Characterization by scanning tunneling microscopy of silver oxydehydrogenation catalysts

P. Gallezot *, S. Tretjak
Institut de Recherches sur la Catalyse, CNRS, 69626 Villeurbanne Cedex, France

Y. Christidis, G. Mattioda, A. Schouteeten
Société Française Hoechst, Centre de Recherches et d'Applications, 93240 Stains, France

Yip-Wah Chung and T.S. Sriram
Center for Catalysis and Surface Science, Northwestern University, Evanston, IL 60208, USA

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A silicon carbide-supported silver catalyst used in the oxydehydrogenation of ethylene glycol to glyoxal has been studied by scanning tunneling microscopy. The surface morphology depends upon reaction conditions. Silver particles normally sinter into large plates covering the support. However, in the presence of diethylphosphite there is a chemical erosion which results in a tortuous and fractal-like surface.

Keywords: Scanning tunneling microscopy; silver catalyst STM study of silver catalyst; surface topography of

1. Introduction

Scanning tunneling microscopy (STM) is well known for its unique capability of revealing the structure of surfaces with atomic resolution [1,2]. However, atomic resolution STM studies are mostly restricted to model surfaces and require a great expertise both in the control of the experimental conditions (environment control, tip reproducibility, ...) and in the interpretation of images which represent the local density of states on surfaces rather than the mere atomic patterns. On the other hand, STM studies at slightly lower resolution (e.g. 0.4–1 nm) can be used routinely to probe the topography of surfaces in three dimensions [3]. This cannot be done easily by other techniques.

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* To whom correspondence should be sent.

For example scanning electron microscopy (SEM) has a lower resolution and transmission electron microscopy requires thin samples and gives a projected image which does not tell much on the surface relief. This work is to our knowledge the first STM study of a real catalyst after use in a micropilot reactor. More specifically, we have studied the surface topography of a silicon carbide-supported, silver catalyst used in the oxydehydrogenation of ethylene glycol (CH_2OHCH_2OH) into glyoxal (CHOCHO). Our aim was to monitor possible changes in the catalyst morphology induced by small amounts of diethylphosphite (DEP) added in the gas phase to enhance the selectivity to glyoxal.

2. Experimental

A 5 wt% Ag/SiC catalyst was prepared by impregnation of carborundum (SiC) grains (≈ 1 mm diameter) with water solutions of silver nitrate. After drying at 100°C, the metal salt was reduced at 500°C under flowing hydrogen.

The oxydehydrogenation of ethylene glycol was carried out at 550°C in a quartz flow reactor. Water solutions of ethylene glycol were vaporized in a stream of a preheated oxygen and nitrogen mixture. In some experiments, small amounts of diethylphosphite were added to ethylene glycol solutions. Reactions were conducted at high conversion for 100 h, the catalyst being in a steady state.

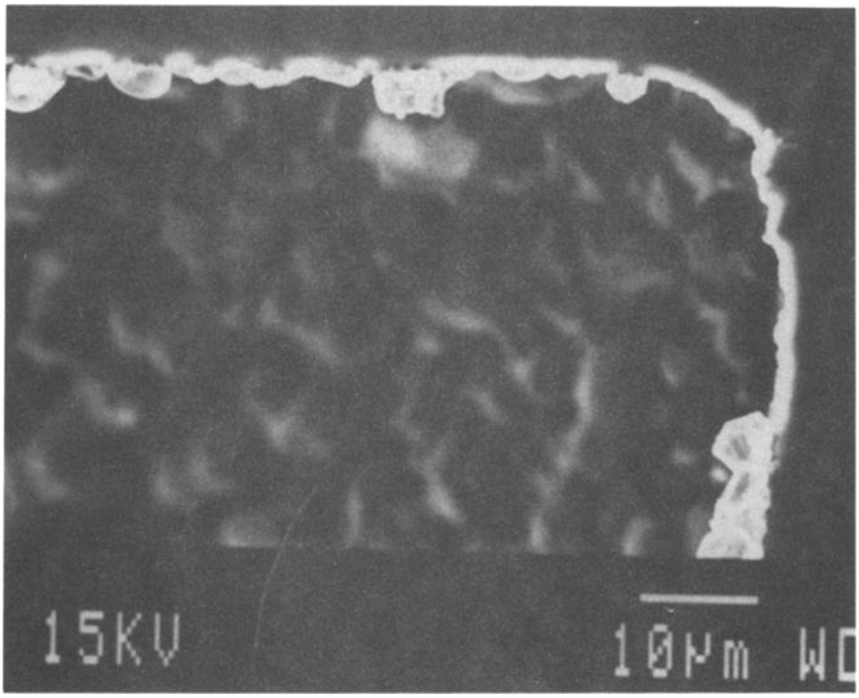

Fig. 1. SEM view of a broken grain of the fresh Ag/SiC catalyst.

After stopping the reactant flow, catalysts were cooled to room temperature under flowing nitrogen. The fresh and used catalysts were characterized by SEM and STM.

STM studies were performed by a Digital Instruments Nanoscope II, operating at a nominal specimen bias 25 mV and a tunneling current of 1 nA. The sample was glued to the specimen platform using conductive silver paint. Images were acquired as 400 × 400 integer arrays at a rate of 80–160 s per image. Sharp

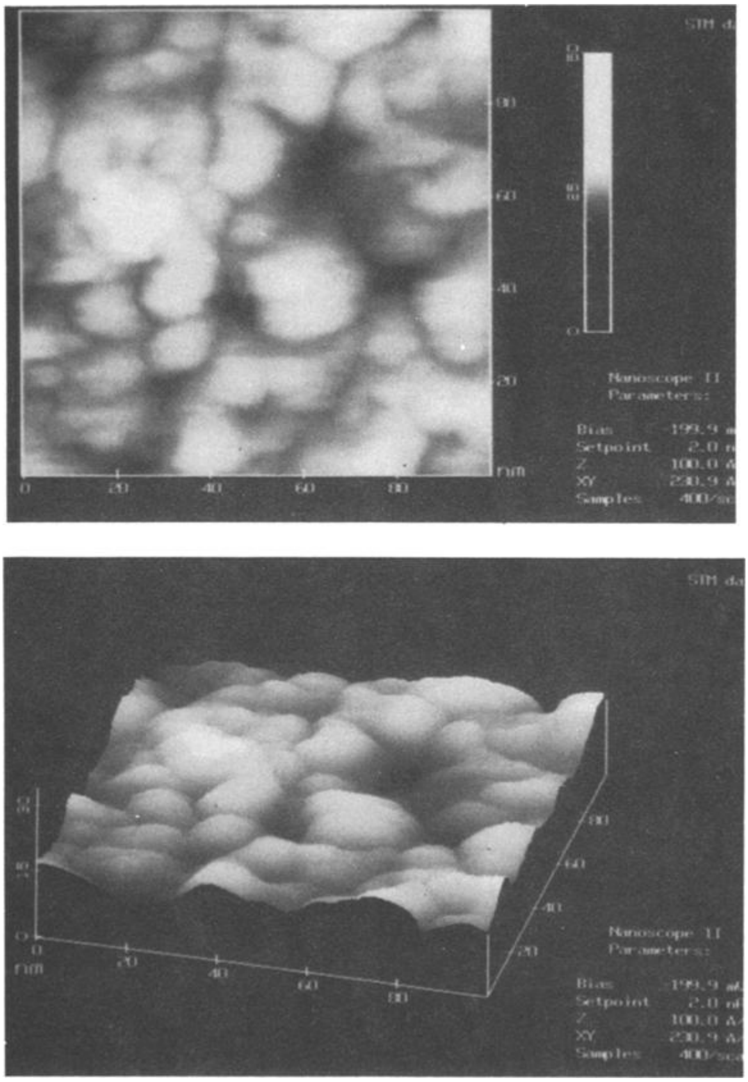

Fig. 2. STM view of the fresh Ag/SiC catalyst; scanned area (100×100) nm^2. Upper part, top view; lower part, side view.

Pt–Ir tips (tip radius less than 25 nm with a 15° opening angle extending over several microns) were used to minimize tip artifacts.

3. Results and discussion

3.1. FRESH CATALYST

Fig. 1 gives an SEM view at low magnification of a catalyst grain broken purposely. The section shows that silver forms a crust covering the entire surface

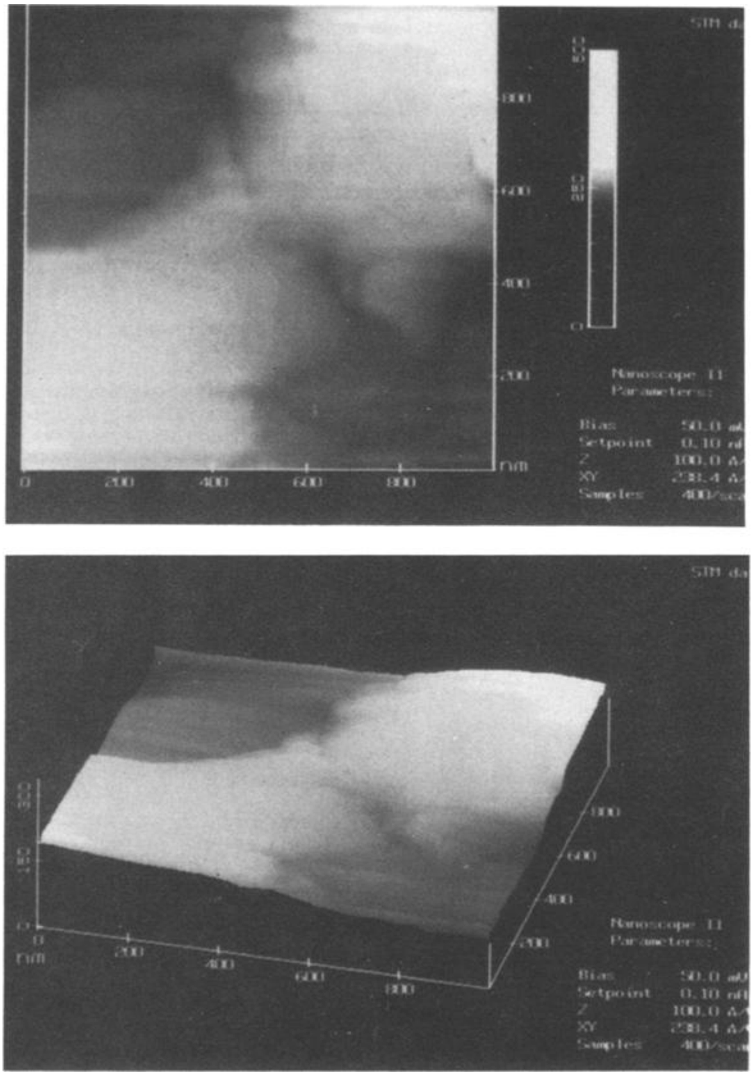

Fig. 3. STM view of Ag/SiC after reaction without diethylphosphite; scanned area (1000×1000) nm^2. Upper part, top view; lower part, side view.

of the glassy, non-porous silicon carbide carrier. Views at higher magnifications indicate that the SiC surface is covered by a thin continuous layer of silver on which loosely packed silver particles are attached.

Fig. 2, upper part (top view) and lower part (side view), are STM images of a (100 × 100) nm^2 area. Most of the particles are in the size range 5–20 nm.

3.2. CATALYST AFTER REACTION

The Ag/SiC catalyst described above was used in the ethylene glycol oxydehydrogenation reaction at 550°C for 100 h without DEP in the feed. The catalyst morphology is deeply modified as shown by the STM views given in fig. 3. The silver particles have sintered into plates in the size range 1–10 nm. However, the surface of these plates is not smooth. The top view (fig. 3, upper part) shows that there are terraces on the surface with steps forming contour lines. These terraces have been also detected by SEM.

3.3. CATALYST AFTER REACTION IN PRESENCE OF DEP

The Ag/SiC catalyst has been used under the same reaction conditions as previously except that 20 ppm of DEP were added to the vaporized ethylene glycol solution. Figs. 4–6 are STM views corresponding to successively smaller scanned areas. The images of the silver surface show bud-like particles. Interestingly, the images do not change much whatever the magnification, i.e. small

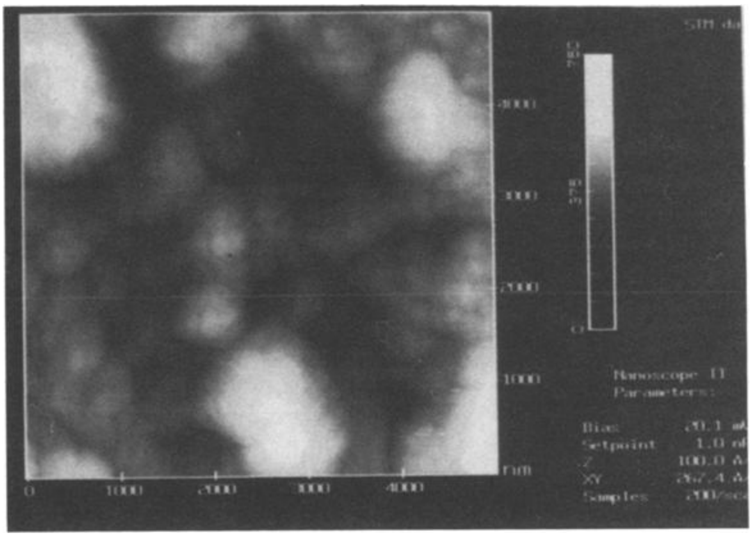

Fig. 4. STM view of Ag/SiC after reaction with 20 ppm of diethylphosphite; scanned area (5000×5000) nm^2; top view.

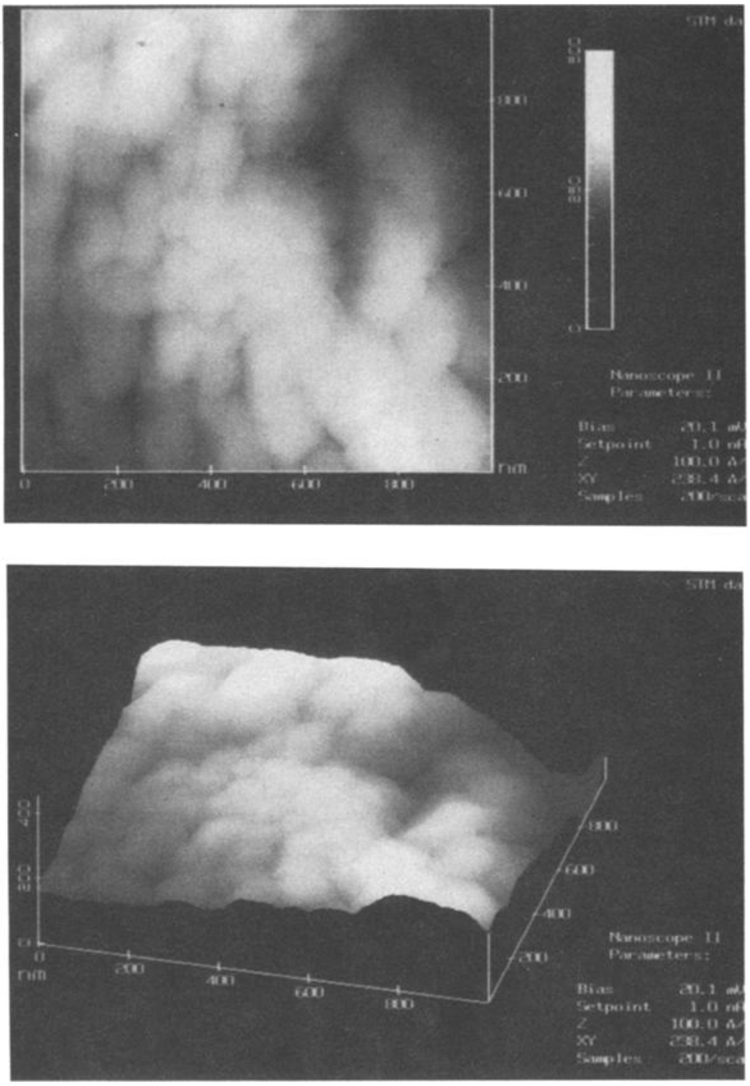

Fig. 5. STM view of Ag/SiC after reaction with 20 ppm of diethylphosphite; scanned area (1000 × 1000) nm^2. Upper part, top view; lower part, side view.

particles seem burgeoning out of larger ones, suggesting that the surface of silver could be fractal. This particular morphology could be the result of chemical erosion occurring during the reaction in the presence of DEP. Indeed, chemical analysis after the reaction shows that part of the silver was leached away probably because a volatile Ag-P compound was formed on the surface. The morphology of the surface is due either to the erosion itself or to a reconstruction process following the erosion.

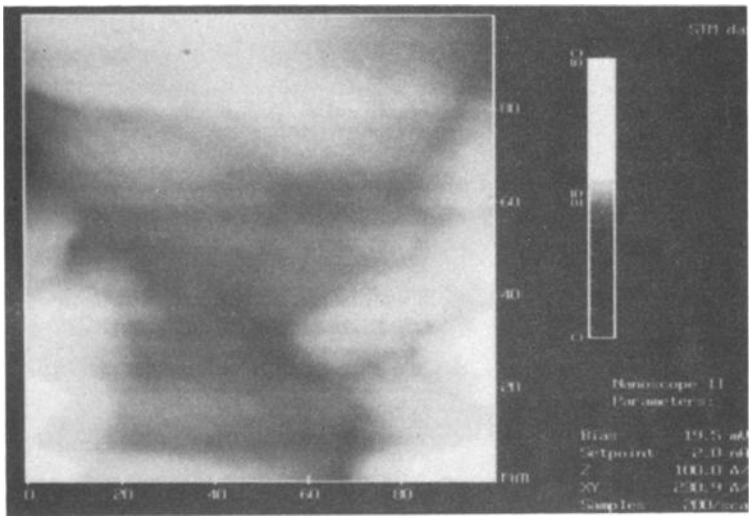

Fig. 6. STM view of Ag/SiC after reaction with 20 ppm of diethylphosphite; scanned area $(100 \times 100)\ \mathrm{nm}^2$; top view.

4. Conclusions

The surface morphology of the catalyst in the absence of DEP is due to a sintering process whereby the small silver particles coalesce and reconstruct into large terraced silver plates. On the other hand, the surface morphology of the catalyst used in the presence of DEP cannot be described by a sintering process which would minimize the surface free energy. Instead, hemispherical particles seem burgeoning out of larger ones possibly in a fractal scheme due to the continuous chemical erosion of the surface. This study demonstrates that (i) silver surface atoms have a high mobility under reaction conditions and the actual surface morphology depends upon slight variations in the feedstock composition, (ii) STM is a very good tool to probe the surface morphology of the conductive silver layer wetting the SiC support. Three-dimensional images have been obtained on a routine basis with higher resolution, specially in the Z direction, than with an SEM which is more expensive to buy, to maintain and to house than an STM.

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