

Liquid Phase Oxidation of Cumene over Heterogeneous Catalysts

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Summary: Liquid phase selective oxidations are normally catalysed homogeneously. Significant interest has recently arisen in the use of solid catalysts for liquid-phase oxidations. Unlike similar studies[1-8] carried out on silver and gold, the present work is aimed at understanding the oxidation of copper and silver rather than the nature of adsorbed oxygen species. An inhibition technique was used to measure the radical initiation rate during liquid-phase cumene oxidation over copper and silver. The radical initiation rate was only slightly reduced by changing from an oxygen to an argon atmosphere. It was concluded that oxygen decomposed directly to radicals on the surface. In studies of homogeneously catalysed oxidations, the difficulty of eliminating traces of hydroperoxide has become clear. This has given spurious results. The present study does not, therefore, offer conclusive proof of an initiation mechanism other than hydroperoxide decomposition.

Introduction

The activities of copper, silver and gold as catalysts for cumene oxidation has been compared. With supported catalysts, silver was found considerably more active than copper, while gold was found totally inactive.

Copper and silver have been in use as industrial catalysts for selective oxidation reactions since the early years [9-11] of this century. Although there have subsequently been many investigations [12-16] of these processes, a number of problems still remain. The oxidation of copper and silver and adsorption of oxygen on copper and silver has been examined by a variety of techniques including LEED, XPS, ESR, electron microscopy as well as DTA studies.

Experimental

After an initial chemisorption of oxygen on a (100) copper surface to

give an ordered ($\sqrt{2} \times \sqrt{2}$) R 45° structure, further oxidation at temperatures greater than 290°K resulted in the formation of a thin layer of copper (I) oxide. This involved a rearrangement of the surface to yield a ($\sqrt{2} \times \sqrt{2}$) R 45° structure. The oxygen 1s binding energy is around 531 eV, which corresponded well to the 530.8 eV observed for copper (I) oxide. In addition, at low temperatures a peak at 532 - 533 eV was observed after further oxygen adsorption on the ($\sqrt{2} \times \sqrt{2}$) R 45° structure. This oxygen species desorbed on heating to 290°K. An oxygen peak also appeared at 670°K. By analogy with silver-oxygen system, it is possible that this high binding energy oxygen peak can be ascribed to an adsorbed form of molecular oxygen. Further oxidation of copper surface at temperatures of 290°K or above resulted in the formation of a polycrystalline copper (II) oxide phase as judged by the copper

2p XPS signal and by DTA measurements. After heating in vacuo, the ordered copper (I) oxide phase disappeared, reflecting the thermodynamic stability of copper (I) oxide relative to copper (II) oxide.

A clean silver surface adsorbs oxygen in a dissociated form. LEED studies showed that on the Ag (III) face oxygen adsorbed to form a stable (4 x 4) superstructure. This was interpreted as a lattice coinciding between the Ag (III) plane and the (III) plane of silver (I) oxide. There was evidence that oxygen adsorption of faces other than Ag (III) resulted in the formation of Ag (III) facets. Incorporation of oxygen into the subsurface appeared to be rather slow in the presence of molecular oxygen, but alternate cycles of oxidation and reduction with carbon monoxide resulted in the buildup of a thin subsurface layer of oxidised silver. This surface could now adsorb oxygen in an associative form. The presence of paramagnetic oxygen species was detected with ESR and the species was characterised as \overline{O}_2 . With one exception no paramagnetic Ag (II) species was detected. Only 0.02% oxygen was present as \overline{O}_2 , at saturation coverage at 298°K. It appeared that \overline{O}_2 was attached end-on to a single silver ion and had an activated surface mobility. The desorption mechanism was second order on oxygen coverage, which confirmed that most of the oxygen present was in the dissociated form.

The nature of the subsurface oxide formed by adsorbed oxygen could not be defined. When a relatively thick layer has been built up by successive oxidation-reduction cycles, electron diffraction indicated the presence of silver (I) oxide. The oxygen 1s binding energies measured using XPS helped to clarify the situation. When

oxygen was adsorbed on a clean polycrystalline silver an oxygen peak was observed with a binding energy of 530.5 eV. Further exposure to higher pressures of oxygen led to the formation of a second oxygen 1s peak with a binding energy of about 532 eV. These peaks were assigned to adsorbed oxygen and lattice oxygen respectively. The results were interpreted in terms of inhibition of a free-radical reaction by oxygen adsorbed on silver. At least part of the chain propagation was believed to occur in the liquid phase. A possible reaction scheme is given as under.

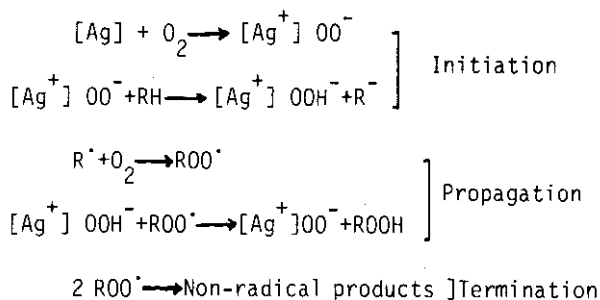


Table 1 shows a comparison of the activities and selectivities of copper and silver as catalysts for cumene oxidation.

Results and Discussion

Characteristics of the reaction:

The essential characteristics of a catalytic reaction are the same whether the catalyst is soluble or insoluble:

(a) The effect of a catalyst is purely kinetic. It does not make a thermodynamically impossible reaction favourable, but it can dramatically accelerate a possible reaction by providing a pathway for a low energy of activation.

(b) The microscopic catalytic site operates in a cycle fashion through a series of reactions that are repeated each time a molecule of substrate is transformed.

Table-1: Activities and selectivities of copper and silver for liquid phase cumene oxidation at 290°K.

Metal	Activity		Cumene	Aceto-	Dimethyl-
	mole l ⁻¹	cm ⁻² H ⁻¹	hydroperoxide %	phenone %	phenylcarbinol %
Cu	0.29		69 - 77	3 - 6	20 - 25
Ag	0.26		83 - 91	0.8 - 1.4	8 - 16

(c) The active catalytic species is not necessarily the same compound that is put into the reaction mixture as a catalyst. Many transformations of the nominal catalyst may occur.

In view of above, the main controversy regarding the mechanism of this reaction concerns the part played by heterogeneous and homogeneous, free-radical processes. Van Ham et al [17] advocated a cumene mechanism based on diatomic oxygen adsorption. This proposal arose from the correlation between activity for this reaction and the catalysts' ability to absorb molecular oxygen as demonstrated by its selectivity.

Addition of an oxygen inhibitor stopped the reaction for a time dependent on the amount of the inhibitor used, indicating a radical-chain mechanism. This technique was also used to measure the rate of radical initiation by cumene hydroperoxide decomposition. In the absence of oxygen, t-butyl hydroperoxide was decomposed over the catalyst at a rate similar to that calculated for initiation of cumene oxidation. On this basis, free-radical initiation by silver catalysed cumene hydroperoxide was proposed as the oxidation mechanism. However, in the light of the cumene hydroperoxide decomposition experiment showing oxygen inhibition, this mechanism is less likely than one based

on initiation by the reaction of adsorbed oxygen with the hydrocarbon.

In contrast to silver catalysed oxidation, the evidence concerning the mechanism of copper catalysed reaction favours radical initiation *via* surface cumene hydroperoxide decomposition. Depending on the catalyst surface area and surface oxide species present, a certain critical hydroperoxide concentration was necessary in order to produce a catalytic reaction. At lower hydroperoxide levels, the reaction was inhibited by the oxidised copper surface. XPS surface analysis of the copper catalysts showed a correlation between catalysis and $\text{Cu}^{2+}/\text{OH}^-$ species. Assuming that the catalysis and inhibition arised from cumene hydroperoxide decomposition to give radical and non-radical products respectively, the reaction was successfully modelled to show the abrupt change from inhibition to catalysis on increasing the hydroperoxide concentration. This behaviour of different oxygen species may explain the range of activities observed for copper catalysts in liquid phase oxidations.

Conclusion

The chemistry involved in the types of oxidation reaction discussed is rather diverse. It is difficult to make any general conclusions concerning the efficacy of copper and silver

catalysts for these reactions. However, it is possible to comment on the individual systems. The difference in partial oxidation product produced by silver catalyst, as opposed to copper, reflects a difference in adsorption. On copper (I) oxide, the lattice oxygen acts as the hydrogen abstraction agent. The overall oxidation state of the silver surface, under reaction conditions, appears to lie somewhere between Ag^{I} and Ag^{O} . It can thus be compared to a reduced form of copper (I) oxide. Under these conditions, abstraction of the proton does not readily occur and the reaction is forced to proceed via an interaction between gas-phase and associatively adsorbed oxygen as the partial oxidation product. On copper, the reactive species is the adsorbed intermediate. When this interacts with adsorbed molecular oxygen, unsaturated products are formed. It is possible that a similar mechanism applies to silver but unfortunately very little is known about the nature of oxygen species present at low temperatures.

When a supported copper salt, which has been pre-reduced with hydrogen, is in contact with propene/oxygen mixture, propane oxide is initially produced. The selectivity depends on the anion present, but can be as high as 70-80%. The reaction is a co-oxidation of copper and propene rather than a catalytic system and propene oxide production rapidly falls as the copper catalyst is re-oxidised. This effect demonstrates that the oxygen chemistry occurring on copper (I) oxide is closer to that occurring on silver, despite the difference in the partial oxidation products.

For both copper and silver catalysts, the complete oxidation mechanism involves atomic oxygen. On copper this involves the irreversible adsorption of

the alkene to give adsorbed carboxylate species after cleavage of the C=C double bond. These species are subsequently oxidised to carbon dioxide. The mechanism on silver is different and a surface glucoxide species is probably formed. Abstraction of hydrogen from this species by atomic oxygen is likely to be the rate determining step for the reaction on silver.

The selective dehydrogenation involves hydrogen abstraction and hence atomic oxygen becomes the selective species on copper. The mechanism on silver is probably similar to that on copper. The weakly adsorbed, possibly molecular, oxygen species appears to be responsible for the unselective reaction which proceeds by oxygen addition.

Differences between copper and silver have been found for the heterogeneously catalysed liquid phase oxidation of cumene. Copper appears to initiate the reaction by decomposition of the hydroperoxide. There is some evidence that silver initiates this process via an adsorbed molecular oxygen species. If this is correct, then this species is reacting in a different manner when compared to its reaction with gas phase alkenes. In the latter, O-O bond cleavage occurs while the cumene oxidation mechanism would necessarily involve Ag-O bond cleavage.

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