JOURNAL OF CATALYSIS **116**, 590–594 (1989)

Effects of Dopants on Performance of Metal Crystallites

3. Influence on Kinetic Parameters in CO/H_2 and CO/O_2 Reactions

It has often been demonstrated in the literature that chemisorptive and catalytic properties of supported metal crystallites can be influenced by the nature of the carrier employed in catalyst formulation. Early work by Schwab (*1*) and Solymosi (*2*) attributed the origin of certain types of metal–support interactions to the electronic state of the carrier. During the last decade, the concept of SMSI (*3*) has dominated the literature in this field. The origin of the SMSI phenomenon has been attributed to migration of TiO_x species to the surface of metal crystallites (*4–6*) and to an electronic factor operating concomitantly (*7, 8*).

The effects of altervalent cation doping of TiO_2 carriers on the chemisorptive properties of Pt crystallites were discussed in previous publications (*9, 10*). It was shown that small Pt particles supported on TiO_2 doped with higher valence cations (Sb^{5+}, Ta^{5+}, W^{6+}) exhibit significantly reduced chemisorption capacity for H_2, O_2, and CO. Weakened CO adsorption was also revealed by FTIR studies. On the basis of TEM and ESCA characterization and on measurements of electrical conductivity and activation energy of electron conduction (*11*), the observed alterations in the chemisorptive properties of Pt particles supported on higher-valence doped TiO_2 were attributed to long-range electronic interactions at the metal–support interface, on the basis of the physics of metal–semiconductor boundary layers.

In the present communication, the effects of altervalent cation doping of TiO_2 carriers on the catalytic performance of Pt and Rh crystallites are presented. Carbon monoxide hydrogenation and oxidation are used as probe reactions.

EXPERIMENTAL

Preparation and characterization of doped supports and Pt catalysts used in this investigation have been described previously (*9–11*). Rh catalysts were prepared by incipient wetness impregnation of the support with appropriate amounts of aqueous solutions of $RhCl_3$ at approximately 80°C. The impregnated supports were dried overnight at 90°C and then reduced in flowing hydrogen at 200°C for 2 h. Rhodium content was invariably 0.5 wt%.

A fixed bed, plug flow reactor was used for kinetic studies, and it was operated in the differential mode. Feed flow rates were measured and controlled by high-precision thermal mass flow meters and control valves. Analysis of the reaction mixture was performed by an on-line gas chromatograph equipped with thermal conductivity and flame ionization detectors, temperature programming capability, and a reporting integrator. Kinetic experiments in CO hydrogenation were performed at atmospheric pressure, in the temperature range of 170 to 325°C with a feed composition consisting of an H_2/CO molar ratio of 3. Kinetic experiments in CO oxidation were also conducted at atmospheric pressure, within the temperature range of 240 to 300°C, with a CO/O_2 ratio of 0.45 and 2% CO in the feed stream.

RESULTS

Platinum catalysts employed in CO hydrogenation and oxidation have been characterized in terms of H_2, O_2, and CO chemisorption capacity and by measurement of

0021-9517/89 $3.00

their electrical conductivity and activation energy of electron conduction under various atmospheres. They have also been studied by TEM, ESCA, and FTIR of adsorbed CO (*9–11*). For ease of reference, catalyst configurations are designated as $x\%M/TiO_2$ (*D*), where *x* indicates metal content, *M* the metal, and *D* the doping material.

A summary of kinetic results of CO hydrogenation on Pt catalysts is presented in Table 1. Turnover frequencies of methanation and water–gas shift reactions are based on exposed metallic areas obtained by H_2 chemisorption on undoped samples. TEM analysis has shown that the 0.5% Pt/TiO_2 (*D*) catalysts suffered no measurable reduction in the degree of dispersion of Pt, as compared to the undoped catalysts, while the 2% Pt/TiO_2 (*D*) catalysts suffered a minor reduction in dispersion (*9*). Specific rates of higher-valence doped catalysts are significantly lower than those of undoped or lower-valence doped catalysts. Activation energies obtained over various catalysts are also shown in Table 1. It is observed that activation energies are not significantly affected by the doping process, since the variation of ±1 kcal/mol observed seems to be random.

To determine the influence of dopant concentration in the carrier, a number of catalysts were prepared on carriers with variable Ta_2O_5 concentration, and their activity was determined under CO hydrogenation conditions. Turnover frequencies of methanation and water–gas shift reactions at 275°C as a function of dopant concentration in the carrier are shown in Fig. 1. It is apparent that the activity of Pt particles is a function of dopant concentration or, alternatively, of the electron state of the carrier.

TABLE 1

Summary of Kinetic Results of $Pt/TiO_2(D)$ in $CO–H_2$ Reaction at 548 K

Catalyst	$N_{CH_4} \times 10^3$ (μmol/s-m² Pt)	$N_{CO_2} \times 10^3$ (μmol/s-m² Pt)	E_{CH_4} (kcal/mol)	E_{CO_2} (kcal/mol)
2% Pt/TiO_2	180	110	16.8	19.1
2% $Pt/TiO_2(Sb^{5+})$	2.9	2.3	17.2	19.7
2% $Pt/TiO_2(Ta^{5+})$	2.3	1.7	16.8	19.4
0.5% Pt/TiO_2	120	82	16.6	18.2
0.5% $Pt/TiO_2(Mg^{2+})$	108	77	18.2	19.0
0.5% $Pt/TiO_2(Sb^{5+})$	1.1	1.0	18.8	19.5
0.5% $Pt/TiO_2(Ta^{5+})$	0.9	0.8	18.6	19.9

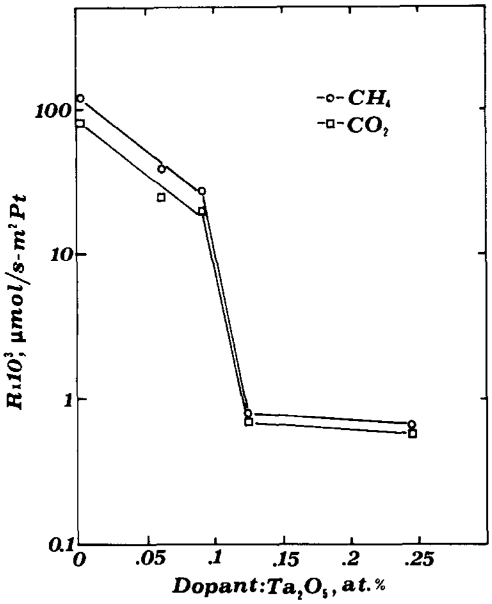

FIG. 1. Variation of CO hydrogenation activity of 0.5% $Pt/TiO_2(Ta^{5+})$ catalysts with dopant content of carrier at 275°C.

The influence of carrier doping on catalytic properties of Pt was also investigated under CO oxidation conditions. Specific activity and activation energy results are summarized in Table 2. A suppression of specific activity is observed when Pt is supported on carriers doped with higher-valence cations, while no significant changes are observed when the carrier is doped with lower-valence cations. Reduction of specific activity in CO oxidation is significantly smaller than that in CO hydrogenation. Contrary to the CO/H_2 case, activation energies of CO oxidation seem to be affected by the doping process. Activation energies of higher-valence doped catalysts are higher by as much as 45%.

The influence of carrier doping was also investigated on the catalytic performance of Rh particles under CO hydrogenation conditions. The effects of doping TiO_2 with WO_3 on the catalytic performance of Rh in

TABLE 2

Summary of Kinetic Results of $Pt/TiO_2(D)$ in $CO-O_2$ Reaction at 533 K

Catalyst	N_{CO} (μmol CO/s-m^2 Pt)	E (kcal/mol)
0.06% Pt/TiO_2	109.3	16.4
0.06% $Pt/TiO_2(K^+)$	126.3	16.6
0.06% $Pt/TiO_2(Mg^{2+})$	100.6	16.9
0.06% $Pt/TiO_2(Sb^{5+})$	4.4	21.4
0.06% $Pt/TiO_2(Ta^{5+})$	6.2	23.9
0.06% $Pt/TiO_2(W^{6+})$	8.2	21.1
0.5% Pt/TiO_2	277.6	16.7
0.5% $Pt/TiO_2(Mg^{2+})$	209.2	17.3
0.5% $Pt/TiO_2(Sb^{5+})$	98.4	22.4
0.5% $Pt/TiO_2(Ta^{5+})$	60.9	21.0
0.5% $Pt/TiO_2(W^{6+})$	90.2	21.9

CO hydrogenation at 210°C are shown in Fig. 2 as a function of the dopant concentration in the carrier. It is apparent that turnover frequencies of CO conversion, methanation, and water–gas shift reactions are significantly enhanced by the doping process and the activity enhancement in a function of the dopant concentration. Activation energies, shown in Table 3, are also affected by higher-valence doping of the carrier. The apparent activation energy of CO hydrogenation is reduced by as much as 25% while a somewhat smaller reduction is observed in the apparent activation energy of methanation. A small but consistent shift in product distribution was also observed in the $Rh/TiO_2(D)$ system, as shown in Fig. 3. Catalysts formulated on doped carriers exhibit significantly higher rates of production of saturated C_2 and C_3 hydrocarbons at the expense of corresponding unsaturated molecules. Thus, the ratio of ethane to ethylene of the undoped catalyst is 0.5 while that of the doped catalyst (2 wt% WO_3) is 14. Similarly, the ratio of propane to propylene of the undoped catalyst is 0.07, while that of the doped one is 1.4.

DISCUSSION

The alterations of catalytic activity of Pt and Rh supported on higher-valence doped carriers are explained in terms of extended electronic interactions between the metal particles and the support which alter the electronic configuration of surface metal atoms, a model first proposed by Schwab (*1*) and Solymosi (*2*). Electron transfer from the semiconducting support to the metal particles originates from the requirement that the Fermi energy level of the two solids in contact must be the same at the interface. Doping TiO_2 with cations of higher

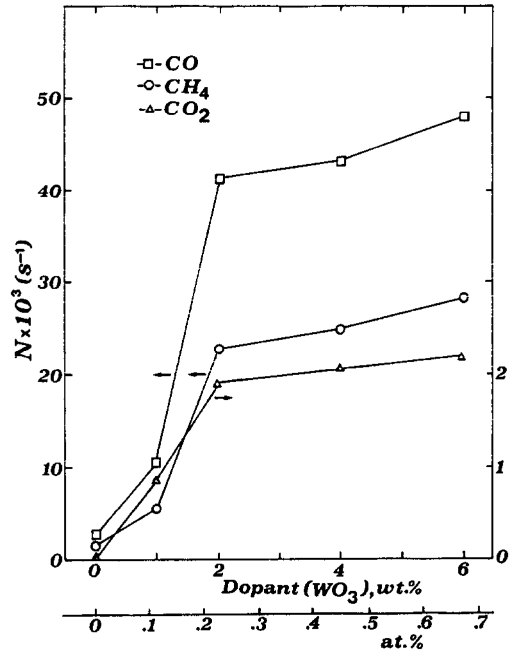

FIG. 2. Variation of turnover frequency of CO hydrogenation over 0.5% $Rh/TiO_2(W^{6+})$ catalysts with dopant content of carrier at 210°C.

TABLE 3

Apparent Activation Energies of CO Hydrogenation over 0.5% $Rh/TiO_2(W^{6+})$ Catalysts

Dopant concentration		E_{CO} (kcal/mol)	E_{CH_4} (kcal/mol)
Wt%	At.%		
0	0	31.4	30.5
1	0.112	25.8	30.4
2	0.224	24.8	25.7
4	0.448	23.8	24.7

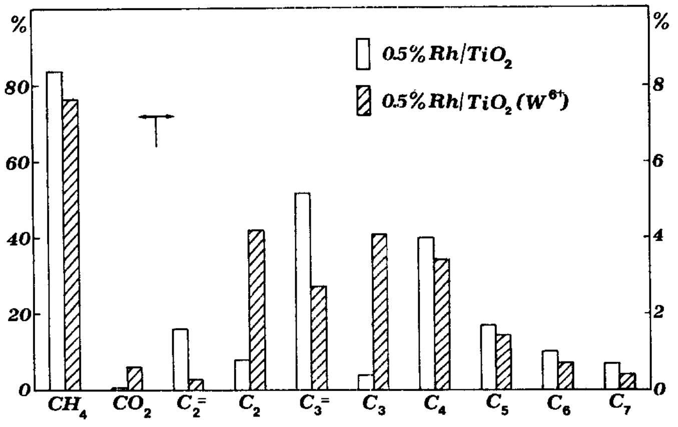

FIG. 3. Effects of carrier doping on product distribution in CO hydrogenation over 0.5% Rh/TiO$_2$ catalysts.

valence results in an increased Fermi energy level or a decreased work function. Since the work function of Pt and Rh is higher than that of the semiconducting supports, electrons are transferred into the Pt and Rh particles until the Fermi energy levels at the interface are at equal heights.

Charge transfer into Pt atoms tends to saturate their empty *d* orbitals which is detrimental for their capacity to chemisorb H$_2$, CO, and O$_2$. As a result of reduced adsorbed population of these species, the activity of Pt in CO hydrogenation and CO oxidation is significantly reduced. The activation energy of CO hydrogenation is not affected because the rate-controlling step (CO dissociation) proceeds as an acceptor reaction. Greater availability of electrons in the surface Pt atoms does not significantly reduce the resistance of the rate-controlling steps; thus, activation energy is not affected. The opposite is true in CO oxidation in which the rate-controlling step proceeds as a donor reaction. The charge which has been transferred into the Pt atoms via electronic interactions with the doped carrier offers increased resistance to this step due to the fact that transfer of electrons into an already saturated bonding orbital is difficult. This enhanced resistance to the rate-controlling step is manifested as increased activation energy.

As Tables 1 and 2 indicate, the degree of suppression of activity of the two reactions is different. This fact can be explained by results of *in situ* measurements of electrical conductivity (*11*). Under CO hydrogenation, electrical conductivity was found to be approximately five orders of magnitude higher than that under CO oxidation condition. Lower conductivity indicates reduced Schottky barrier height and a smaller amount of charge transferred into the Pt crystallites and smaller effect of the dopant on the catalytic activity of the Pt particles.

The effect of higher-valence doping of TiO$_2$ on the catalytic performance of Rh is opposite to that observed on Pt. In the case of Rh, turnover frequencies of methanation and water–gas shift reactions increase upon doping of TiO$_2$. The activity enhancement is a function of the concentration of the dopant in the carrier, in qualitative agreement with observations made by Solymosi *et al.* (*12*). Furthermore, apparent activation energies of CO conversion and methanation seem to be reduced. These phenomenological contradictions can be explained on the basis of the electron transfer model if the electronic configuration of the two metals and the mechanistic differences of the reactions on the two different metals are considered.

Pt has a d^9 configuration which tends toward d^{10} upon acceptance of charge, transferred from the carrier. This d^9 to d^{10} transformation results in a significant loss of the capacity of Pt to chemisorb H_2 and CO. As a result of reduced CO and hydrogen surface coverage under reaction conditions, the activity of the surface is also reduced, while the activation energy is essentially unchanged. On the other hand, Rh has a d^8s^1 configuration which, upon acceptance of charge, probably tends toward d^9s^1. Thus, the ability of Rh to adsorb reactant molecules is not reduced, as adsorption studies indicate. In both cases, as a result of charge transfer, CO adsorption is weakened, and the C–O bond is strengthened. In the case of Pt, breaking of the C–O bond is the slow step, which might be a secondary reason for the observed activity reduction. Nevertheless, there is a strong indication in the literature (*13, 14*) that, in the case of Rh, breaking of the C–O bond occurs readily and the slow step is the hydrogenation of carbon. The weakened metal–carbon bond facilitates carbon hydrogenation which is translated into enhanced catalytic activity and reduced activation energy.

These explanations must be considered tentative since no mechanistic studies have been conducted in our laboratory. Such studies, which aim toward understanding the observed differences between Pt/$TiO_2(D)$ and Rh/$TiO_2(D)$ systems are currently in progress.

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Received June 1, 1988; revised October 5, 1988