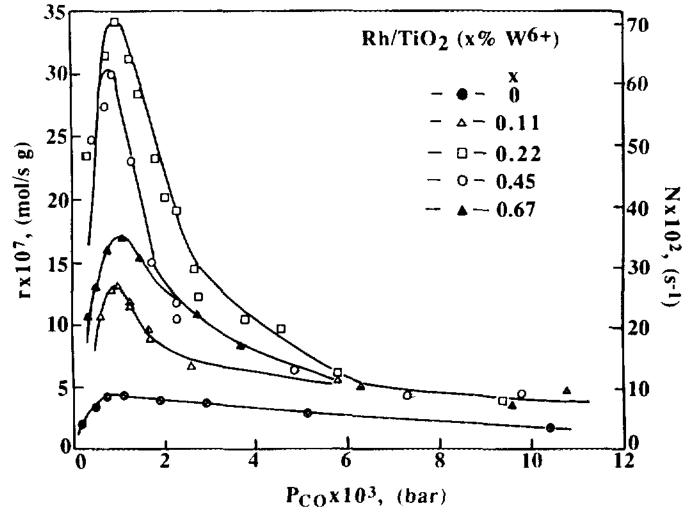

FIG. 2. Influence of CO partial pressure on the rate of oxidation at constant oxygen partial pressure of 0.06 bar and temperature of 120°C.

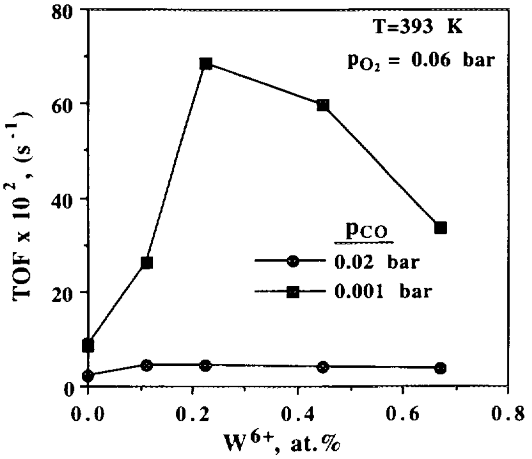

FIG. 3. Influence of W^{6+}-dopant concentration in the TiO_2 matrix on the specific rate of CO oxidation at CO partial pressures of 2 × 10^{-2} and 1 × 10^{-3} bar.

on the specific rate of CO oxidation at two CO partial pressures is illustrated in Fig. 3. At a high CO partial pressure (2 × 10^{-2} bar), where CO hinders oxidation activity (Fig. 2), the doped catalysts are only slightly (50–90%) more active than the undoped catalyst. At a CO partial pressure of 1 × 10^{-3} bar, however, where the maximum specific rate is observed, the activity of the doped catalysts is 3–8 times higher than that of the undoped one, as illustrated in Fig. 3. Maximum activity enhancement is observed when the carrier contains 0.22 at% W^{6+}. The oxidation activity decreases at higher dopant concentrations.

The results shown in Fig. 3, especially those at high CO partial pressures, provide additional evidence that the observed alterations in the adsorption capacity (1) and specific activity of doped catalysts are not due to alterations in metal dispersion, caused by altervalent doping of the carrier. The dispersion of the undoped 0.5% Rh/TiO_2 catalyst was found by hydrogen chemisorption techniques to be approximately 0.10. Taking into account the structure insensitive character of the CO/O_2 reaction and assuming that at a CO partial pressure of 0.02 bar doping does not influence the oxidation activity of the catalysts, the results shown in Fig. 3 can be used to estimate the dispersion of doped catalysts, which comes out to be between 0.15 and 0.19. From TEM analysis, the dispersion of the 0.5% Rh/TiO_2(0.22% W^{6+}) catalyst was estimated to be 0.17 (1). A good agreement in the estimation of the dispersion of the doped catalysts is observed. Furthermore, it is clear that any changes in the degree of dispersion of the metal upon doping of the carrier are not sufficient to account for the large variations in chemisorption capacity and activity which have been observed.

The reaction order with respect to CO, at high CO partial pressures, where the rate is inhibited, was estimated by plots of the logarithm of the observed rate versus the logarithm of the CO partial pressure. The reaction orders with respect to CO are given in Table 3 for the different dopant (W^{6+}) concentrations in the TiO_2 matrix. The classical Langmuir–Hinshelwood model predicts a reaction order of −1. The order observed over the undoped catalyst is significantly lower than this value, but at dopant concentrations higher than 0.22%, the model value is approached.

The influence of oxygen partial pressure on the rate of CO oxidation was investigated over the undoped and 0.22% W^{6+}-doped catalyst, at a CO pressure of 5 × 10^{-3} bar, in the temperature range of 110–130°C. Typical kinetic results obtained over the undoped and 0.22 at% W^{6+}-doped catalyst are shown in Fig. 4. In all cases, the reaction order with respect to oxygen was found to be very close to unity, unaffected by the process of doping the carrier. At high O_2 pressures and at 130°C, oscillations were observed in the case of Rh/TiO_2, but not in the case of the doped catalyst.

The apparent activation energy of the reaction was determined at two different CO pressures, namely 2 × 10^{-2} bar, which is in the rate-inhibiting region, and 1 × 10^{-3} bar, which corresponds to the maximum rate of oxidation. The apparent activation energy at the two CO pressures, for different dopant concentrations, is reported in Table 4. At the CO pressure of 2 × 10^{-2} bar, the apparent activation energy is in the region of 84–103 kJ · mol^{-1}, in agreement with values reported in the literature (15, 16), and it is not affected by carrier doping. On the other hand, at a P_{CO} of 1 × 10^{-3} bar, the apparent activation energy of the doped catalysts is 20 to 30 kJ · mol^{-1} higher than that of the undoped catalyst. However, the apparent activation energy does not seem to be affected by the concentration of the dopant in the carrier.

(c) *Temperature-Programmed Surface Reaction of Adsorbed CO*

The reactivity of CO adsorbed on Rh particles was investigated employing temperature-programmed surface

TABLE 3

Influence of Dopant Concentration of 0.5% Rh/TiO_2(x% W^{6+}) Catalysts on Reaction Order with Respect to CO at High CO Partial Pressures

Dopant content (at%)	n_{CO}
0	−0.60
0.11	−0.58
0.22	−1.01
0.45	−0.84
0.67	−0.88

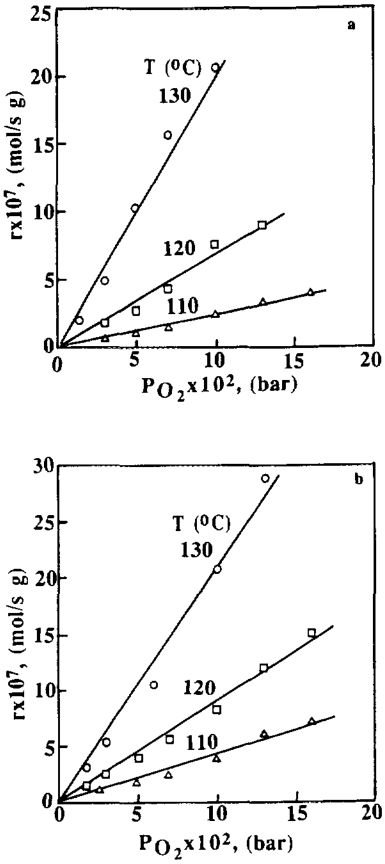

FIG. 4. Influence of oxygen partial pressure on the rate of CO oxidation over (1) 0.5% Rh/TiO_2 and (b) 0.5% Rh/TiO_2(0.22% W^{6+}) catalysts at a CO partial pressure of 5 × 10^{-3} bar.

reaction (TPSR) techniques. CO was adsorbed on the catalyst at 25°C under continuous CO flow for 15 min. The flow was then switched to He for 3 min to clean the reactor and the lines, following which the sample was placed under H_2 flow, while temperature increased in a programmed manner (23°C/min). The only products of the reaction of H_2 with adsorbed CO were found to be CH_4 and H_2O. No CO was observed to desorb prior to reacting.

TABLE 4

Apparent Activation Energy of CO Oxidation over 0.5% Rh/TiO_2(x% W^{6+}) Catalysts at CO Partial Pressures of 2 × 10^{-2} and 1 × 10^{-3} Bar

Dopant content (at%)	E(kJ · mol^{-1})[a]	
	P_{CO} = 2 × 10^{-2} bar	P_{CO} = 1 × 10^{-3} bar
0	90 ± 7	85 ± 5
0.11	91 ± 7	105 ± 13
0.22	103 ± 7	109 ± 5
0.45	84 ± 11	115 ± 11
0.67	94 ± 5	106 ± 3

[a] Errors were estimated from the error of the slope of the Arrhenius plot for 95% confidence.

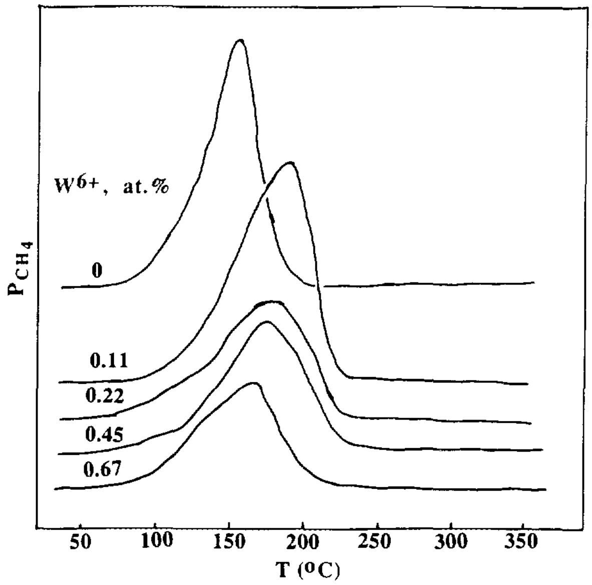

FIG. 5. CH_4 profiles during H_2 TPSR of CO adsorbed on the 0.5% Rh/TiO_2(x% W^{6+}) catalysts (β = 23°C/min).

TPSR profiles obtained over the 0.5% Rh/TiO_2(x% W^{6+}) family of catalysts are shown in Fig. 5. Doping of the carrier with W^{6+} cations results in alterations of the shape and position of the CH_4 peak, which shifts to higher temperatures. The largest shift is observed when the catalyst contains 0.11 at% W^{6+}, but the shift is gradually reduced at higher levels of doping. The shape of the CH_4 peak appears somewhat distorted, on the lower temperature side, for catalysts containing more than 0.22 at% W^{6+}. The temperature of initiation of reaction, T_i, the peak temperature, T_m, and the temperature of completion of the reaction, T_f, are reported in Table 5. With the exception of

TABLE 5

Temperature of Initiation of Reaction, T_i, Peak Temperature, T_m, and Temperature of Completion of Reaction, T_f, during TPSR of CO Adsorbed on 0.5% Rh/TiO_2(x% W^{6+}) Catalysts with H_2

Dopant content at%	T_i (°C)	T_m (°C)	T_f (°C)	Relative quantity of CH_4 produced
0	78	155	205	1.0
0.11	90	190	230	1.60
0.22	67	183	230	1.14
0.45	71	175	240	1.12
0.67	66	165	221	0.87

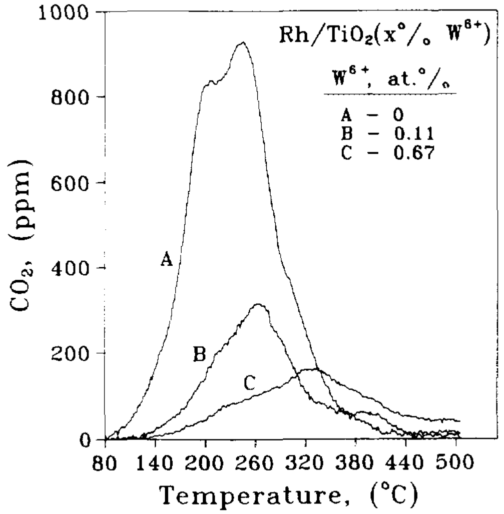

FIG. 6. CO_2 profiles during TPO of carbon formed by exposing the catalysts to a $CO/H_2/He$ mixture at 210°C for 60 min (β = 20°C/min).

the catalyst containing 0.11 at% W^{6+}, the temperatures of initiation of the reaction of the doped catalysts are lower than that of the undoped one. However, T_m and T_f are higher by 10–35°C and 16–35°C, respectively. The quantities of CH_4 produced, normalized over the quantity produced on the undoped catalyst, are also shown in Table 5. The quantity of CH_4 produced is not significantly affected by doping of the carrier, although an increase is observed at the 0.11 at% W^{6+} dopant level followed by a gradual reduction at higher levels of dopant concentration.

(*d*) *Dissociation of CO*

The amount of surface carbon formed on the catalysts from dissociation of CO in the presence or absence of H_2 was determined by measuring the amount of CO_2 formed during TPO, as described in the Experimental section. Typical CO_2 profiles during TPO are shown in Fig. 6 for the case of exposure of the catalysts to a CO/H_2 mixture at 210°C for 60 min. Oxidation of surface carbon leads to a rather broad peak of CO_2 with peak maximum in the temperature range of 250–320°C. On the 0.67 at% W^{6+}-doped catalyst, a shift of the CO_2 peak towards higher temperatures is observed. The quantity of CO_2 formed is significantly less on doped catalysts and appears to be a decreasing function of the W^{6+} content in the TiO_2 support. The amount of surface carbon deposited, as deduced from the CO_2 profiles during TPO, is given in Table 6. The amount of carbon formed from CO dissociation in the presence of H_2 is larger than in the absence of H_2. This is in agreement with results obtained by Solymosi *et al.* (13) and implies that H_2 promotes CO dissociation. W^{6+}-doping of TiO_2 does not seem to enhance CO dissociation on supported Rh. In the absence of H_2, the quantity of carbon deposited is similar on the undoped and the 0.11% W^{6+}-doped catalysts, while it is only half on the 0.67% W^{6+}-doped catalyst. In the presence of H_2, the amount of carbon formed is approximately 3–4 times less on doped catalysts. These results are not in harmony with results obtained by Solymosi *et al.* (15) for similar Rh/TiO_2 (W^{6+}) catalysts. The possible reasons for this disagreement are discussed in a subsequent section.

DISCUSSION

The observed alterations in specific catalytic activity of Rh dispersed on W^{6+}-doped TiO_2 carriers can be explained by evoking the results of equilibrium H_2 and CO adsorption and TPD of H_2 and CO (1), the results of TPSR of adsorbed CO in the presence of H_2, and TPO of surface carbon formed from CO dissociation, the metal–semiconductor boundary layer theory, and results obtained by other investigators concerning mechanistic aspects of the reactions of interest.

Concerning the CO hydrogenation reaction, Efstathiou and Bennett (3) have shown that two types of carbon exist on the surface of Rh/Al_2O_3 catalysts. The catalytically active carbon, which is the main intermediate for the formation of products, occupies only a small fraction of the surface, which is primarily covered by adsorbed CO and inactive carbon. Adsorbed hydrogen also corresponds to a small surface coverage. Although the decom-

TABLE 6

Amount of Surface Carbon Transformed into CO_2 during TPO from Rh/TiO_2 (W^{6+}) Catalysts

Catalyst x in $Rh/TiO_2(x\%\ W^{6+})$ (at%)	Amount of carbon transformed (μmol/g.cat)	
	$CO/H_2/He$ pretreatment at 210°C, 60 min	CO/He pretreatment at 210°C, 60 min
0	16.2	2.0
0.11	5.9	2.2
0.67	4.2	1.0

position of adsorbed CO is generally considered to be the rate-controlling step, the accumulation of inactive carbon might indicate that the step of hydrogenation of surface carbon is equally critical, since the surface coverage of adsorbed hydrogen is very low.

The experiments of TPO of carbon formed from CO dissociation in the presence or absence of H_2, showed that less carbon is formed on W^{6+}-doped catalysts. This implies that in the absence of H_2, CO dissociates less readily on doped catalysts. In the presence of H_2, which seems to promote CO dissociation, two possibilities exist: (a) doping hinders CO dissociation and (b) doping promotes CO dissociation, but hydrogenation of produced carbon is even more promoted, so that less carbon build-up is observed. Solymosi *et al.* (15) reported exactly the opposite results for CO dissociation on Rh catalysts dispersed on W^{6+}-doped TiO_2. The reasons for this discrepancy are not quite clear. The temperature used in Ref. (15) for carbon deposition was 300°C. The temperature employed in this study was 210°C, because the catalyst samples used in the present work were more than an order of magnitude more active than the ones used in Ref. (15). To examine the effect of temperature, some experiments were also performed at 250°C and the same results were obtained. Another possible explanation for the observed discrepancy might be related to adsorbed species remaining on the surface prior to the TPO experiment. It was observed that the catalyst had to be heated to 450°C under He in order to desorb all chemisorbed species. During this treatment, CO, CH_4, and CO_2 were detected in the gas phase. From the undoped catalyst, CO was the main desorption product, accompanied by small amounts of CO_2 and CH_4. From the doped catalysts, the quantity of desorbed CO decreased, while the quantities of CO_2 and especially of CH_4 increased. Thus, exposure of the catalysts to sufficiently high temperatures prior to TPO appears to be necessary for removal of all desorbable species.

Two distinct pathways for CH_4 formation during TPSR of CO adsorbed on Ni, Pd, or Pt dispersed on Al_2O_3 or TiO_2 have been observed by Falconer and co-workers (25–28), namely hydrogenation of CO bound to the metal and hydrogenation of a support-bound methoxy species. The conditions of the TPSR experiments in this work do not favor the formation of methoxy species, as has been shown in a previous publication (23). Based on this, the peak of CH_4 produced during TPSR must be attributed to hydrogenation of CO adsorbed on the Rh surface. A comparison of the results reported in Tables 1 and 5 demonstrates that no correlation between peak temperature of CH_4 produced under TPSR conditions and steady state activity of the catalysts under CO hydrogenation conditions exists. The TPSR experiments of adsorbed CO showed that, upon doping the carrier with W^{6+} cations, the activity of adsorbed CO is reduced. This can be related to the reduced dissociation rate of CO on doped catalysts. Consequently, the rate enhancement under steady state conditions cannot be attributed to enhanced activity of adsorbed CO. This apparent discrepancy can be explained by the fact that, under steady state conditions, the activity of the catalyst depends on the surface coverage of Rh with CO and H_2. Thus, a reduction of activity of adsorbed CO could be compensated by an increase in the hydrogen surface coverage. The enhancement of H_2 surface coverage could be the result of enhanced competitiveness of H_2 relative to CO for the same adsorption sites due to reduced strength of the Rh–CO bond, as illustrated in a previous paper (1). The steady state rate enhancement must then be sought in the weakening of the CO adsorption bond, which was revealed by TPD experiments, and in the enhancement of H_2 adsorption capacity, which was observed in both equilibrium and TPD experiments. Thus, it is proposed that doping of the carrier with W^{6+} cations results in reduced surface coverage of CO and inactive carbon and higher surface coverage of hydrogen. These factors would lead to enhanced hydrogenation rates, as observed in this study. The observation of better stability of doped catalysts with time on stream can also be explained by the finding that carbon build-up is less on these catalysts. The observed shift of selectivity towards saturated hydrocarbons is also explained by the increased surface coverage of hydrogen during reaction. The reduced apparent activation energy of doped catalysts might reflect reduced energy requirements for the hydrogenation of the active carbon and reduced activation energy for the desorption of CO.

Based on the above discussion, a possible scheme for the hydrogenation of CO on Rh is the following:

$$
\begin{array}{lll}
(1) & CO & \rightleftharpoons CO_{(a)} \\
(2) & H_2 & \rightleftharpoons 2H_{(a)} \\
(3) & CO_{(a)} & \rightleftharpoons C_{(a)} + O_{(a)} \\
(4) & C_{(a)} + 4H_{(a)} & \rightarrow CH_4 \\
(5) & O_{(a)} + 2H_{(a)} & \rightarrow H_2O \\
(6) & O_{(a)} + CO_{(a)} & \rightarrow CO_2
\end{array}
$$

Step (3) is believed to be slower on doped catalysts. The activity enhancement must be attributed to acceleration of step (4), for the reasons stated earlier.

Concerning the CO oxidation reaction, a significant enhancement of turnover frequency is observed when Rh is dispersed on W^{6+}-doped TiO_2 carriers, with feed composition in the area in which maximum rate is observed, i.e., for large O_2/CO ratios. Smaller enhancement of turnover frequency was observed at lower O_2/CO ratios, in the area in which CO inhibits oxidation activity. It was further observed that the activity enhancement depends on the dopant concentration in the carrier, going through a maximum at a level of 0.22 at% W^{6+}.

The kinetic behavior of the CO oxidation reaction (Fig. 2) can be approximated by a typical Langmuir–Hinshelwood model which assumes adsorption of CO and O_2 on the surface, and as slow step the surface reaction (17)

$$(1)\quad CO \overset{K_{CO}}{\rightleftharpoons} CO_{(a)}$$

$$(2)\quad O_2 \overset{K_{O_2}}{\rightleftharpoons} 2O_{(a)}.$$

$$(3)\quad O_{(a)} + CO_{(a)} \xrightarrow{k_R} CO_2$$

The resulting rate expression is

$$r = \frac{k_R K_{CO} K_{O_2} P_{CO} P_{O_2}}{(1 + K_{CO} P_{CO} K_{O_2} P_{O_2})^2}. \qquad [2]$$

The kinetic behavior is described qualitatively by the Langmuir–Hinshelwood model if it is assumed that CO is adsorbed more strongly than O_2, although the heat of adsorption of O_2 on Rh is significantly higher than that of CO (17, 18). In order to explain this discrepancy it has been suggested that the presence of CO on the surface reduces the heat of adsorption and the probability of adsorption of O_2 (17). The position of appearance of maximum rate describes, on the basis of the model above, the relative strength of adsorption of CO and O_2. Thus, the results shown in Fig. 3 indicate that the relative strengths of adsorption of CO and O_2 are not significantly altered when Rh is dispersed on W^{6+}-doped TiO_2 carriers. The activity enhancement which is observed over the doped catalysts in the region of maximum rate is probably due to reduced strengths of the CO and oxygen adsorption bonds with the surface, assuming that the surface reaction is the rate-controlling step of the process. At high CO partial pressures the activity enhancement is small, because the surface is heavily saturated with adsorbed CO. The same reasoning can also explain the observed increase in the apparent activation energy of the reaction, especially at the low CO partial pressure (Table 4). Since the interaction of CO with the surface is weaker upon doping the catalyst, the activation of the adsorbed CO molecule is probably of lower intensity and its reaction with the adsorbed oxygen will require higher energy. This is reflected in increased activation energy requirements.

The hysteresis effect in the rate of CO oxidation which was observed when the kinetic measurements started from low CO pressures can be attributed to deactivation due to partial oxidation of the Rh surface. It has been reported in the literature (19) that Rh can be oxidized at high O_2/CO ratios. The oscillations in the reaction rate observed at high O_2 pressures in the case of the undoped catalyst might be due to periodic reduction–oxidation of the Rh surface. The finding that oscillations were not observed in the case of the doped catalyst might imply that Rh is more resistant to oxidation when supported on W^{6+}-doped TiO_2.

The alterations in chemisorptive and catalytic properties of Pt and Rh crystallites dispersed on TiO_2 doped with altervalent cations have been attributed to electronic interactions at the metal–support interface, which alter the electronic structure of the interface and surface metal atoms (1). The CO oxidation activity behavior of the W^{6+}-doped catalysts illustrated in Fig. 2 can be explained if it is assumed that the intensity of the electronic interactions at the metal–semiconductor interface is a function of the composition of the gaseous atmosphere which surrounds the catalysts, primarily, in this case, of the O_2/CO ratio. The number of electrons transferred between the metal crystallites and the semiconducting carrier, which defines the intensity of the interaction, depends on the relative position of the Fermi level of the metal and of the semiconductor (support), or, alternatively, of the work function of the two solids (15). The work function is affected by the nature and coverage of adsorbed species, not only on the metal crystallites, but also on the semiconducting carrier. Therefore, the relative positions of the Fermi levels of the metal and the semiconductor would be expected to vary with the O_2/CO ratio. As a result, the intensity of the electronic interaction at the metal–semiconductor interface would be expected to vary with the same parameter. The fact that the electronic structure of the solids depends on the gaseous atmosphere surrounding them has been demonstrated by measurement of the activation energy of electron conduction which was found to be a strong function of this parameter (1, and references therein).

The observed alterations in specific catalytic activity, activation energy, and selectivity under CO hydrogenation and CO oxidation conditions upon doping of the TiO_2 carrier with altervalent cations have been attributed to changes in the mode of adsorption of the reactants on the metal crystallites. An explanation for this phenomenon has been offered in a previous publication (1), based on the theory of metal–semiconductor contacts. It was proposed that charge is transferred from the doped semiconducting carrier to the metal crystallites and, as a result, the work function of surface metal atoms is altered (long range effect). Simultaneously, the electronic properties of the interface metal atoms are significantly changed (short range effect). Which is the dominant factor, long or short range, cannot be easily assessed at this moment.

CONCLUSIONS

The hydrogenation and oxidation of CO were used as probe reactions to study the influence of altervalent doping of TiO_2 on catalytic parameters of supported Rh. For the CO/H_2 reaction, the activity of Rh was found to increase monotonically with increasing W^{6+}-dopant concentration in the TiO_2 matrix; the apparent activation energy was found to decrease by approximately 20 $kJ \cdot mol^{-1}$, while selectivity was found to shift towards smaller chain saturated hydrocarbons. For the CO/O_2 reaction, the specific activity of Rh was found to pass through a maximum at a W^{6+}-dopant content of 0.22 at% and to decrease at higher dopant concentrations, in the feed composition region in which maximum rate is observed with respect to CO concentration. The composition at which maximum rate is observed was found not to be affected by carrier doping. At higher CO partial pressures, in the region in which CO inhibits oxidation activity, doping of the carrier was found to have a very small influence on specific activity of the supported Rh crystallites. The apparent activation energy was also found to vary with dopant content, especially at low CO partial pressures.

These results are discussed in terms of alterations in the mode of H_2 and CO adsorption which have been observed over the same catalysts (1). To explain changes in chemisorptive and catalytic parameters of Rh crystallites dispersed on doped TiO_2 carriers, the metal–semiconductor boundary layer theory is invoked.

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