

LETTERS TO THE EDITORS

Comments on "Catalytic Conversion of Alcohols
VI. Selectivity of Indium Oxide"

A recent paper by Burtron H. Davis (1) deals with the selectivity of indium oxide for the dehydration and dehydrogenation reactions of secondary alcohols. A mechanism involving a common intermediate (i.e., one involving the initial adsorption of the $C^\alpha-H$ as a hydride on the metal ion and the subsequent removal of a $C^\beta-H$ to form a carbanion-like structure) has been proposed since this broadly takes into account the fact that the same temperature coefficient has been obtained for both reactions on the surface. Although it is stated that the mechanism is a speculative one, it involves an unusual mode of adsorption of alcohol on the catalyst surface as a precursor for both reactions; hence this letter. Neither the initial adsorption of the alcohol through the hydroxyl oxygen (in the case of dehydration) nor the removal of the hydroxyl hydrogen as a proton (in the case of dehydrogenation) has been envisaged in the delineation of the mechanism of these reactions. On the other hand, the author's choice of β -hydrogen abstraction for dehydrogenation and of the common intermediate, involving coordination of the α -hydrogen to a Lewis site, for both dehydration and dehydrogenation has to be considered for critical discussion.

Davis' scheme as indicated in Eq. (3) requires elimination of the α -hydrogen for dehydrogenation and a "flip-flop" to hydroxyl coordination, followed by elimination of the hydroxyl, for dehydration. Since both occur at the same site (Lewis acid site) and involve negatively charged groups (H^- and OH^-) poisoning should affect both reactions equally. But from the results provided in Table 4, it is clear that the

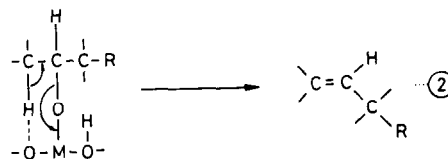
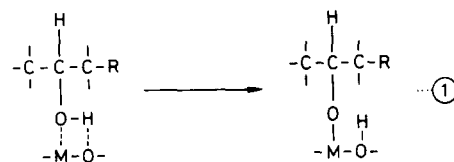
dehydration/dehydrogenation selectivity changes with time. Hence, it is reasonable to state that dehydrogenation and dehydration need not occur via the same intermediate with ElcB character. It should be said, however, that the ElcB nature of the intermediate proposed by Davis is in conformity with the selectivity of 1-olefin over india. But there are catalysts (e.g., hydroxyapatite) (2) which exhibit both dehydration and dehydrogenation activities but have different olefin selectivities vis-à-vis indium oxide. Despite the fact that they do not have transition states for dehydration with ElcB character, they catalyze the dehydrogenation of alcohols when the surface has the required arrangements of Lewis acid centers. Davis' postulate requires that substitution of both β -carbons should inhibit the β -hydrogen abstraction and thus lower the rates of both dehydration and dehydrogenation. But his own data for india (Tables 1 and 4, Ref. (1)) and Lundeen and Van Hoozer's data for thoria (Table III, Ref. (3)) concur in that the rate of dehydration is slowed greatly but that of dehydrogenation is not. Since these point to the fact that dehydrogenation does not require the loss of β -hydrogen, it can be concluded that β -hydrogen abstraction may not be involved in dehydrogenation on any of the oxide catalysts.

Infrared studies confirming the presence of surface alcoholates on thoria have been reported (4). It is worthwhile to note that Davis has found that india is similar to thoria in the sense it exhibits a distinct selectivity for 1-olefin formation from secondary alcohols and is active for both dehydration and dehydrogenation. The mecha-

nism for dehydration as represented by Eq. (3) involves an interaction between the hydroxyl group of the alcohol and the metal ion only as a transition state stemming from the common intermediate proposed for both reactions. Unless the absence of a surface alcoholate is conclusively known experimentally it is difficult to conceive of an adsorption that does not involve the hydroxyl oxygen of the alcohol and Lewis acid center of the catalyst. Though the selectivity for 1-olefin formation over india favors C^β -H cleavage as the first step in dehydration, there is no good reason why coordination to the α -hydrogen is presupposed in dehydration. However, Davis himself notes that his mechanism cannot account for the rapid conversion of tertiary alcohols.

In dehydrogenation also, it is dubious why the C^α -H adsorption as a hydride on the metal ion is considered as being more facile than the dissociative adsorption of the hydroxyl group. Even if the initial coordination of the α -hydrogen is not unreasonable for dehydrogenation, it can be argued that it is the hydroxyl hydrogen that can be better eased out as a proton compared to the C^β -H, since O-H is more heteropolar than C-H. The ir evidence for the surface alcoholate in no way eliminates the possibility of adsorption by the α -hydrogen but logically it eliminates the possibility of a β -hydrogen being lost further as a proton during dehydrogenation. It is true that Hauffe's proposal (5) for the mechanism of dehydrogenation of alcohols over zinc oxide involves the initial adsorption of the C^α -H but it is also followed by the removal of the hydroxyl proton by the surface. Hence we are of the opinion that both dehydrogenation and dehydration could proceed from an alkoxide (or alcoholate) species, as represented in Eqs. (1), (2), and (3).

While dehydration (Eq. (2)) involves the elimination of β -hydrogen and hydroxyl group adsorbed on adjacent oxygen and metal ions respectively, dehydrogenation (Eq. (3)) involves the expulsion of α -hydro-



gen and hydroxyl hydrogen of the alcohol adsorbed on adjacent metal ions. Even in the event of a lack of adjacent exposed cations on the surface, the α -hydrogen transfer could still proceed to the proton of an adjacent surface hydroxyl (2). Though this concerted mechanism is also speculative, it explains the sequence without involving prior coordination of α -hydrogen for dehydration and abstraction of β -hydrogen for dehydrogenation.

The importance of the hydroxyl group participation in dehydration and dehydrogenation reactions has also been pointed out by Wolkenstein (6), who suggested that the initial adsorption, depending upon whether the C-OH bond cleaves or the O-H bond cleaves, determines whether dehydration or dehydrogenation will take place.

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