CO dissociation and oxidation on small supported rhodium particles: SSIMS and TPR study

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The dissociation and oxidation of carbon monoxide on small rhodium particles prepared by vapour deposition of Rh on either MgO or alumina substrate has been investigated by means of static secondary ion mass spectrometry (SSIMS), and temperature programmed reaction (TPR). The intensity ratios Rh_nC^+/Rh_n^+ measured by SSIMS, have been used to monitor the build-up of surface carbon concentration. It was shown that a part of the CO molecularly adsorbed on clean particles undergoes dissociation during heating. The dissociation is more important for smaller particles. This behaviour is explained in terms of increase of CO dissociation probability in the case of CO adsorption near structural irregularities of a surface (edges, corners, steps). During the reaction of CO oxidation the intermediate carbon formation, which is more pronounced for smaller particles, is observed. The temperature dependent carbon concentration exhibits a maximum resulting from a counterbalance between CO dissociation first and carbon reaction with adsorbed oxygen consequently.

Keywords: Rh/alumina catalyst; Rh/MgO catalyst; CO oxidation; size effect; SSIMS; TPR

1. Introduction

Metal catalysts used in the most industrial processes consist of small metal particles ranging in size from 1 to 50 nm supported on a porous oxide substrate. It has been shown long ago that, for so-called structure sensitive reactions, the particle size can affect the catalytic activity by the way of size dependent distribution of crystal planes on small metal particles [1–3]. In our previous papers [4–6] we have reported the unexpected structure sensitivity for C–O bond breaking on small Pd particles supported on substrate materials such as alumina, MgO and mica. These results emphasise the importance of size effects in adsorption processes. In

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the case of CO adsorption on palladium the appearance of CO dissociation has been correlated with the surface roughness [7,8].

Rhodium is one of the more widely used noble metal catalysts – one of the most important applications is in automobile catalytic converters, where addition of Rh provides high conversion for both the NO–CO and the CO–O_2 reactions [9]. The theoretical results obtained for CO adsorption on rhodium show that the bonding interaction with the $2\pi^*$ antibonding orbital increases with the co-ordination number [10] and adsorption to steps has a very favourable interaction [11,12]. Partial CO dissociation was reported to occur on open Rh surfaces [13–16]. On the other hand the densely packed Rh surfaces [17–20] were never found capable of breaking the C–O bond. A few CO adsorption studies on particulate Rh model catalysts have been made in the past. These studies indicate a small influence of particle size variation on CO adsorption mechanism [3,21].

Static secondary ion mass spectrometry (SSIMS) provides a very powerful tool for CO adsorption studies. Studies on a wide range of single-crystal surfaces over a number of years have demonstrated that SSIMS is able to discern clearly between the dissociative and the molecular states of adsorption of CO (the occurrence of the $M_mC_n^+$ ion clusters in a SSIMS spectrum is indicative of carbon on the surface of a metal M) [22–24].

In the present paper we report on results obtained in an investigation of CO dissociation and catalytic oxidation over small Rh particles deposited on both alumina and MgO substrates.

2. Experimental

The studies reported here were performed in a specially designed UHV system at the background pressure of 1×10^{-8} Pa. This system contains two chambers that can be isolated from each other. The main analysis chamber has facilities for SIMS and temperature programmed experiments. The second preparation chamber was used for sample preparation and for temperature programmed reaction. Rhodium particles were grown by vapour deposition on chosen substrates. The Rh source was a specially designed micro-electron bombardment evaporation source, the atomic flux of which was electronically stabilised and calibrated by a quartz micro-balance. The usual flux employed for rhodium deposition was 1×10^{13} atoms cm^{-2} s^{-1}. After the Rh deposition the samples were pre-treated by heating in CO/O_2 mixture for 1 h in order to obtain stabilised particle structure and morphology. It has been shown that the vacuum vapour deposition of Rh gives larger particles on the alumina support than on the MgO one. Similarly the heating under CO/O_2 mixture causes more important coalescence in the case of Rh/alumina particles. More details about the results of rhodium growth study will be published in a special paper [25].

In order to obtain two particle populations different in size we used both thermally oxidised aluminium foil and MgO(001) cleavage as supports for metal particle growth. In the case of deposits on Al_2O_3, the alumina layers were prepared by thermal oxidation (24 h / 600°C under air) of pure 25 µm thick Al foil. The back side of the oxidised Al foil was lightly scribed by a steel needle and the samples were submerged in 10% NaOH water solution in order to create very small windows (several µm) by dissolution of aluminium. These windows appeared in the places of the holes created by the scribing and were covered by an intact alumina layer on the front side. After the experimental run disks of 3 mm diameter were cut from the samples and mounted on the electron microscope grid holder (without grid) for transmission electron microscope (TEM) observation. The particles deposited on MgO were removed from the substrate using the method of transfer replica [26].

The secondary-ion intensities are sensitive to the amount of surface species X (X = CO, C, O) and to the work-function change induced by adsorption [4–6, 22–24]. Thus as X coverage increases on a surface of the metal M, the secondary-ion intensities increase non-linearly as a consequence of both of these parameters. It was established that, while the formation of M_nX^+ ion species was sensitive to both coverage and work function, the M_n^+ ion signal also increased but only as a consequence of the work-function change. It was suggested that if the ratio M_nX^+/M_n^+ was used, it would only be sensitive to coverage. The total coverage θ_X of X species on the Rh surface should be represented by the sum of ion intensity ratios,

$$S_X = \sum_n Rh_nX^+/Rh_n^+ \quad (n = 1,2; X = CO, C, O) . \tag{1}$$

The experimental conditions were examined in order to optimise signal intensities and to minimise the damage caused to the sample surface during the analysis. Thus a low primary ion current density was used (5 nA cm^{-2} at 3 keV), such that the crystallographic and chemical integrity of the surface layer was preserved during the period of study. The conservation of the integrity of the surface layer was verified by the stability of the SSIMS signals. The sample electrostatic charge, due to the polarisation of insulator supports under the ion impact, was neutralised by a low energy electron beam of 200 eV.

3. Results and discussion

In order to be able to compare the CO dissociation and oxidation on particle populations very different in size and density, the experiments have been performed on two samples: (A) Rh particles deposited on MgO(001), average particle size $\varnothing = 1.3$ nm and average particle density $d = 1.0 \times 10^{13}$ cm^{-2}; (B) Rh/Al_2O_3, $\varnothing = 3.3$ nm, $d = 2.9 \times 10^{12}$ cm^{-2}.

3.1. CO DISSOCIATION

Before the beginning of the experiments the samples were heated during 30 min in 1×10^{-5} Pa of oxygen at surface temperature $T = 550$ K in order to remove residual carbon from the Rh surface. Then T was changed to the chosen value and kept constant during the experiment. The surface carbon and oxygen concentrations were monitored as a function of time by the SSIMS intensity ratios S_C, and S_O (eq. (1)), respectively. At time $t = 0$ s, we have introduced 5×10^{-6} Pa of CO in the chamber. It can be seen that surface oxygen, adsorbed during heating under O_2 atmosphere is rapidly removed from the surface by its reaction with CO while surface carbon concentration increases. The slope of carbon curves depends on T indicating the temperature dependence of the carbon formation rate. In fig. 1 the characteristic curves of surface carbon and oxygen concentration, obtained for Rh/MgO (A) and Rh/Al_2O_3 (B), are shown. The curves of 400 K correspond to the maximum of CO dissociation rate. We can see that the carbon formation rate is larger for sample A than for B. The origin of slope variations, i.e. CO dissociative activity, could be explained by the effect of self-poisoning by carbon.

The occurrence of CO dissociation at metallic surfaces is usually interpreted by mutual enhancement occurring between donation of electrons from CO 5σ orbital into unoccupied metal orbitals and back donation from metal orbitals into the CO $2\pi^*$ (antibonding system). A large filling of these states upon chemi-

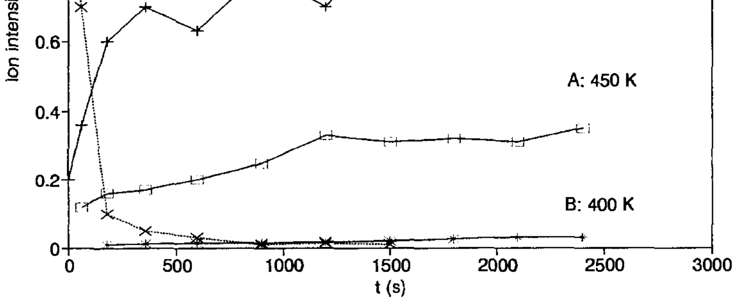

Fig. 1. Variations of $\sum_n Rh_nC^+/Rh_n^+$(—) and $\sum_n Rh_nO^+/Rh_n^+$(...) as a function of heating time under CO at surface temperatures of 400 and 450 K respectively: (A) 1.3 nm Rh particles on MgO; (B) 3.3 nm Rh particles on alumina.

sorption weakens the C–O bond considerably and may even lead to its dissociation. It was shown for Rh that in the case of structural irregularities of a surface on the atomic scale there is a very favourable $2\pi^*$ interaction resulting in the higher $2\pi^*$ orbital occupancy [11]. In the case of small supported particles the number of edge, corner and step atoms related to the number of plane atoms increases with decreasing particle size. For this reason it seems reasonable to explain the surface carbon formation on particle surface by dissociation of CO adsorbed near the surface irregularities (like in the case of Pd particles [27]). This interpretation is in agreement with the observation of two different CO-desorption features α and β, where the α peak is due to molecular CO desorption and the β one to C_{ad}–O_{ad} recombination [28].

We have used two different supports for particle growth. Thus it could be possible theoretically that the mechanism of CO adsorption was influenced not only by the effect of particle size but also by the effect of different metal–support interactions. On the other hand it is generally assumed that alumina and MgO are materials of a low metal–support interaction [29,30]. Thus it is legitimate to rule out an origin of observed "size effect" due to an interaction of Rh with the support.

3.2. CO OXIDATION

In figs. 2 and 3 the results of a temperature programmed reaction (TPR) of CO oxidation over samples A and B are shown. The oxygen pre-treated samples were heated under CO/O_2 mixture at $P_{CO} = P_O = 5 \times 10^{-6}$ Pa. The temperature was increased step by step up to 600 K and after each step we waited for stabilisation in order to obtain steady-state values. Variations of relative ion intensities S_X ($X = $ CO, O, C) exhibit different trends. At low temperature the CO- and O-ion ratios are high while those of carbon are low. Thus molecular CO adsorption is the dominating process under these conditions. Increasing temperatures lead to decreasing CO SSIMS signal as to be expected for a depletion of the CO_{ad} layer due to the thermal desorption or reaction. At high temperatures the CO_{ad} concentration is low, however oxygen chemisorbs on the surface as evidenced by significant oxygen SSIMS intensities. The carbon signal first increases with rising temperature, T, reaches a maximum at medium values of T, and decreases again later on. This behaviour is explained in terms of partial CO_{ad} decomposition first and reaction of the deposited carbon subsequently. At the maximum of the intensity curve the rates of carbon production and consumption counterbalance. It can be seen that the steady C_{ad} concentration obtained under identical conditions is higher in the case of smaller particles which is in agreement with the results from fig. 1.

The qualitatively same behaviour was observed on small palladium particles and explained in detail previously [4–6]. The only difference is in the initial stage of experiment. Oxygen deposited on the surface during sample pre-treatment under O-atmosphere (carbon removing) remains on the surface under CO/O_2 catalytic mixture at room temperature (in the case of Pd it is reacted off via reaction with

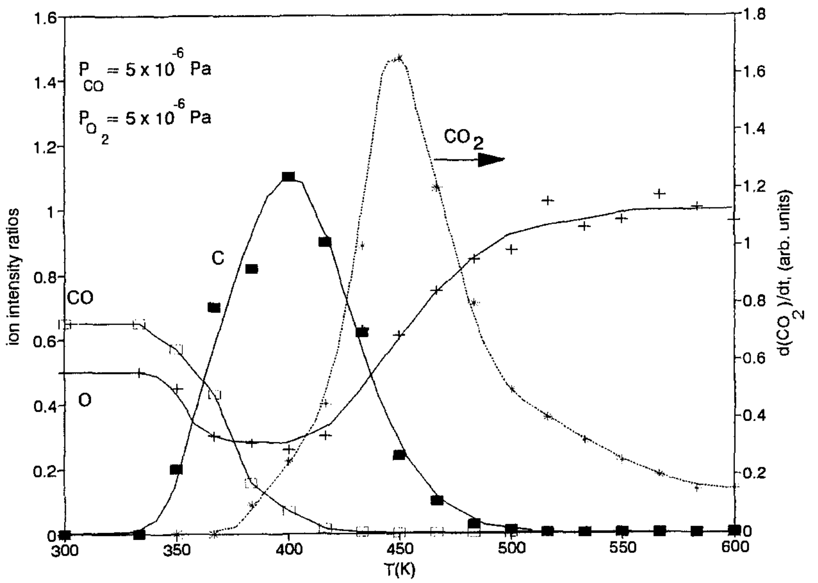

Fig. 2. Variations of $\sum_n \mathrm{Rh}_n\mathrm{X}^+/\mathrm{Rh}_n^+$ secondary ion intensity ratios (X = CO (□), C (■), O (+); $n = 1, 2$) and CO_2 production rate $d(CO_2)/dt$ (*) as a function of surface temperature under catalytic CO/O_2 mixture: 1.3 nm Rh particles on MgO.

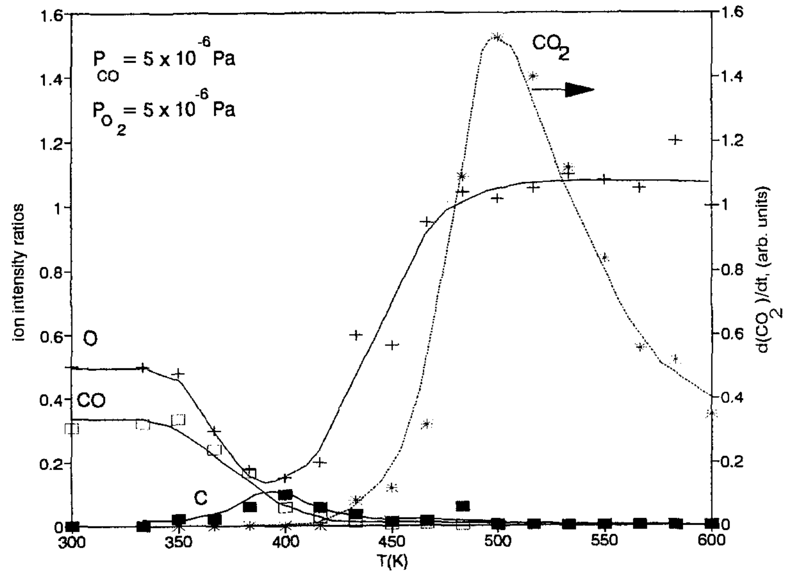

Fig. 3. Variations of $\sum_n \mathrm{Rh}_n\mathrm{X}^+/\mathrm{Rh}_n^+$ secondary ion intensity ratios (X = CO (□), C (■), O (+); $n = 1, 2$) and CO_2 production rate $d(CO_2)/dt$ (*) as a function of surface temperature under catalytic CO/O_2 mixture: 3.3 nm Rh particles on Al_2O_3.

CO). We can see in figs. 2 and 3 that at the first stage of the experiments ($T < 350$ K) CO molecules are co-adsorbed with oxygen which starts to be removed from the surface at higher temperature. The CO saturation SSIMS ratios obtained on samples A and B for C- and O-free surface have values between 0.8 and 0.9. By comparing these values with the maximum CO-ion intensity ratios from figs. 2 and 3 it can be seen that the surface oxygen reduces the adsorption capacity for CO. It appears that site blocking is occurring in this case which is in agreement with the results obtained on Rh(210) [15].

The production of CO_2 – measured by means of quadrupole mass spectrometer as a variation of CO_2 partial pressure – shows that the reaction rate reaches maximum when the CO_{ad} steady concentrations decrease nearly to zero and oxygen adsorbs on the surface. The same behaviour has been observed on Pd [6] particles indicating the same mechanism of CO oxidation: adsorbed CO migrates on the surface and interacts with dissociatively adsorbed oxygen (Langmuir–Hinshelwood reaction). The results represented in figs. 2 and 3 show that in the case of smaller particles the maximum reaction rate occurs at lower temperature (450 K) under the same CO/O_2 pressure conditions. This could be explained by a size dependent decrease in the activation energy of reaction.

In a previous study on small Rh particles [28] the surface carbon has been observed to inhibit the CO and oxygen adsorption on the metal surface. Consequently it has to inhibit the CO oxidation reaction (similarly as in the case of palladium [31]). On the other hand we find that the deposited carbon is removed during the CO oxidation. Thus our results constitute surface carbon as an intermediate species of the steady state reaction. The significance of this behaviour increases with decreasing particle size. Therefore the CO oxidation over small Rh particles must be considered as a structure sensitive reaction as long as the reaction involves the Rh particles with diameter smaller than 3 nm.

4. Conclusion

(1) The application of temperature programmed SSIMS has revealed that adsorbed CO partially dissociates on supported Rh particles. CO dissociation is an activated process and the kinetics depends on particle size and surface temperature. It was shown that the smaller the particle size, the higher are the CO dissociation rates.

(2) The deposited carbon is rapidly reacted off the surface by its reaction with oxygen.

(3) During the reaction of CO oxidation steady state surface concentration of CO, C, and O results from equilibrium between different processes: CO adsorption/desorption, CO dissociation/carbon removing, CO_2 production rate.

(4) The surface carbon is formed as an intermediate species during the steady

state reaction. The CO oxidation over small Rh particles is structure sensitive in the case of Rh particles smaller than 3 nm.

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