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NOTES

The Oxidation of Cumene on Silver and Silver–Gold Alloys

Silver has a unique selectivity for the oxidation of ethene to ethene oxide. Worbs (*1*) and numerous other authors ascribe this property to the presence of undissociated, diatomic oxygen, e.g. O^-_{2ads}, on the surface of silver. In spite of considerable efforts, however, no unambiguous experimental proof for this adsorption complex has been found. A review on this subject is given in Ref. (*2*). A possible clue to the existence of diatomic, adsorbed oxygen might be seen in an observation reported by Fortuin (*3*). This author studied the oxidation of liquid cumene to cumene hydroperoxide and found that the induction period characteristic for this free radical chain reaction in a glass vessel was considerably reduced when a copper vessel was used. As it is conceivable that in the formation of cumene hydroperoxide a pair of oxygen atoms is inserted in one reaction step, De Boer (*4*) proposed that an adsorbed diatomic-oxygen species is adsorbed on copper in a manner analogous to the above-mentioned complex on silver. It therefore appears desirable to study the catalytic effect of silver for this reaction.

Flank and Beachell (*5*) studied the oxidation of ethene to ethene oxide on silver, gold and silver–gold alloys. They observed that alloys containing up to 10% Au had a considerably higher selectivity for this reaction than pure silver. In terms of Worbs' reaction mechanism, this result seems to indicate that the ratio of diatomic to monoatomic oxygen adsorbed on the surface would be higher on this alloy than on pure silver. If De Boer's view that the diatomic oxygen species is also a reaction intermediate in the oxidation of cumene is correct, an activity maximum for this reaction would be expected for the same alloy. As no systematic investigation of the metal catalyzed oxidation of cumene to cumene hydroperoxide is known to us, we decided to study this reaction not only with silver, but also with copper, gold and silver–gold alloys as potential catalysts.

EXPERIMENTAL

Ag/SiO_2 and $Ag/\gamma\text{-}Al_2O_3$, $Cu/\gamma\text{-}Al_2O_3$, and $Au/\gamma\text{-}Al_2O_3$ catalysts were prepared by impregnating the carrier with an aqueous solution of either $AgNO_3$ or $Cu(NO_3)_2$ or of the Au complex obtained by dissolving elementary Au in aqua regia. The $Ag\text{–}Au/\gamma\text{-}Al_2O_3$ catalyst was prepared by impregnating a $Ag/\gamma\text{-}Al_2O_3$ catalyst with a chlorine-free "gold-nitrate"-solution prepared by removing Cl_2 from the Au complex as described in Ref. (*6*). All the catalysts were reduced with hydrogen at 200–300°C.

From the line broadening in the X-ray diffraction patterns, a particle size varying between 40 and 400 Å was calculated. Specific silver surface areas were determined with a Perkin–Elmer Shell model 212D sorptometer by measuring the quantity of hydrogen necessary for removing preadsorbed oxygen.

The method used for measuring the rate of cumene oxidation was essentially the same as that described by Fortuin (*3*). The oxidation was carried out in the liquid phase at temperatures between 80 and 110°C. The reaction was followed by measuring the oxygen consumption at constant pressure with the aid of a gas burette. The

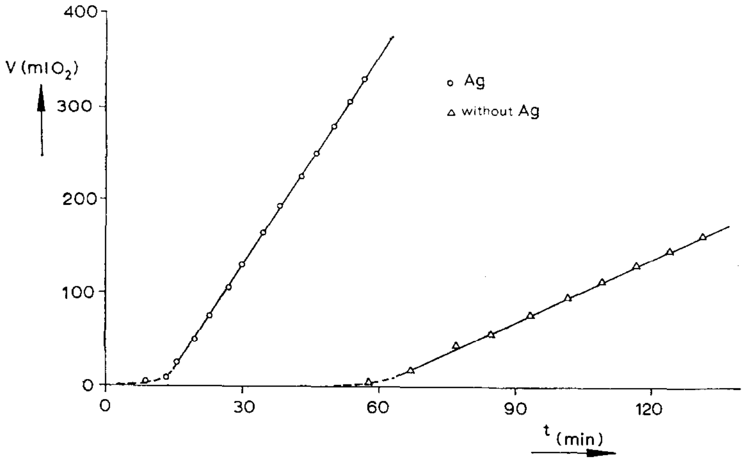

FIG. 1. The amount, V, of oxygen reacted with cumene with and without silver vs reaction time, t, at a temperature of 90°C.

products of reaction were analyzed by peroxide titration with NaI and Na_2SiO_3 and by GLC.

RESULTS AND DISCUSSION

Figure 1 shows the course of oxidation of cumene with and without silver at a temperature of 90°C. In the presence of silver, the induction period is drastically shortened and the steady-state rate of oxidation is markedly increased. With copper the reaction rate is only slightly higher than without a catalyst. Gold is totally inactive. Removing the silver catalyst from the reaction vessel results in the same reaction rate as in the absence of silver, as shown in Fig. 2. This result proves that the rate increase caused by silver is due to its action as a heterogeneous catalyst and *not* to the removal of an impurity, or the formation of an active dissolved compound. By varying the temperature, we found an activation energy of 10.7 kcal/g-mole for the reaction with silver. For the noncatalyzed reaction, we found an activation energy of 17 kcal/g-mole in fair agreement with Fortuin (*3*) reporting 16 kcal/mole. Table 1 shows a linear dependence of the reaction rate with respect to the relative silver surface area. The result of alloying silver with gold can be seen in Fig. 3. A pronounced maximum in the activity is found at about 5 at. % Au. By analyzing the reaction mixture, we found that part of the cumene hydroperoxide formed is subsequently decomposed by silver. By

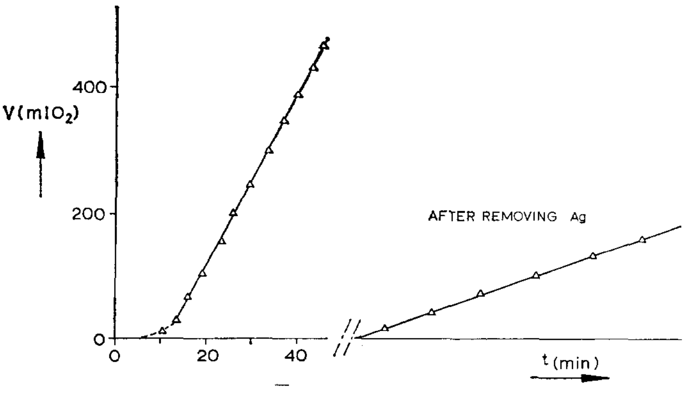

FIG. 2. The influence of removing Ag from the reaction mixture.

TABLE 1
The Oxidation Rate of Cumene as a Function of the Silver Surface Area

Ag weight (g)	Surface area, A (arbitrary units)	Oxidation rate, B (ml/h)	B/A
0.075	273 ± 5	74	0.27
0.100	523 ± 5	146	0.28
0.157	899 ± 5	243	0.27
0.250	1138 ± 5	300	0.26

filling the apparatus with nitrogen and a known amount of cumene hydroperoxide, it appears that in the presence of silver about 75% of the hydroperoxide is decomposed after 40 min.

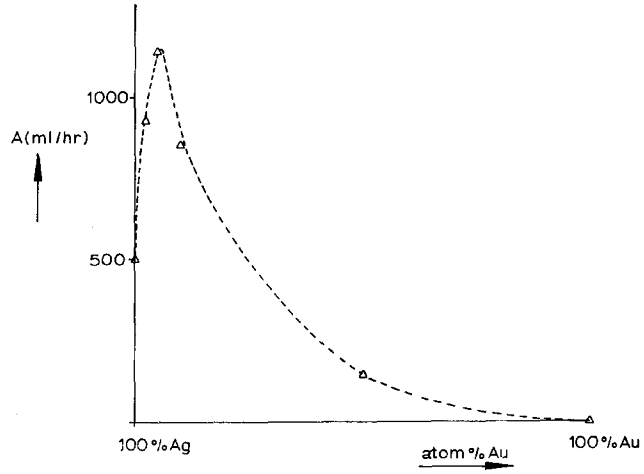

Fig. 3. The oxidation rate as a function of the alloy composition at a temperature of 90°C.

The pertinent results of this work, viz.:

(a) drastic shortening of the induction period by silver;
(b) increase in steady-state oxidation rate by silver, proportional to its surface area;
(c) significant lowering of the activation energy by silver;
(d) virtual absence of these effects for copper and gold;
(e) pronounced increase in oxidation rate over the value found for silver by those silver–gold alloys which are reported to possess a high selectivity in catalyzing the formation of ethene oxide, allegedly using O^-_{2ads};

are consistent with the mechanism proposed by De Boer:

$$[Ag] + O_2 \rightarrow [Ag]O_2^-$$
$$[Ag]O_2^- + RH \rightarrow [Ag] + ROOH$$

with $R = C_6H_5C(CH_3)_2$.

The present results, however, do not categorically exclude other mechanisms. It is still possible, e.g., to speculate about free radical chain reactions, in which case the role of the silver would be to increase the steady-state concentration of free radicals by decomposing hydroperoxides present as trace impurities from the very beginning. It would seem to us that abstraction of a free radical from a metal surface would be a highly endothermic process; moreover, it appears difficult to reconcile such an alternative mechanism with observations (c) and (e) without invoking additional ad hoc postulates. We, therefore, prefer at present De Boer's mechanism as the simplest rationale for the observations known, but we hope that future work including a study of the catalytic behavior of silver–gold alloys in decomposing cumene hydroperoxide will lead to results permitting more definite statements.

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N. H. A. VAN HAM
B. E. NIEUWENHUYS
W. M. H. SACHTLER

Afdeling Heterogene Katalyse
Gorlaeus Laboratorium
Rijksuniversiteit Leiden
The Netherlands

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