

Nature & Role of Metal-Oxygen Bond in the Activity of a Zn-Cr-Fe Oxide Catalyst

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The type of metal-oxygen bonds and their role in the reaction of propan-2-ol on a Zn-Cr-Fe oxide catalyst is studied. A change of character of the metal-oxygen bond neither influences the decomposition or oxidation of propan-2-ol nor does it affect the activity of the catalyst.

IN metal oxides the presence of a band in the IR region $900\text{--}1000\text{ cm}^{-1}$ may be attributed to a metal-oxygen bond having a double bond character¹. Such metal-oxygen bonds are present in solids like molybdates² which are active oxidation catalysts, while they are absent in the inactive ones. This band is also absent in catalysts, such as Fe, Ni and Co oxides³ which cause profound oxidation of hydrocarbons.

The catalytic behaviour of molybdates and the role of metal-oxygen bonds with double bond character can be rationalized on the basis of an oxidative dehydrogenation mechanism which is the same for all the molybdates. In order to check whether the metal-oxygen terminal bonds are involved directly or indirectly in the mechanism of the reaction of propan-2-ol over Zn-Cr-Fe ternary oxide catalyst, the IR spectra and catalytic activity of different samples have been studied. A catalyst of composition 1:1:1 on the basis of metal was chosen because of its good selectivity.

Materials and Methods

All the chemicals were of analar (BDH) grade and used as such.

Preparation of catalysts — The Zn-Cr-Fe catalyst was prepared by the slurry method described by Batist⁴. $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ were obtained by precipitation from nitrate solutions by the slow addition of analar ammonia (BDH) keeping the system stirred. A zinc oxide paste made with distilled water was added to the mixture of freshly precipitated thoroughly washed $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ and heated for 10 hr on a water-bath with vigorous stirring. After the reaction the solid was filtered, dried overnight at 110° and calcined at 550° for 5 hr.

Binary oxides, Zn/Cr, Zn/Fe and Cr/Fe were prepared by the slurry method as adopted for Zn-Cr-Fe system and dried and calcined as before.

For the preparation of mechanical mixtures of Zn/Cr+Zn/Fe, Zn/Fe+Fe/Cr and Zn/Cr+Fe/Cr, the binary systems Zn/Cr, Fe/Cr and Zn/Fe were powdered separately in a mortar, mixed to get the respective combinations, ground in an agate mortar and heated at 550° for 5 hr. Reactions were carried out in a flow type reactor functioning

at atmospheric pressure. The packing of the reactor and experimental procedure has been described in an earlier paper⁵. The IR spectra in KBr were recorded on a Perkin-Elmer 257 spectrometer.

Results and Discussion

Propan-2-ol forms acetone when reacted over the Zn-Cr-Fe catalyst. The IR spectrum of a fresh catalyst indicates a broad band around $900\text{--}1000\text{ cm}^{-1}$ which actually vanishes after reaction with propan-2-ol at 400° . The regenerated catalyst exhibits the original band at the same position.

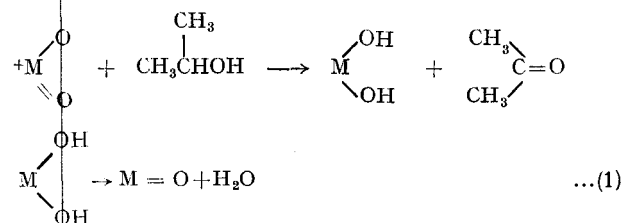
The selectivity of the oxidizing agent is attributed to the presence of surface metal oxygen bonds with double bond character^{1,2}. These groups act as chemical oxidizers and are replenished by molecular oxygen. This double bonded oxygen situated at the surface projects out of the catalyst plane⁶ and therefore it is very likely that this oxygen species is reduced first.

Reaction of the substrate with the oxygen of the catalyst is typical of an oxidation mechanism of the oxyreductive type⁷ which has been proposed for catalysts containing a metal-oxygen bond having double-bond character. Reaction of propan-2-ol with the oxygen of the catalyst must be taking place as a first step in the case of Zn-Cr-Fe.

The influence of the double-bonded oxygen in the dehydrogenation of alcohol in the presence of oxygen in the feed has also been investigated. After 15 min. of reaction of alcohol mixed with oxygen over the catalyst the IR spectrum of the catalyst recorded at room temperature shows that the absorption is shifted to a higher wave number ($1050\text{--}1000\text{ cm}^{-1}$) as compared to the fresh sample ($900\text{--}1000\text{ cm}^{-1}$).

There are reports that by decreasing the number of terminal oxygens, the double bond character of the metal-oxygen bond increases and the corresponding band is shifted towards higher wave numbers⁸⁻¹⁰. In the present case (i.e. with the sample after 15 min. reaction of a mixture of alcohol and oxygen) it is quite possible that the decrease in number of terminal oxygen bonds may be the cause for the shift in the band towards higher wave numbers. If we assume that there are two terminal oxygen

bonds to start with, then the following mechanism (Eq. 1) may be considered:



The samples of Zn/Cr, Fe/Cr and Zn/Fe of 1:1 composition were prepared and the IR spectra of the three samples recorded. The IR spectra of Zn/Cr and Fe/Cr exhibit a band at the same position as in Zn-Cr-Fe catalyst. Zn/Fe fails to exhibit a band in the region of interest. This suggests that Zn/Cr or Cr/Fe or both the systems may be responsible for the observed activity of the Zn-Cr-Fe catalyst.

The mechanical mixtures of all the three phases of Zn/Cr, Zn/Fe and Cr/Fe were prepared and calcined at 500°. None of the three mixtures, i.e. Zn/Cr+Fe/Cr, Fe/Cr+Zn/Fe and Zn/Fe+Zn/Cr gave any band in the IR region of interest.

All the three systems Zn/Cr, Zn/Fe and Fe/Cr and their three mechanical mixtures were tested for the reaction of propan-2-ol. Only the system Zn/Cr+Fe/Cr shows catalytic activity and a trend in the variation of activity with the duration of the run that is similar to that exhibited by the Zn-Cr-Fe catalyst (Fig. 1). The complete system which is active in Zn-Cr-Fe catalyst might not have formed in the Zn/Cr+Fe/Cr mechanical mixture to give an IR band and it is clear that the mechanical mixture contains only the active phases, i.e. Zn/Cr and Fe/Cr which by themselves gave IR bands.

The data for the X-ray analysis of the various samples using iron filtered Co-K α radiation are given in Table 1. X-ray data for the mechanical mixture (b) and ternary oxide system (a) reveal that they do not differ in structural features.

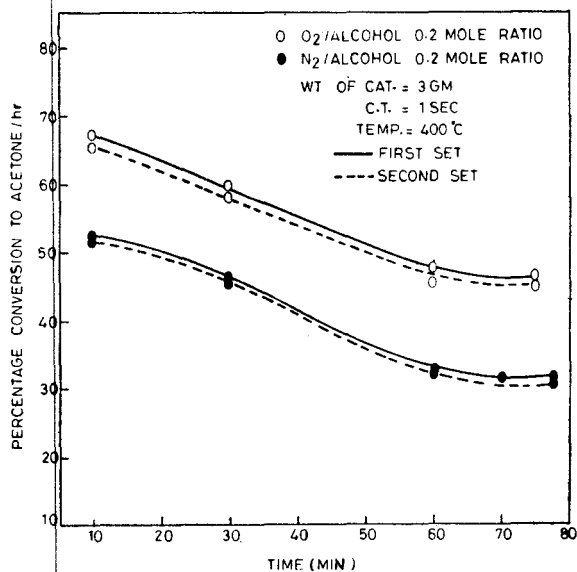


Fig. 1 — Effect of time on conversion of propan-2-ol

TABLE 1 — d -VALUES OF VARIOUS SAMPLES

(a) Zn-Cr-Fe	0.4564
	0.4084
	0.3981
	0.2554
	0.1574
(b) Zn/Cr + Fe/Cr	0.4564
	0.4084
	0.3981
	0.2554
	0.1232
(c) Zn/Fe + Fe/Cr	0.6455
	0.4556
	0.4071
	0.3081
	0.2642
(d) Zn/Cr + Zn/Fe	0.4084
	0.3070
	0.2724
	0.2312
	0.2101
(e) Zn/Cr	0.4056
	0.4084
	0.3870
	0.2436
	0.2162
(f) Zn/Fe	0.4744
	0.4383
	0.4071
	0.3820
	0.3383
(g) Fe/Cr	0.5310
	0.4229
	0.3981
	0.3626

From the above observations, it can be stated that the presence of the IR band at 900-1000 cm^{-1} , indicative of the presence of $\text{M}=\text{O}$, does not seem to be very important for the catalytic behaviour of the systems. It may be expected that the change of the character and the number of bonds on the metal atoms might lead to a change of catalytic activity. However, the present results do not appear to support such a generalization, as there are cases like Zn/Cr+Fe/Cr mixtures where the IR spectrum indicates a difference in the type of metal oxygen bonds from those present in Zn-Cr-Fe and yet exhibit the same pattern of activity.

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