The Structure of Alkali Promoters on Catalysts Prepared by Traditional versus Surface Science Methods: A Case Study with Cs on Ag(111)

I. INTRODUCTION

Patents issued to commercial manufacturers of industrial ethylene oxide catalysts suggest that alkali promoters are often added to supported catalysts by impregnation with an aqueous solution of the alkali salt, followed by heating until dry in air. In surface science studies of the effects of alkali additives, the alkali is often added by vapor deposition under ultrahigh vacuum. We show here that these two methods give the same final surface structure for Cs additives on Ag catalysts for selective ethylene oxidation. This structure consists of a crystalline surface cesium oxide, $\sim Ag_xCsO_3$, characterized by a $(2\sqrt{3} \times 2\sqrt{3})R30°$ LEED pattern on the Ag(111) surface. In one case it is generated by vapor-depositing Cs onto clean Ag(111), followed by use as a catalyst in the reaction mixture (20 Torr ethylene, 150 Torr O_2, 490–563 K). In the other case, it is generated by dropping aqueous solutions of Cs_2CO_3, CsOH, or $CsNO_3$ onto the Ag(111) surface, then drying, and cooling in air. This result lends credibility to surface science methods for studying alkali promotion of other transition metal catalysts.

As the basis for a two billion dollar per year industry, the selective oxidation of ethylene to ethylene oxide ($C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$) as catalyzed by silver has been the subject of intense practical and fundamental research (1–4). Cesium has received much attention as an additive in basic studies and in patents and patent applications for catalysts useful in this reaction (5–12). We recently addressed the role of cesium

promoters on silver catalysts by using adsorbed cesium on the clean Ag(111) surface as a model catalyst (5). Patented catalysts often consist of small (~ 0.1 μm) Ag particles supported on an oxide such as Al_2O_3 (10, 11). In our experiment we had no support material, since a single crystal of pure Ag was studied (5). In this way, we could isolate and study the influence of Cs addition to that part of supported Ag catalysts which resembles metallic silver, and remove the influence of the support material. We studied the Ag(111) plane which, due to its thermodynamic stability, should predominate on the surfaces of Ag particles in technical catalysts. Similar studies have also been reported by Grant and Lambert (6, 7).

In our study (5) we found that, under reaction conditions where ethylene oxide was being produced with high steady-state rates on our Ag(111) surface (0.5–4 molecules/site/s at 20 Torr ethylene, 150 Torr O_2, 490–563 K), the added Cs always assumed the form of a surface cesium oxide with a characteristic $(2\sqrt{3} \times 2\sqrt{3})R30°$ LEED structure. This should be called a surface cesium oxide since the Cs and oxygen existed on the surface, with no other elements present except Ag, in a constant stoichiometric ratio of O/Cs = 3.1 ± 0.4. This ratio was independent of the amount of Cs initially added to the silver (up to one monolayer coverage). It is clear from this ratio that at least some of the oxygen atoms bond to both Cs and surface Ag atoms. This "surface CsO_3" or Ag_xCsO_3 decomposed in vacuo at ~ 600 K to yield simultaneous evolution of

gaseous Cs and O_2. Its presence in proper concentration on the surface under conditions of selective ethylene oxidation led to a slight enhancement in the selectivity for ethylene oxide formation (5), similar to the results for Cs addition to catalysts reported in patents and patent applications (11, 12) and in another study on Ag(111) (7).

At this point, one might already be convinced that we had clarified to a significant extent the structure and function of Cs promoters which could be extrapolated to more cost-efficient, supported Ag catalysts. However, one major criticism of this extension has been the method with which the Cs was initially dosed onto the Ag surface. We vapor deposited Cs onto clean Ag(111) under ultrahigh vacuum prior to high-pressure reaction studies; but, in patents and patent applications (11, 12) the Cs is typically deposited from salts (CsOH, $CsNO_3$, Cs_2CO_3) in aqueous solutions, after which the catalyst is heated in air to evaporate the liquid. Our results will be proven most pertinent if Cs salts deposited in this latter fashion are also converted to the $(2\sqrt{3} \times 2\sqrt{3})R30°$ surface CsO_3 either during the heating in air or under steady-state reaction conditions. The present study was undertaken to show that, indeed, Cs deposited from aqueous salt solutions onto Ag(111) converts to this very same surface cesium oxide during the heating/drying process in air.

II. EXPERIMENTAL

The experimental apparatus has been described in detail previously (4), as have the cleaning and preparation methods for Ag(111) (13). The sample was cleaned and characterized under ultrahigh vacuum (UHV) with Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). It was then rapidly retracted to a loading position (where it is exposed to atmospheric air), dosed at room temperature with a drop of water containing the Cs salt, heated in air for 1–2 min at 490 K to dry up the drop, cooled in air to almost room temperature, and then translated rapidly (~20

s) back to UHV for surface analysis at room temperature. The Cs salts were from Alpha Products, 99.9% purity as solids (Cs_2CO_3 and $CsNO_3$) or as a water solution (CsOH). These were mixed with ultrahigh purity (HPLC grade) water and diluted to make solutions containing ~2.5×10^{14} Cs^+ ions per drop (~10^{-5} moles/liter). This was sufficient to give a coverage of cesium, θ_{Cs} $\simeq 0.2$ on the front face of the 7 mm $\times$ 10 mm Ag(111) single crystal. (Coverages, θ, are defined relative to the number of Ag surface atoms, 1.38×10^{15} cm^{-2}.) The drops spread reasonable uniformly over the sample face.

Great care was required in handling the water used in this work to avoid other metal ions contaminating the water and therefore the surface, particularly Cu and Zn. The best results were obtained by using only polyethylene labware meticulously treated according to the recipes in (14), which have been developed for handling samples in trace elemental analysis. For these experiments, we found no differences between HPLC-grade water and the same water which was also subjected to pyrodistillation to remove carbon residues, except that the pyrodistilled water had a better chance of picking up metal impurities.

III. RESULTS

After dosing the clean Ag(111) surface with water solutions of the Cs salts in air, then heating and cooling in air, a $(2\sqrt{3} \times 2\sqrt{3})R30°$ LEED pattern was immediately observed upon translation into UHV, as shown in Figs. 1a–1c. These structures are not due to any electron-beam damage, since they were invariant with time or rapid translation of the sample thru the electron beam over distances considerably larger than the electron beam. These $(2\sqrt{3} \times 2\sqrt{3})R30°$ patterns were observed without ever heating the samples in vacuo. That is, these structures were characteristic of the species existing on the sample surface in atmospheric pressure after the heating/drying/cooling cycle, except for the influence
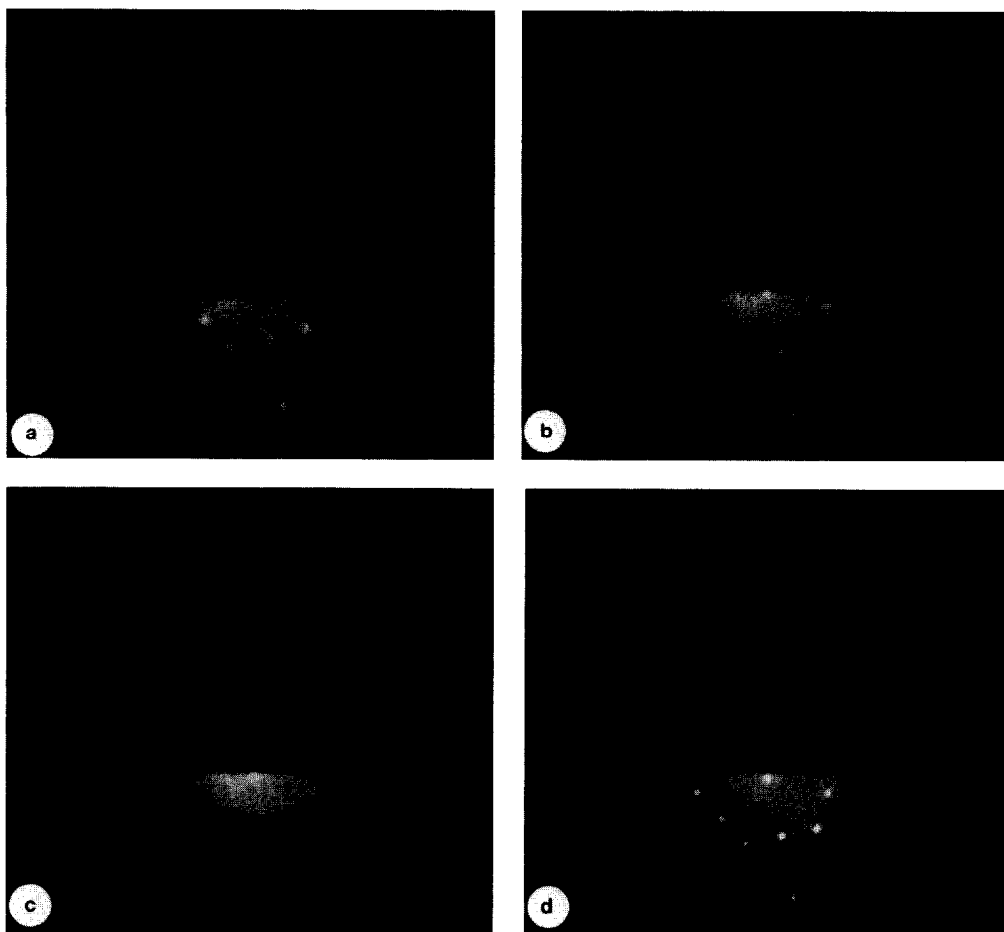
FIG. 1. Low-energy electron diffraction patterns showing the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure of surface cesium oxide (Ag_xCsO_3) generated in various ways on Ag(111): Aqueous solutions of (a) Cs_2CO_3, (b) CsOH, and (c) $CsNO_3$ were dropped onto the Ag(111) surface, which was then heated to 490 K for 1–2 min in air to dry, then cooled in air. (d) shows the same structure, prepared in Ref. (5) by vapor-depositing Cs onto clean Ag(111) in UHV, then treating the sample with a mixture of 20 Torr ethylene and 150 Torr O_2 at 490–563 K. All patterns taken with an electron beam of 63–69 eV, incident a few degrees off normal, at ~310 K.

of weakly adsorbed species which desorbed during the rapid evacuation at room temperature.

For comparison, in Fig. 1d we show the $(2\sqrt{3} \times 2\sqrt{3})R30°$ LEED pattern of surface cesium oxide $(\sim Ag_xCsO_3)$, produced in Ref. (5) by vapor-depositing atomic Cs onto clean Ag(111) and either heating in low pressures of O_2 or high pressure of $(O_2 + C_2H_4)$ mixtures. Clearly the structures seen by dosing Cs from the aqueous salt solutions are the same as those generated in the experiments of Ref. (5). Similar minima

and maxima in the LEED intensity versus voltage behavior further confirm this assignment.

The lower intensity and higher background in the case of $CsNO_3$ (Fig. 1c) correlated with the presence of observable (by AES) amounts of Cu impurities after dosing the nitrate solutions, a problem which could not be eliminated. This copper appeared to exist on the surface as some disordered form of copper oxide, which was stable to ~820 K in vacuo (see below). In any case, all three salts gave the $(2\sqrt{3} \times$

$2\sqrt{3})R30°$ pattern as a major feature on the surface.

After LEED observation but prior to heating the sample in vacuo, the structures of Figs. 1a–1c were analyzed by AES. The results are shown in Fig. 2, which includes for comparison the clean Ag(111) spectrum. One can see that the O(KVV) and Cs(MNN) regions of spectra b and c are very similar to those for the $(2\sqrt{3} \times 2\sqrt{3})R30°$ surface cesium oxide ($\theta_{Cs} \simeq 0.24$) of Ref. (5). (The difference for spectrum d will be discussed below.) Compared to clean Ag, the surfaces with the Cs oxide overlayer show a small difference at ~266 eV, which may be related to low-level carbon impurity or to a greater extent of Ag surface oxidation here. Unfortunately, this region of the spectrum is rich with Ag structure, and difficult to analyze. However, in
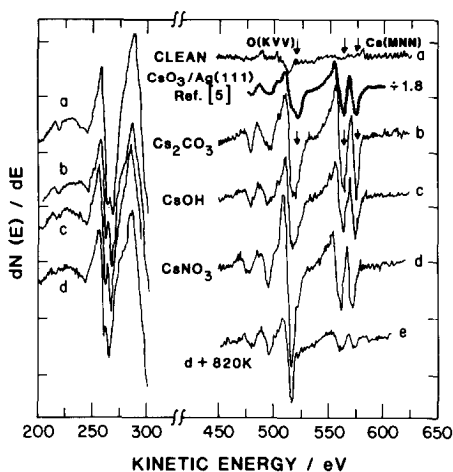

FIG. 2. Auger electron spectra of (a) clean Ag(111), (b)–(d) Ag(111) after Cs salt deposition to produce the LEED patterns of surface cesium oxide shown in Figs. 1a–1c. For comparison, the dotted curve shows the spectrum corresponding to the LEED pattern of Fig. 1d, taken from Ref. (5). (Scaling factor obtained by equating Ag intensities.) In (d), the N(KVV) region was also examined on the same sensitivity as for the O(KVV) region, and no nitrogen could be found. (Beam-damage effects were eliminated by moving the beam on the sample.) Curve (e) shows oxygen signal after heating (d) to 820 K to decompose the $(2\sqrt{3} \times 2\sqrt{3})R30°$ surface Cs oxide. The residual oxygen is attributed to copper impurities from the water. Spectral conditions: pass energy = $\frac{1}{4}$ × kinetic energy, V_{mod} = $5V_{p-p}$ normal detection.

our experience monolayer-level carbon impurity on Ag usually appears at a kinetic energy (~275 eV) which is noticeably higher than seen here. In any case, this could be due to some small extent of hydrocarbon contamination adsorbed during sample transfer. (This structure in the AES spectra at ~266 eV was also seen in a number of cases using the preparation methods described in Ref. (5).)

Finally, the thermal stability of the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structures of Figs. 1a–1c were tested by heating to successively higher temperatures in vacuo and cooling to room temperature for LEED observation. The $(2\sqrt{3} \times 2\sqrt{3})R30°$ patterns were completely stable up to 505 K, but disappeared by 615 K to yield a sharp and bright $p(1 \times 1)$ pattern characteristic of clean Ag(111). This again is completely consistent with the $(2\sqrt{3} \times 2\sqrt{3})R30°$ structure of surface CsO_3 from (5), which decomposes at ~600 K in thermal desorption spectra to liberate gaseous Cs and O_2.

After heating to 615 K, some residual oxygen remained on the surface in AES, and was stable to our highest annealing temperatures (~820 K). This was attributed to oxides of trace metal impurities from the water droplet, since all oxygen desorbs from Ag surfaces by 700 K (20). It was also present after dosing the pure water (no Cs salts) as above in a blank experiment. This residual oxygen was largest after dosing $CsNO_3$ solution, as can be seen in curve e of Fig. 2. In that case, it was associated with significant Cu impurity, as was evidenced by an AES peak at ~920 eV. Contribution from this oxidized Cu impurity explained the extra large O(KVV) signal of curve d in Fig. 2. It also may explain why the $(2\sqrt{3} \times 2\sqrt{3})R30°$ LEED spots were weaker and less ordered (streaked) in the case of $CsNO_3$ dosing.

IV. DISCUSSION AND CONCLUSIONS

It is typical in patent preparations to introduce alkali additives to supported cata-

lysts by impregnating with aqueous solutions of the alkali salts, after which the catalyst is dried by heating in air (11, 12). On the other hand, fundamental surface science studies of the effects of alkali additives often start by vapor depositing the alkali atoms onto the clean surface under ultrahigh vacuum, followed by reaction studies (5–9, 15–19). We have shown conclusively that, for the case of Cs on Ag(111) catalysts used for ethylene oxidation, these two methods give the same final form of the alkali: a crystalline surface cesium oxide of approximate stoichiometry $CsO_3(Ag_x)$, displaying a $(2\sqrt{3} \times 2\sqrt{3})R30°$ LEED pattern. This result should be considered as a success for the surface scientific approach to catalysis, and lends more credence to the many recent and ongoing studies of alkali promotion on this and other metal/alkali systems (4–9, 15–19).

This success can be attributed to the fact that the final structure of the alkali is really controlled by the most stable structure formed in the gaseous environments experienced during heating. Both the reaction mixture (O_2 + ethylene) and air are relatively oxidizing environments, where apparently both adsorbed cesium atoms and the Cs salt overlayers are readily oxidized to the final Ag_xCsO_3 form. In the later case, the nitrogen, carbon, or hydrogen of the original salt must be liberated as gases such as NO_2, CO_2, and H_2O during the heat treatment in air. The starting form of the alkali plays an insignificant role compared to the thermodynamics which drive the system to its most stable form. That is *not* to say, however, that the final form of the alkali is as adsorbed atoms. On the contrary, if one wished (for example) to study the influence of Cs additives on individual elementary steps in this reaction mechanism on silver, one should use Cs in the form of this surface CsO_3, and not as isolated adatoms. One can, nevertheless, begin such a study with alkali adatoms, and allow the high-pressure reaction mixture to generate their final structure. This structure would

then be tested with respect to individual reaction steps.

We should reiterate that our structural analyses here were made without ever heating the sample above room temperature in vacuo. One can therefore conclude that the observed surface structures are the same as those existing on the sample after dosing the salts, heating, and then cooling in atmospheric air, except for weakly adsorbed species which desorb already at room temperature in vacuo. Such weakly bonded species will certainly not play a major role in the function of the catalyst additive at elevated temperatures, where desorption is much more rapid, unless such species are somehow also continuously replenished by adsorption from the reaction mixture.

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