the concentration range studied. This is also in agreement with Sheffer's work[4,9] and other work[3] which indicate that the molecular weight of the colloid is not extensively changed by solvent dilution. Thus, the drag reduction data confirm what the recorded physicochemical data explicitly state: that these colloidal soaps do not change their micellar molecular weights with concentration. Some comparison in drag reduction efficiencies may be made between these disoap preparations reported here and the well known Polyox materials. The intrinsic concentrations of the dilaurate and dipalmitate were respectively 522 and 50 p.p.m. corresponding to Polyox polymers of 130,000 and 275,000 in their efficiency[8]. Thus, it would seem that any soap critical concentration required for drag reduction in non-aqueous systems must be the result of events taking place on a molecular level, that is, the competition between the disoap anions and the polar impurities for the soap cations as the soap concentrations is varied. The remarkable micellar changes which take place as a function of polar additive type and concentration have been well pointed out by Singleterry and his coworkers for other linear soap colloids in benzene[10-13].

R. C. Little

Naval Research Laboratory,
Washington, DC 20375

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Chlorine-catalysed Rearrangement of Silver Catalysts

THE oxidation of ethylene to ethylene oxide over supported silver catalysts is usually carried out on a commercial scale in the presence of a moderator[1-3]. Compounds such as chlorine, bromine, sulphur and ethylene dichloride[3] improve the selectivity of the reaction to ethylene oxide at the expense of the production of carbon dioxide. There is evidence that silver chemisorbs, for example, Cl^-, which partly poisons the silver for the chemisorption of oxygen and hence reduces the yield of highly oxygenated products.

Previous investigation of the reaction in the absence of moderators showed that considerable rearrangement of the metal could occur under reaction conditions[5,6]. This rearrangement, which was catalysed by oxygen, was described in terms of a surface energy-driven surface self diffusion. Here we report that a similar process occurs in the presence of the moderators chlorine and ethylene dichloride.

The preparation, annealing, characterisation and observation of thin evaporated silver on amorphous silica films have been previously reported[5,6]. Both chlorine and ethylene dichloride were passed into the reactor in a stream of nitrogen, ethylene dichloride being picked up by nitrogen on passing through two bubblers maintained at a preset temperature ($\pm 0.1°$ C).

The microstructural changes in the annealed specimen were studied by transmission and scanning electron microscopy. Electron micrographs taken at different stages of sintering were photographed and used to measure the projected metal-silica area using a Metals Research Quantimet image analysing computer. Statistical methods were used to reduce the error to $\pm 1\%$.

Graphs of the projected metal area vs time were obtained over the temperature range $200°$-$300°$ C in the presence of chlorine or ethylene dichloride maintained at a concentration of 8% of the nitrogen flow: this corresponds to the conditions of the industrial reaction as quoted by Bond[7]. Values of the induction time, during which there was no change in projected metal area, were then plotted on an Arrhenius-type plot. Both chlorine and ethylene dichloride gave similar results, corresponding to an apparent activation energy of 5.0 kcalorie mol^{-1} (± 0.1 kcalorie mol^{-1}). Following the theory presented in ref. 5, this value represents the approximate activation energy for surface diffusion.

Comparison of the activation energy in chlorine (5.0 kcalorie mol^{-1}) with the value in oxygen (14.9 kcalorie mol^{-1}; ref. 5) shows that oxygen-catalysed rearrangement becomes more important at higher temperatures. The relative importance of the two alternatives at $200°$ C probably depends much more on the relative concentration of moderator and oxygen. No evidence of preferred faceting was obtained in either case.

M. Moayeri
D. L. Trimm
P. M. Williams

Department of Chemical Engineering
and Chemical Technology,
Imperial College, London SW7

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