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Mobile Ruthenium Oxide Species on Platinum Observed by Pulsed Field Desorption Mass Spectrometry

The oxidation of ruthenium metal restricts its use in supported metal catalysts (*1*). In addition, the question of the mobility of one metal oxide over another metal is one of considerable importance in the use of bimetallic catalysts (*2*). Bimetallic systems containing ruthenium are currently under active research. These include Ru–Cu (*3* and references therein), Ru–Au (*4*), Ru–Fe (*5*), and Ru–Pt (*6*) catalytic systems. The Ru–Pt system is the subject of this study.

In earlier experiments designed to study the dynamic processes associated with ruthenium oxidation, we applied the technique of pulsed field desorption mass spectrometry (PFDMS) to directly detect the intermediates formed. During experiments with PFDMS, a surface reaction proceeds with continuous supply of reactive gas at pressures up to 0.1 Pa. After a certain reaction time ($10\ \mu s < t_R < 10$ s), a field pulse ($F_P < 5 \times 10^8$ V/cm) is applied in order to remove all surface species, i.e., chemisorbed molecules, reaction intermediates, and products from the surface. The analyzed surface area consists of ≈ 100 sites. If during longer reaction times, molecules diffuse from the shank into the monitored area, then they too will be analyzed. Electric fields are applied only during the short pulse times of ≈ 100 ns and have minor influences on the reaction and diffusion. The desorbed ions are identified by time-of-flight mass spectrometry.

During oxidation of ruthenium tips, ruthenium oxides up to the tetroxide were identified and it was postulated that RuO_4^+ and cluster ions, $Ru_2O_m^+$ (m = 4–6) were formed from mobile precursors like RuO_2 and RuO_3 molecules (*7, 8*). However, direct proof of the mobility of these species has been lacking though recent theoretical calculations by Anderson support the idea of mobile RuO_x (x = 1–3) species on ruthenium surfaces (*9*).

We want to report a special experiment designed to examine the mobility of RuO_x species during oxidation of ruthenium. In this experiment, a thin ring of Ru metal was electrodeposited from a $RuCl_3$ solution onto the shank of a freshly prepared platinum field emitter. The deposit was a 1-mm broad ring of about 100 monolayers thickness; it was located ≈ 2 mm behind the apex of the tip. During the electrodeposition, care was taken to keep the apex region free of the $RuCl_3$ solution. The prepared tip was mounted in the PFDMS apparatus and examined after a bakeout of the system. The residual gas pressure was 2.6×10^{-7} Pa. Field evaporation of the emitter at 300 K produced only Pt^{2+} ions, proving that no Ru was at the apex. No ruthenium or ruthenium oxide ions appeared even when the tip was heated to 850 K *in vacuo* during the field pulses (Fig. 1). This shows that even at this temperature, Ru species do not migrate over distances in the order of 2 mm on a platinum surface within the total measuring time (10^3–10^4 s). However, when oxygen (pressure: 7.5×10^{-4} Pa) was introduced to the heated tip, RuO_2^{n+} and RuO_3^{n+} (n = 1, 2) were observed in the mass spectrum as shown in Fig. 2. Platinum-containing ions, e.g., Pt^{2+}, Pt^+, PtO^{2+}, PtO^+, and PtO_2^+ were also seen. No RuO^+ ions were seen in this investigation, indicating that a metallic ruthenium surface may be necessary for RuO-production and stability. Any ruthe-

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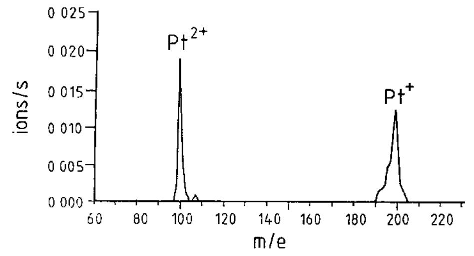

FIG. 1. Mass spectrum of field evaporated Pt tip with deposited Ru ring on the shank. Temperature of tip = 850 K, desorption pulse frequency = 10 Hz.

nium monoxide produced on the deposited ruthenium layer has to diffuse over a platinum surface on its way to the monitored zone at the apex of the tip; during this process it will probably be further oxidized by reaction with surface oxygen or platinum oxides.

Our study shows that in the presence of oxygen, RuO_x species ($x = 2, 3$) are formed and that these species are mobile on a platinum surface. The migration of the ruthenium oxides from the deposited layer is further confirmed by varying the desorption field strength and the frequency of the desorption pulses. Cocke *et al.* (*10*) have thoroughly investigated the application of PFDMS to the study of diffusion kinetics.

Information on the mobilities of ruthenium oxides will help in the formulation of models for the nucleation stage of oxidation, and this in turn will contribute to the development of better means to control the loss of ruthenium from supported catalysts. Since ruthenium oxide species wet a platinum surface, their mobility leads to coverage of platinum and loss of active surface area. Therefore, to understand the factors affecting the movement of ruthenium oxides on platinum is very useful for those researchers designing Ru–Pt catalysts that must undergo the oxidizing environment of a calcination or rejuvenation process.

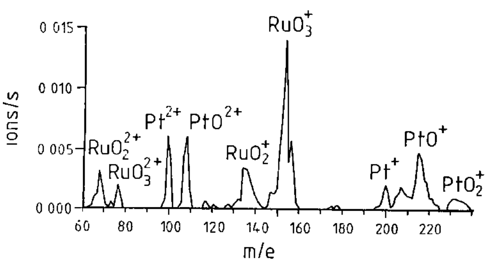

FIG. 2. Mass spectrum of the same tip on exposure to oxygen (Pressure: 7.5×10^{-4} Pa). Temperature of tip = 850 K, desorption pulse frequency = 10 Hz.

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