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THE ROLE OF SURFACE EXCESS OXYGEN IN THE CATALYTIC DEHYDROGENATION OF 2-PROPANOL ON $ZnCrFeO_4$ SPINEL

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AMONG the many physical and chemical properties of the oxides considered to explain their observed catalytic activities, the amount of surface excess oxygen has been a useful variable to correlate with catalytic activity. Such a correlation has been demonstrated for the oxidation of ammonia on nickel oxide and manganese oxide catalysts¹ and the decomposition of hydrogen peroxide on nickel oxide² and chromia catalysts³. A similar correlation is attempted in $ZnCrFeO_4$. This catalyst system has been chosen because of its good selectivity for the dehydrogenation of 2-propanol.

Zinc chromium ferrite was prepared by the slurry method described by Batist⁴. 2-Propanol and acetone were purified by standard procedures⁵ and their purity confirmed by vapour phase chromatography. Nitrogen and hydrogen were purified by passing through a vanadium(II) solution and the moisture removed by passing through towers packed with anhydrous calcium chloride.

Catalytic reactions were carried out in a differential tubular flow reactor operating at atmospheric pressure, mercury being used to displace the reactant from a feeder into the reactor⁶. The liquid products were condensed in a cold trap and analysed by vapour phase chromatography using a carbowax column maintained at 65°C and hydrogen as the carrier gas. The surface

excess oxygen was estimated by the method reported by Uchijima *et al.*⁷.

$ZnCrFeO_4$ is selective and promotes the dehydrogenation of 2-propanol. The incorporation of Cr in the $ZnFe_2O_4$ spinel lattice increases both the activity and the selectivity. The Cr^{+3} incorporated into the octahedral sites of the spinel lattice inhibits the bulk reduction of the Fe^{+3} to an oxidation state lower than Fe^{+2} as can be concluded from the absence of reduction of the Fe^{3+} to the metallic state when Cr^{3+} is present. Neither $ZnFe_2O_4$ nor $ZnCr_2O_4$ exhibit the selectivity shown by $ZnCrFeO_4$.

The surface excess oxygen on $ZnCrFeO_4$ samples subjected to various pretreatments and their catalytic activities are given in table 1.

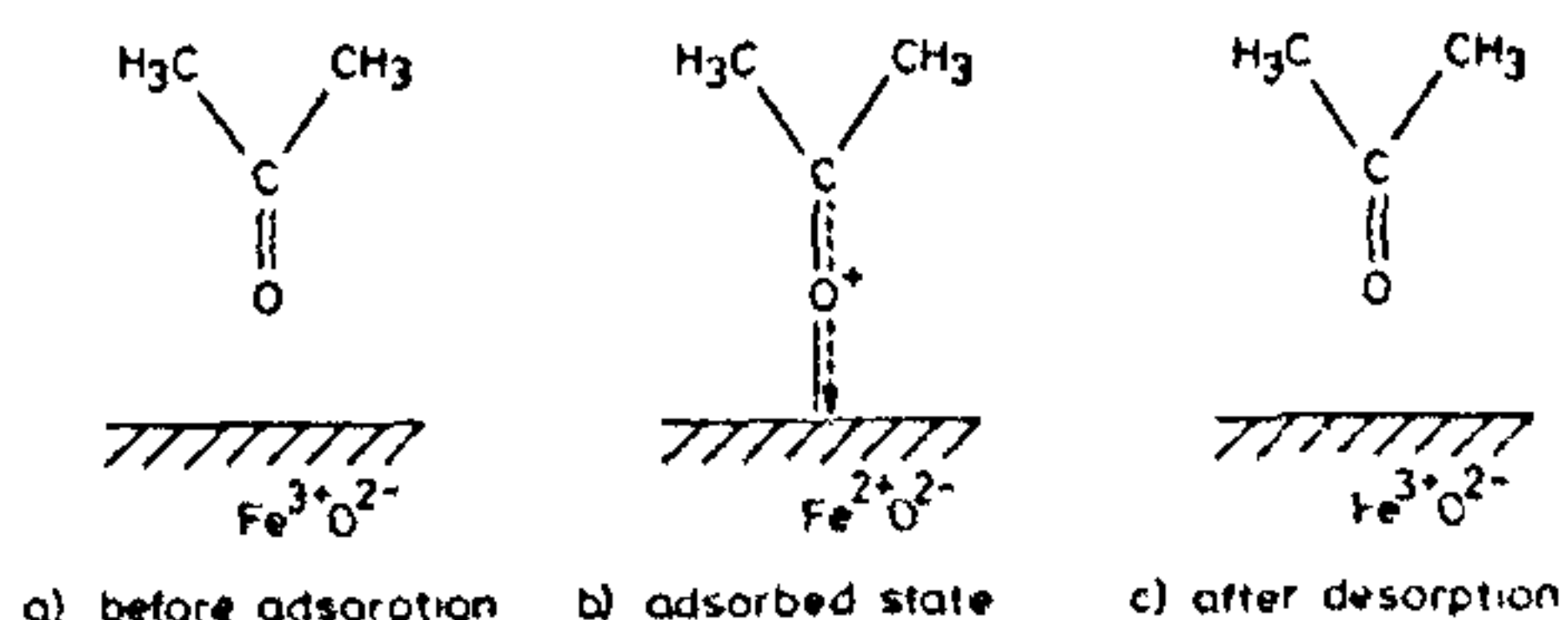
Table 1 Influence of various pretreatments on the surface excess oxygen of $ZnCrFeO_4$ and the catalytic activity

Type of pretreatment	Condition of pretreatment	Percentage conversion of 2-propanol	Surface excess oxygen mM/g
Hydrogen	500°C, 3 hr	57.5	0
2-propanol	"	52.5	0.030
Fresh catalyst	"	47.2	0.073
Air	500°C, 3 hr	45.2	0.087
Oxygen	"	40.0	0.109

It is clear from these results that increase in the surface excess oxygen which can be related to oxidation of the catalyst brings down the dehydrogenation activity while reduction increases it.

Adsorption of acetone on Fe_2O_3 is a donor process⁸. Ferric oxide is a semiconductor in which the density and the nature of current carriers are known to change when it is subjected to slight oxidation or reduction⁹. As in Fe_2O_3 the active site in $ZnCrFeO_4$ is also likely to be iron since the chromium present in the catalyst does not undergo any change in the oxidation state so readily. The decrease in the formation of acetone with an increase in the surface excess oxygen can be rationalized on the basis of the following mechanism.

The adsorption and desorption of acetone may be visualised as follows.



Acetone will be more strongly held on an oxidised catalyst. Separate experiments on poisoning studies show that acetone strongly inhibits the reaction. Hence the desorption of acetone can be considered to be the rate-determining step. The competitive adsorption of acetone and 2-propanol shows that the active sites for the adsorption of acetone and the adsorption of 2-propanol are the same.

When Fe^{+2} is surrounded by Fe^{+3} ions there would be delocalisation of electron charge from Fe^{+2} to Fe^{+3} resulting in acetone, which is adsorbed by a donor mechanism, being held strongly to the surface. This results in a reduction in the adsorption of 2-propanol. When the number of Fe^{+2} ions present in the vicinity of the point of adsorption is large, the desorption of acetone becomes easier. Therefore, the reduction of the catalyst increases the activity of the catalyst for dehydrogenation and oxidation reduces it. A used catalyst shows more activity than a fresh one.

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PHOTOCYCLIZATION OF 2'-HYDROXY-3'-BROMO-5'-METHYLCHALCONE

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THE photocyclization of stilbene and *N*-benzylidene-aniline¹⁻³, *N*-(2-propylidene)-2-aminobiphenyls⁴, pyridiniumylide⁵, transnitrones⁶, azobenzene⁷, 4-phenylvinyl-2-pyridones⁸, *N*-2-alkenyl and *N*-3-alkenyl phthalimide⁹ and flavone^{10,11} has been studied and reviewed by various workers.

In the present study the photocyclization of 2'-hydroxy-3'-bromo-5'-methylchalcone has been reported.

2'-hydroxy-3'-bromo-5'-methylchalcone, benzophenone and ethanol used were chemically pure. The chalcone (200 mg) was dissolved in ethanol (50 ml) and benzophenone (0.5 mg) was added to this solution. It was made alkaline by adding five drops of NaOH solution (0.1 M) and irradiated with a medium arc lamp (Phillips, 80 watt) kept at 8 cm. After 10 hr, a solid started separating out from the reaction mixture and the separation was nearly complete after 15 hr.

The solid was filtered, washed with ethanol and recrystallized from benzene [yield 90 mg, m.p. 228°C and mole formula $\text{C}_{16}\text{H}_{11}\text{O}_2\text{Br}$]. It gave a positive test for bromine.

$$\text{UV } (\lambda_{\text{max}}^{\text{benzene}}) = 276, 255 \text{ and } 244 \text{ nm.}$$

The UV spectrum of the parent compound showed a peak at 322 nm indicating the presence of a conjugated system which had shifted towards shorter wavelength (276 nm) in the product, showing the disappearance of conjugation.

$$\text{IR}-(\text{KBr})^{\text{cm}^{-1}}-3420, 2920, 1700, 1640, 1600, \\ 1470, 1385, 1265 \text{ and } 1150.$$

The IR spectrum of the product resembles that of the parent compound except for a slight shift towards larger wave numbers and the strong absorption at 1700 cm^{-1} which may be attributed to a cyclopentanone ring.

The mass spectrum (m/e 316) indicated the formation of a compound with the same molecular weight. Other intense peaks obtained were at m/e 217 and 77 (Scheme 1).

The effect of photon in the photocyclization was confirmed by carrying out the reaction in the absence of UV radiation when no product was formed. In the