JOURNAL OF CATALYSIS **142**, 729–734 (1993)

Oxidative Dehydrogenation of Ethylene Glycol into Glyoxal: Effect of Diethylphosphite on SiC-Supported Silver Catalysts

Because of its bifunctionality, glyoxal or ethanedial ($CHOCHO \cdot 2H_2O$) is a highly reactive molecule which has found many applications (*1*) as a synthon in organic chemistry and as a cross-linking agent acting as a hardener in various materials (natural and synthetic polymers, textiles, papers, cements, and soils). Also, because of its lower toxicity it tends to replace formaldehyde, e.g., as a reducing agent. Water solutions of glyoxal are prepared industrially either by nitric acid oxidation of acetaldehyde or by oxidative dehydrogenation of ethylene glycol; the latter reaction is documented only in the patent literature (*2–8*). The reaction is conducted either at moderate temperatures (623 to 723 K) or at high temperatures (773 to 873 K). Reactions at high temperatures which give the highest productivity are catalysed by copper or silver catalysts. Processes are based mostly on unsupported catalyst; however, the recent patent from Mitsui Toatsu (*8*) claims a high glyoxal yield on a silver catalyst supported on silicon carbide. All the patents report the use of promoters, especially phosphorous compounds, which are added to the reactant flow to boost the selectivity to glyoxal at the expense of more deeply oxidized products. However, the mode of action of these promoters remains totally unknown. A surface science study of ethylene glycol dehydrogenation to glyoxal at low temperatures (220–380 K) on the (110) crystal face of silver has shown that the reaction proceeds via a 1,2-ethanedioxy intermediate bridge-bonded to the surface which is further dehydrogenated into glyoxal (*9, 10*).

The scarcity of data on the factors controlling the selectivity of the reaction at high temperatures prompted us to undertake a detailed study combining physical characterizations of catalysts and reaction data to better understand the effects of the catalyst morphology, reaction conditions, and presence of phosphorous additives on the selectivity to glyoxal. A first report on the characterization of a Ag/SiC catalyst by scanning tunnelling microscopy has been published (*11*). The present paper deals with the effect of diethylphosphite on the composition and catalytic properties of two SiC-supported silver catalysts used in the oxydehydrogenation of ethylene glycol.

Two silver catalysts supported on SiC were studied. Catalyst 8% Ag/SiC was an industrial catalyst used in the oxidative dehydrogenation of methanol into formaldehyde. It was kindly supplied by CDF Chimie. Catalyst 5% Ag/SiC was prepared by impregnation of a silicon carbide support with water solutions of silver nitrate in required amounts. The SiC support was in the form of roughly spherical, nonporous grains of ca. 1 mm diameter; its specific surface area was lower than 0.1 $m^2\ g^{-1}$. After elimination of the solvent in a rotary evaporator at 80°C and overnight drying at 373 K, the impregnated support was treated at 773 K under flowing H_2 for 24 h.

The silver content was determined by atomic absorption spectroscopy after acid dissolution of silver. The morphology of the catalyst surface was studied by scanning electron microscopy (Hitachi S800) and by scanning tunnelling microscopy (Nanoscope II, Digital Instruments) in the conditions described previously (*11*). Because of the electron conductivity of the silver layer, SEM and STM measurements were conducted directly on the catalyst without

0021-9517/93 $5.00

prior coverage with sputtered gold. The surface composition was determined with an Auger scanning spectrometer (Riber Nanoscope) and by secondary ion mass spectrometry (IMS 3F Cameca). SIMS measurements were conducted on the surface eroded at various depths with Cs^+ ions.

The oxidative dehydrogenation of ethylene glycol (EG) was performed in a quartz reactor. Water solutions of ethylene glycol (50 wt%) were injected with a peristaltic pump in a mass-controlled flow of nitrogen at the entrance of an oven heated at 450°C. The design of this vaporizer was optimized to give a smooth, continuous vapor flow of ethylene glycol and water which was admitted in the upper part of a 300-mm-long, 20-mm-large quartz reactor. These vapors were mixed with a downward flow of a preheated mixture of nitrogen and oxygen whose composition was set with Brooks mass-flow controllers. Under standard reaction conditions the molar ratios with respect to EG were: $EG:O_2:H_2O:N_2 = 1:1.45:3.40:35$. The concentration of EG in the flow was 2.48%, i.e., outside the domain of explosivity. At 550°C the total flow was as high as 212 liter h^{-1} and the residence time in the catalyst bed was 0.03 s. The catalyst was retained with quartz wool in the lower part of the reactor. The space between the catalyst bed and the condenser was kept as small as possible to quench reaction products. The condenser was cooled with circulating cold water, liquids, and noncondensed vapors were trapped at liquid-nitrogen temperature.

The diethylphosphite (DEP) promoter was dissolved in required amounts in the ethylene glycol-water mixture. Gaseous products (CO, CO_2) were analyzed on line by gas chromatography. The condensed products were residual EG and aldehydes. EG was reacted with HI at 423 K to give ethyl iodide which was measured by gas chromatography. Part of the ethylene glycol was not measured because EG combined with water formed an aerosol which was very difficult to condense even in the trap cooled by liquid nitrogen. Therefore a good carbon balance between reactant and products was obtained only at high conversion, i.e., when negligible amounts of ethylene glycol were left. Aldehydes were converted into oximes and then measured by HPLC with an internal standard.

At 823 K the free energy of the oxidative dehydrogenation of ethylene glycol into glyoxal (by the reaction below) is 460 kJ mol^{-1} but parallel and consecutive oxidation reactions are also highly favoured; therefore the selectivity to glyoxal (GL) is highly dependent upon the choice of catalyst.

$$CH_2OHCH_2OH + O_2 \rightarrow CHOCHO + 2H_2O.$$

Preliminary blank experiments without catalyst were conducted at 823 K in stainless steel reactors of various lengths. The EG conversion was as high as 50% with GL and formaldehyde (FOR) as main products and was dependent upon the geometric area of the reactor walls. The presence of diethylphosphite (DEP) in the feed had no effect on the conversion and product distribution. Subsequent blank reactions in a quartz reactor gave only 5% conversion. Clearly these experiments show that no metal should enter in the reactor design at least on a micropilot scale, where the area of reactor walls is important with respect to that of the catalyst. Although most patents describe the use of unsupported silver crystals, we directed our effort toward the design of supported silver catalysts in order to optimize the amount of silver. At high temperature the contact time of the reactant and reaction products with the catalyst surface should be as small as possible to avoid total oxidation and therefore microporous supports were discarded. It appeared that even low-specific-area (1.5 m^2 g^{-1}), macroporous supports (silica, alumina, silico-alumina ceramics) gave a very low glyoxal

TABLE 1

Reaction Data (823 K; O_2/EG = 1.45)

Run	Catalyst	DEP (ppm)	Conversion (%)	Product distribution (%)						Selectivity (%)
				GL	GLA[c]	C_1[c]	FOR[c]	CO_2	CO	
1[a]	8% Ag/SiC	0	98	50	0	48				51
2[a]	8% Ag/SiC	5	96	60	1	35				62.5
3[a]	8% Ag/SiC	20	95	62	4	29				65
4[a]	8% Ag/SiC	40	86	64	1	21				74
5[a]	5% Ag/SiC	0	96	53	1	42				55
6[a]	5% Ag/SiC	5	95	62	2	31				65
7[a]	5% Ag/SiC	20	92	66	4	22				72
8[b]	5% Ag/SiC	20	98.5	72	1.5	25	9	11	5	73
8[b]	5% Ag/SiC	20	98	72	1	25	9	11	5	73
8[b]	5% Ag/SiC	20	96	70	1.5	24.5	11	9	4.5	73
8[b]	5% Ag/SiC	20	97.5	71	1.5	25	11	9	5	73

[a] Residence time 0.03 s; data after 2 h on stream.

[b] Residence time 0.06 s; data after different periods of time on stream: 3, 27, 72, and 96 h.

[c] GL, glyoxal; GLA, glycolic acid; FOR, formaldehyde; C_1 = FOR + CO_2 + CO.

yield and more deeply oxidized products. Therefore our choice was oriented toward silicon carbide which is totally nonporous and presents the additional advantage of being a good heat conductor which should ease the dissipation of the large reaction heat.

Table 1 gives the reaction data on catalyst 8% Ag/SiC as a function of the amount of DEP added to the EG-water solution (runs 1 to 4). The presence of DEP in the feed increases the glyoxal yield at the expense of C_1 products (HCHO + CO_2 + CO). However, the main effect is obtained with only 5 ppm of DEP; larger amounts improve slightly the yield but decrease the conversion. Catalyst 5% Ag/SiC under the same reaction conditions exhibits a similar behavior (Table 1, runs 5 to 7) but gives slightly higher selectivities. Table 1 gives the results obtained on catalyst 5% Ag/SiC after different periods of time on stream (run 8; 3, 27, 72, and 96 h) in the presence of 20 ppm of DEP. The residence time in the catalyst bed is twice as large as in previous experiments; higher conversion (98.5%) and higher selectivity (73%) were obtained. This means that GL once formed is not oxidized further, at least as long as the contact time is still very short; we checked that residence times larger 0.06 s lead to lower glyoxal yields. Another interesting result is the high stability of the catalyst which did not give any significant change in conversion and selectivity after 4 days on stream. It would be interesting to study the behavior of the catalyst initially, but this is not easy to do experimentally. In another experiment, not reported in Table 1, the concentration of DEP in the EG–water solution was increased and then decreased. It was shown that the conversion and glyoxal yield can take back their initial values as long as the DEP concentrations remained lower than 100 ppm. This means that DEP should be injected permanently to maintain the catalyst performance.

Table 2 gives the amount of silver present in the 8% and 5% Ag/SiC catalysts. It is noteworthy that in the absence of DEP the percentage of silver in 8% Ag/SiC hardly changes after reaction, whereas a substantial loss of silver is observed after reaction conducted with 20 ppm of DEP in the feed.

TABLE 2

Effect of DEP on the Catalyst Composition

Catalyst	Reaction	Ag (wt%)	
		Before reaction	After reaction
8% Ag/SiC	100 h without DEP	8.4	8.0
8% Ag/SiC	120 h with 20 ppm of DEP	8.2	6.2
5% Ag/SiC	96 h with 20 ppm of DEP	5.6	4.8

A loss of silver is also observed for the 5% Ag/SiC catalyst when reaction proceeds in the presence of DEP. Chemical analyses of both catalysts after reaction failed to detect any phosphorus in the catalyst, the limit of detection being 40 ppm. The analysis of the catalyst surface by Auger electron spectroscopy did not reveal the presence of phosphorus on the surface which, given the sensitivity of the technique, means that there is less than 1% P-atoms on the surface, if any. Using SIMS it was possible to detect ^{31}P on the surface and at various depths underneath, however the amount was too low to give a quantitative estimate. The actual concentration of phosphorus should be very small since the sensitivity of SIMS for phosphorus is extremely high (0.4 ppb of P in a silicon matrix). These different analyses prove that the phosphorus, continuously injected in the form of DEP, does not remain on the catalyst and that silver is leached away in the gas phase, probably as a result of the formation of a compound between silver and phosphorus. The chemistry of the leaching process is not easy to establish given the complexity of the reaction medium including oxygen, water, DEP, and the organic reactant and products at temperatures as high as 823 K. Among possible definite compounds between silver and phosphorus, silver pyrophosphate $Ag_4P_2O_7$ is the most likely since it is stable at the temperature of reaction.

The SEM and STM studies of the morphology of the catalyst surface after reaction with or without DEP in the feed have been reported previously (*11*). Let us recall that in the fresh 5% Ag/SiC catalyst the SiC grains are covered with a continuous thin layer of silver to which 5–20 nm silver particles are attached. After reaction without DEP the silver particles sinter into large 1–10 μm plates whereas with DEP the surface remains highly textured and small particles seem always to be burgeoning out of larger ones suggesting that the surface of silver could be fractal.

From an industrial standpoint, the oxidative dehydrogenation of ethylene glycol to glyoxal should be conducted so as to obtain the best yield at total conversion. Although the objective of the present investigation was not to match the best results reported in the patent literature on highly optimized catalysts and reaction conditions, we note that the performance of the 5% Ag/SiC catalyst compares well with the data obtained on silver crystals. This represents a tremendous improvement in terms of efficiency for metal use since a twenty times smaller silver loading is used. This is because silver is in the form of a continuous thin layer sticking to the SiC surface. The catalyst grain is resistant to attrition and is thermally conductive. The potentialities of SiC-supported catalysts in the oxidative dehydrogenation of EG was confirmed by a recent patent from Mitsui Toatsu published in the midst of our study where a 83% glyoxal yield at 99.9% conversion was claimed (*8*). However, in this patent as well as in the present investigation traces of alkylphosphite compounds were used to boost the selectivity. The main objective of our study was to understand the role of DEP on the selectivity and on the catalyst morphology.

The presence of DEP even in amounts as small as 5 ppm in the reactant feed markedly improves the selectivity to glyoxal, thanks to a decrease of C_1 oxidation products (formic acid, CO, and CO_2) (Table 1).

From our blank experiment in the absence of any catalyst showing that the conversion is very low, it can be concluded that radical type oxidation reactions in the gas phase have a negligible contribution, if any. Thus DEP acts essentially on the surface of the catalyst where the reaction takes place. Accordingly, it is noteworthy that DEP is efficient at concentrations much smaller than those used for flame retardants or radical trapping agents in homogeneous gas phase reactions. The action of DEP on the surface is obvious as far as catalyst composition and morphology are concerned. Thus, the leaching of silver during reaction means that phosphorus brought in the form of DEP reacts with surface oxygen and with surface silver atoms which are extracted. This etching process results either directly, or more probably via a continuous surface reconstruction, in a fractal surface where small particles seem to be burgeoning from larger ones so that whatever the magnification the STM images look similar (*11*). However, at present it is not easy to establish any link between the particular surface morphology and the selectivity improvement except that they are observed simultaneously as long as DEP is present in the feed. At least it can be said that the EG conversion is not related with the surface morphology since to a larger surface area corresponds a lower conversion.

The effect of DEP as a selectivity promoter can be tentatively interpreted from the surface chemistry of EG adsorption and conversion established by Capote and Madix (*9*, *10*) on silver (110) crystal face, albeit at much lower temperatures than in the industrial reaction conditions. According to this mechanism the first step is the adsorption of EG leading to 1,2-ethanedioxy species bonded to silver surface atoms:

$$\mathrm{HOCH_2CH_2OH(g)} \rightarrow \mathrm{HOCH_2CH_2OH(a)} \quad (1)$$

$$\mathrm{HOCH_2CH_2OH(a)} + \mathrm{O(a)} \rightarrow \mathrm{HOCH_2CH_2O(a)} + \mathrm{OH(a)} \quad (2)$$

$$\mathrm{HOCH_2CH_2O(a)} + \mathrm{OH(a)} \rightarrow \mathrm{OCH_2CH_2O(a)} + \mathrm{H_2O(a)}. \quad (3)$$

These species can dehydrogenate into glyoxal

$$\mathrm{OCH_2CH_2O(a)} \rightarrow \mathrm{OCH_2CH{=}O(a)} + \mathrm{H(a)} \quad (4)$$

$$\mathrm{OCH_2CH{=}O(a)} \rightarrow \mathrm{O{=}CHCH{=}O(g)} + \mathrm{H(a)} \quad (5)$$

or react with adsorbed oxygen

$$\mathrm{OCH_2CH_2O(a)} + \mathrm{O(a)} \rightarrow \mathrm{O{=}CHCH_2O(a)} + \mathrm{OH(a)} \quad (6)$$

$$\mathrm{OCH_2CH_2O(a)} + \mathrm{OH(a)} \rightarrow \mathrm{O{=}CHCH_2O(a)} + \mathrm{H_2O(a)} \quad (7)$$

$$\mathrm{O{=}CHCH_2O(a)} + \mathrm{O(a)} \rightarrow \mathrm{HCOO(a)} + \mathrm{H_2C{=}O(g)} \quad (8)$$

to be cleaved into formaldehyde and adsorbed formate which can subsequently give CO or CO_2. Therefore the relative amounts of O(a) and OCH_2CH_2O(a) present on the surface might determine the extent of the two pathways, one leading to glyoxal, the other to C_1 products. At 823 K there is a balance between oxygen in the gas phase, dissociated oxygen on the surface, and even atomic oxygen dissolved in the bulk of silver, as shown by Rehren *et al.* (*12*). The addition of DEP could play a decisive role in this balance by decreasing the amount of adsorbed atomic oxygen to a level where reactions (6)–(8) leading to C_1 products become less probable, thus increasing the amount of glyoxal via reactions (4) and (5). Indeed $P^{(III)}$ in DEP should be oxidized into $P^{(V)}$ by reacting with adsorbed oxygen, thus decreasing the concentration of these species on the surface. This mechanism accounts not only for the increase of selectivity to glyoxal but also for the decrease of conversion as the concentration of DEP increases especially above 20 ppm; then the concentration of adsorbed oxygen may become too low which would decrease the probability of reaction (2) and thus the amount of 1,2-ethanedioxy species. One might expect that the glyoxal formed in reaction (5) should be oxidized further. The stability of GL can be due to the presence of water in the reaction medium which reacts with GL to form the gem-diol $CH(OH)_2CH(OH)_2$ which is quenched in the condenser very close to the catalyst bed. Note that it was not possible to study the kinetics of GL oxidation in the present reaction conditions because GL water solutions cannot be vaporized.

In conclusion the present work throws some light on an important catalytic reaction little studied so far; more specifically the following points are highlighted:

1. Although pilot studies would be required to confirm our laboratory tests, SiC-supported silver catalysts appear to be good substitutes for silver crystals since comparable selectivities to glyoxal can be obtained with much less silver immobilized in the catalyst inventory. However, silver leaching could make the economy of the process questionable since catalysts with low metal loadings might deactivate sooner.
2. The continuous injection of phosphite compounds such as DEP is necessary to keep a high selectivity to glyoxal. These compounds act on the surface of the catalyst by reacting both with oxygen and silver atoms. By depleting the concentrations of adsorbed oxygen they decrease the probability of reaction pathway leading to C_1 oxidized products. By eroding the surface they enhance restructuring processes leading to a fractal surface.

REFERENCES

1. Mattioda, G. and Blanc, A., *in* "Ullmann's Encyclopedia of Industrial Chemistry" (B. Elvers, S. Hawkins, M. Ravenscroft, J. F. Rounsaville, and G. Schulz, Eds.), Vol. A12, p. 491. VCH-Verlag, Weinheim, 1989.

2. Carbide and Carbon, US 2 339 282 (1940).

3. Laporte, DE 1 923 048 (1968); DE 1 967 147 (1968).

4. American Cyanamid, DE 2 634 439 (1975).

5. BASF, EP 3 443 (1978); EP 19 772 (1979); EP 72 912 (1981); EP 287 884 (1987).

6. Nippon Goshei, DE 3 904 829 (1989).

7. Mitsubishi, JP 5 920 3928.

8. Mitsui Toatsu JP 583 8277 (1981); JP 585 9933 (1981); US 4 555 583 (1982); JP 60 100 533 (1983); JP 91 232 835 (1991).

9. Capote, A. J., and Madix, R. J., *J. Am. Chem. Soc.* **111,** 3570 (1989).

10. Capote, A. J., and Madix, R. J., *Surf. Sci.* **214,** 276 (1989).

11. Gallezot, P., Tretjak, S., Christidis, Y., Mattioda, G., Schouteeten, A., Chung, Y. W., and Sriram, T. S., *Catal. Lett.* **13,** 305 (1992).

12. Rehren, L., Isaac, G., Schlögl, R., and Ertl, G., *Catal. Lett.* **11,** 253 (1991).

P. GALLEZOT*,[1]
S. TRETJAK*
Y. CHRISTIDIS†
G. MATTIODA†
A. SCHOUTEETEN†

* *Institut de Recherches sur la Catalyse—CNRS*
2 avenue Albert Einstein
69626 Villeurbanne Cedex, France
† *Société Française Hoechst*
Centre de Recherches et d'Applications
64 avenue Gaston Monmousseau
93240 Stains, France

Received November 18, 1992; revised March 8, 1993

---

[1] To whom correspondence should be addressed.