On Oxygen Mobility During Catalytic Oxidations

Recently, Nováková and Jirů (*1*) have noted that isotopic oxygen exchange may occur between the oxygen atoms of $H_2{}^{18}O$ and the lattice oxygens of some catalysts used for selective hydrocarbon oxidation. On the basis of their observations, they have suggested that the results obtained by Keulks (*2*) and ourselves (*3*) on the selective oxidation of propene over bismuth molybdate catalysts could be explained by rapid exchange of bulk oxygen with H_2O, rather than by high mobility of bulk oxygen. In addition they suggest that study of the ^{18}O content of water and carbon products containing oxygen might reveal that oxidation occurred via water.

Two features of the properties of the lattice oxygen in selective oxidation catalysts must be emphasized. Firstly, Keulks (*2*) and ourselves (*3*) have shown by experiments with ^{18}O that it is the lattice oxygen which is incorporated into the products C_3H_4O and CO_2, without any scrambling of the gas phase oxygen. The participation of lattice oxygen in the initial, rate-determining abstraction of the allylic hydrogen is also likely because the rate and selectivity of acrolein formation is very similar in the absence or presence of gaseous oxygen. In addition, Keulks (*2*) has shown that the isotopic composition of the products C_3H_4O and CO_2 can only be explained by participation in the reaction of oxide ions from approximately 500 layers of the catalyst crystals, pointing to very rapid diffusion of adsorbed oxygen into the bulk and of interior oxygen to the surface.

The results of Nováková and Jirů (*1*) are interesting but it must be remembered that the exchange of any fraction of the oxygen in the solid greater than that which corresponds to movement within the outermost layer implies that an oxygen "containing" species is mobile within the lattice. This is unlikely to be molecular H_2O as such and although hydroxide ion diffusion is a possibility the crucial feature emerging from Keulks' (*2*) results is that the lattice of the catalyst allows for a large degree of anion mobility.

As Nováková and Jirů (*1*) point out, $H_2{}^{18}O$ is known to undergo more rapid exchange with the oxygen of some oxide catalysts than is $^{18}O_2$ at 450–500°C (*4*). Although both exchanges result from dynamic surface equilibria the mechanisms are likely to be different. It is known that oxide surfaces carry hydroxyls and also that they dissociatively chemisorb water. Thus, a partially hydroxylated oxide surface may rapidly exchange its oxygens with those of water vapor by, for example, dissociatively chemisorbing $H_2{}^{18}O$ in the from of surface hydroxyls, followed by the formation of $H_2{}^{16}O$ and a concomitant ^{18}O ion in the lattice. Thus, on selective oxidation catalysts of the type used by Keulks (*2*) and ourselves (*3*), under the conditions where the lattice diffusion is rapid (e.g., 450–500°C), a surface process involving H_2O can lead to a relatively large fraction of the oxygen of the solid appearing in gas phase H_2O without necessarily implying that the H_2O takes part as a reactant in the oxidation process.

REFERENCES

1. NOVÁKOVÁ, J., AND JIRŮ, P., *J. Catal.* **27**, 155 (1972).
2. KEULKS, G. W., *J. Catal.* **19**, 232 (1970).
3. WRAGG, R. D., ASHMORE, P. G., AND HOCKEY, J. A., *J. Catal.* **22**, 49 (1971).
4. WINTER, E. R. S., *J. Chem. Soc. Ser. A*, 479 (1968).

R. D. WRAGG
P. G. ASHMORE
J. A. HOCKEY

Department of Chemistry
University of Manchester Institute of Science and Technology
Manchester M60 1QD, England
Received September 11, 1972