

shallow solar convection zone, an order of magnitude thinner than hitherto accepted models would suggest. I suggest that the boundary condition to be applied at the base of a sunspot when constructing a sunspot model is that the depth of the spot should be set equal to, or less than, the depth of the convection zone. Large spots would then have the natural boundary condition that their depth must be 10,400 km.

Leighton<sup>3</sup> pointed out that values of  $R/H$  in excess of 20 "would pose questions concerning the means by which the submerged field could resist being carried to the surface by the supergranulation circulation". Now supergranule flow has a speed of  $0.5 \text{ km s}^{-1}$  at the upper surface<sup>6</sup>, where the density is about  $2 \times 10^{-7} \text{ g cm}^{-3}$  and the kinetic energy density of this flow is sufficient to drag fields of about 100 gauss towards the supergranule periphery. But at the base of the convection zone, where the density has risen to  $3.5 \times 10^{-6} \text{ g cm}^{-3}$  (see ref. 2), mass conservation requires a speed of about  $0.03 \text{ km s}^{-1}$ . Fields stronger than about 20 gauss can withstand this flow. As root-mean-square fields at the photosphere are about 8 gauss (ref. 7), it would not be surprising if, at the base of the convection zone, r.m.s. field strengths exceeded 20 gauss. Problems of dragging field lines are therefore not too severe.

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<sup>1</sup> Hong Sik Yun, *Astrophys. J.*, **162**, 975 (1970).

<sup>2</sup> Mullan, D. J., *Mon. Not. Roy. Astron. Soc.*, **154**, 467 (1971).

<sup>3</sup> Leighton, R. B., *Astrophys. J.*, **156**, 1 (1969).

<sup>4</sup> Schröter, E. H., in *Solar Magnetic Fields*, IAU Symp. No. 43 (edit. by Howard, R.), 175 (D. Reidel, Dordrecht, Holland, 1971).

<sup>5</sup> Steshenko, N. V., *Izvestia Krimskoi Astro. Observ.*, **37**, 21 (1967).

<sup>6</sup> Leighton, R. B., Noyes, R. W., and Simon, G. W., *Astrophys. J.*, **135**, 474 (1962).

<sup>7</sup> Howard, R., *Astrophys. J.*, **136**, 211 (1962).

## Alteration of Catalyst Surface Composition induced by $\gamma$ -Irradiation

DURING a study of the influence of pre-irradiation of a supported silver catalyst by  $\gamma$ -rays on conversion and yield in the oxidation of ethylene to ethylene oxide and  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , ESCA was employed to ascertain whether or not pre-irradiation altered the chemical composition of the silver catalyst surface. The influence of pre-irradiation on ethylene conversion and yield of ethylene oxide is reported elsewhere (J. J. Carberrry, G. C. Kuczynski and E. Martinez, to be published); in this communication we wish to report changes in the surface chemical composition of the silver. We employed a Varian IEE-15 ESCA with an Mg source; K alpha energy line<sup>1</sup>.

A commercial (Engelhardt) supported silver catalyst was subjected to ESCA before  $\gamma$ -irradiation and then after  $\gamma$ -irradiation in air ( $10^{18} \text{ eV min}^{-1} \text{ g}^{-1}$  for 10 h in a  $^{60}\text{Co}$  source). The principal surface species (Ag) were unaffected by irradiation, but Ca does not appear on the surface of the un-irradiated sample whereas the same sample after irradiation definitely contains surface Ca. That irradiated sample was then reduced in  $\text{H}_2$  for 1 h at  $280^\circ \text{C}$  and then cooled in air. This reoxidized sample then seems to be free of surface Ca. This sample was then re-irradiated—ESCA reveals the reappearance of surface Ca.

Calcium is, of course, an expected impurity at low concentrations in the catalyst, presumably arising as an impurity in the salt solutions used to create the supported silver formulation. Its negligible surface concentration is then not unexpected. The surface concentrating phenomenon induced by  $\gamma$ -irradiation and the reversibility of the phenomenon are indeed novel.

The absence of Ca on the silver surface before irradiation would indicate, in accord with the Gibbs adsorption theorem, that Ca increases the surface tension of Ag. During irradiation bulk calcium is energized and, by translation into kinetic energy, it is ejected to the surface where, in the presence of air, it is fixed by oxygen chemisorption. During reduction at  $280^\circ \text{C}$  for 1 h the calcium, perhaps in a hydride form, rediffuses into the bulk of the material and is re-injected by subsequent energizing irradiation.

We are not aware that such a phenomenon has been observed previously and, although the exact mechanism for the migration of the calcium may be speculative, the ESCA evidence is unambiguous. The implications are that  $\gamma$ -irradiation can cause significant changes in the chemical nature of the catalytic surface with consequent alterations in catalytic activity and yield, insofar as these parameters depend on the chemical nature of the catalytic surface.

In the instance of ethylene oxidation, yield of ethylene oxide is enhanced after  $\gamma$ -irradiation of the supported silver catalyst, because, we believe, of the formation of chemisorbed Ca superoxide at the surface. On the other hand, we suggest that surface concentrating of, say, Mg by irradiation should reveal smaller yields as Mg does not form the desired superoxide but the peroxide, which promotes ethylene combustion to undesired  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . We are now studying this catalyst containing traces of Mg.

We conclude that exposure of a metal catalyst containing impurities to  $\gamma$ -irradiation markedly alters the chemical composition of the surface of the catalyst with respect to the impurities. The influence of alterations on catalytic activity and yield (selectivity) is profound in the case of ethylene oxidation and may be profound in other systems whose kinetic character depends on the nature and surface concentration of the dislodged impurities. The observed surface concentrating effect is reversible and a reasonable mechanism involving irradiation induced "energy spikes" and, on thermal reduction, re-diffusion may be tentatively postulated. ESCA penetration (possibly  $10 \text{ \AA}$  to  $20 \text{ \AA}$ ) seems to be less severe than previously suggested.

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## Significance of Upper Jurassic Sediments in the Knysna Outlier (Cape Province)

MARINE Upper Jurassic sediments of the Knysna Outlier of Cape Province, South Africa, have been recently interpreted to indicate that "the southern part of the East/West Gondwana split cannot be younger than lower Upper Jurassic". This, combined with a "suspected" "complete mid-Jurassic to Upper Cretaceous marine succession" on the Agulhas Bank, forms the basis of a verdict that "a Cretaceous date for the East/West Gondwana split and for the commencement of the construction of the Agulhas Bank (Veevers *et al.*<sup>1</sup>) is clearly incorrect"<sup>2</sup>.

It is clear, both from the present relationships between mid-ocean rises and continental rifts, and from the structure