

LETTERS TO THE EDITORS

A Comment on Oxygen Mobility During Catalytic Oxidation

Recently, Keulks (1) and Wragg, Ashmore and Hockey (2) found a large mobility for the bulk oxygen of a Bi-Mo-O catalyst during the oxidation of propylene. Although no exchange of gaseous oxygen with this mixed oxide was observed at the temperature of catalytic oxidation, the products of the oxidation of propylene with highly enriched ^{18}O oxygen contained a very small fraction of ^{18}O atoms. The authors agreed in conclusion that not only oxide ions in the surface layer participate in the reaction but also oxide ions in deep subsurface layers. The gaseous oxygen once adsorbed undergoes a very rapid diffusion into the bulk.

We tried to make the same experiments for the oxidation of methanol with $^{18}\text{O}_2$ on a mixed oxide of the type Fe-Mo-O and on pure MoO_3 , where the participation of lattice oxygen is commonly supposed [e.g., (3, 4)]. Both oxides exchange their bulk oxygen with $^{18}\text{O}_2$ gas at temperatures above 500°C (5, 6). The temperature of catalytic oxidation of methanol to formaldehyde was found to be $100\text{--}300^\circ\text{C}$ on the Fe-Mo-O catalyst and $300\text{--}450^\circ\text{C}$ on MoO_3 (7).

In agreement with the results of Keulks (1) and of Wragg, Ashmore and Hockey (2) we found no change of the isotopic composition of gaseous 60 atom % ^{18}O oxygen during the oxidation of methanol on MoO_3 at 440°C and on the Fe-Mo-O catalyst at 200°C . In our experimental conditions allowing the determination of an enrichment of at least 5% of ^{18}O in formaldehyde, no such enrichment was observed, but a fraction of H_2^{18}O appeared. This H_2^{18}O amount was higher for MoO_3 at

440°C than for Fe-Mo-O at 200°C , corresponding to several surface layers of oxygen in the first oxide and more in the second one.

Owing to the observed ^{18}O enrichment of water we examined in more detail the exchange of H_2^{18}O with MoO_3 and the Fe-Mo-O catalyst. One gram of sample [described in (7)] was previously heated in a vacuum of 10^{-5} Torr to 450°C and then kept at 10 Torr of oxygen $^{16}\text{O}_2$ at 450°C overnight. Oxygen was pumped off at room temperature. The exchange of 3.2 Torr 70% H_2^{18}O in a volume of 750 cm^3 was measured directly with a mass-spectrometer (8). The results are shown in Fig. 1. In 100 min the following percentages were observed of exchange of the whole of the oxygen in the oxide samples used: for MoO_3 at 440°C , 0.4%; for Fe-Mo-O at 20°C , 0.8%; and for Fe-Mo-O at 200°C , 3%. When the temperature during the exchange on Fe-Mo-O was increased from 20 to 420°C , the amount of bulk oxygen exchanged increased after 40 min to almost 10%. The surface area of Fe-Mo-O was about three times larger than that of MoO_3 (6.9 and $2.6\text{ m}^2/\text{g}$, respectively). There is a large difference in temperature and amount of lattice oxygen exchanged with H_2^{18}O for MoO_3 and Fe-Mo-O in contrast to the exchange of $^{18}\text{O}_2$ gas, where no such differences between MoO_3 and Fe-Mo-O were observed.* The exchange with H_2^{18}O proceeds quickly at the temperature of catalytic oxidation on

*The rapid exchange of H_2^{18}O in comparison with ^{18}O gas has been known from the first papers dealing with ^{18}O exchange (9).

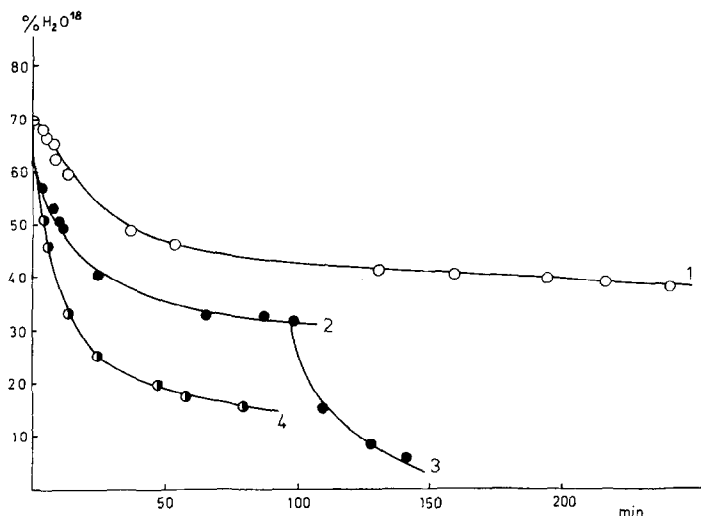


FIG. 1. H_2^{18}O vapor exchange with MoO_3 and Fe-Mo-O catalyst as a function of time: (1) MoO_3 at 440°C ; (2) Fe-Mo-O catalyst at 20°C ; (3) Fe-Mo-O catalyst continued at 420°C ; (4) Fe-Mo-O catalyst at 200°C .

Fe-Mo-O catalyst. Therefore the mobility of oxygen ions during the catalytic oxidation of methanol on Fe-Mo-O might be explained by the rapid exchange of H_2O released. Also the difference of the temperature of catalytic oxidation on MoO_3 and Fe-Mo-O catalyst might be connected with the different ability of H_2O exchange with these oxides.

We followed also the exchange of H_2^{18}O with an industrial Bi-Mo-O catalyst for the selective oxidation of propylene to acrolein. The exchange was found to proceed at room temperature, too, being very rapid at 200°C . For this reason it is possible to explain the results of Keulks (1) and of Wragg, Ashmore and Hockey (2) not only by the large mobility of bulk oxygen during the catalytic oxidation, but also by a rapid exchange of bulk oxygen with H_2^{18}O released. If the amount of ^{18}O during the oxidation were the same in water and carbon oxidation products, the possibility of oxidation of carbon species via water could not be excluded.

More detailed results will be published elsewhere.

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