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Dehydration of Alcohols over Alumina: Effect of Sodium Impregnation on the Mode of Elimination

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Dehydration of secondary alcohols has always been the key to studying reaction mechanisms of reactions catalyzed by oxides. The γ-alumina-promoted reactions always afforded a low S_{12} (1-olefin/2-olefin) and high S_{Ct} (*Cis/trans*). These were shown to proceed by the "anti" mode of elimination of elements of water. The effect of sodium impregnation has been studied, in detail, to understand the mode of elimination operative over these doped catalysts. Studies were conducted with 2-butanol and *threo*-3-methyl-2-pentanol over these catalysts. It appears that although sodium poisoning affected selectivity S_{12}, it did not show any variation in S_{ct}, suggesting no variation in the mode of elimination. The studies conducted with *threo*-3-methyl-2-pentanol confirm that only the anti mode of elimination is operative on these catalysts.

INTRODUCTION

The dehydration studies on secondary alcohols have always been found to be useful in investigating the properties of dehydration catalysts as well as the modes of elimination to yield the various olefins. The reaction is known to be catalyzed by solid acids (*1*) and it has also been pointed out that the basic properties of some oxides also play an important role in dehydration reactions (*2–4*). Studies have been made to correlate the acid–base properties of the catalyst with catalyst activity and selectivity (*5–7*). Though alumina has been shown to eliminate by the anti mode from antiperiplanar conformation, the mode of elimination over sodium-impregnated aluminas has not been fully investigated.

Experiments have been carried out in the present study with 2-butanol and *threo*-3-methyl-2-pentanol to discern the factors underlying the selectivity and activity of alumina catalyst as a result of sodium doping.

Studies carried out by the temperature-programmed desorption technique (TPD) provided useful information without the operation of secondary isomerization processes.

It was observed by Yamaguchi and Tanabe (*5*) that dehydration was dependent on catalyst acidity and they proposed a mechanistic pathway involving a carbonium ion-like intermediate to explain the variation in product distribution. During these TPD studies, it was found that S_{12} was minimal at 150°C, and at temperatures lower or higher, the S_{12} value rose. Similar studies by Carrizova and Manuera (*8*) using anatase also provide the same S_{12} minimum exhibited at 230°C. The latter studies provide interesting observations regarding selectivity varying with temperature (*8*). It appears that during the TPD studies of dehydration a minimum S_{12} is observed at some temperature (though no such report exists in continuous-flow reactions), which may be characteristic of the technique and the catalyst employed. The authors believe that there could be varying contributions of syn and anti modes operative on the system.

It was reported by various workers (*4, 9*) that a correlation exists between the induc-

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tive and steric constants (σ^* and E_S) with different bulky β-substituents. It was also noted that the partial pressure of alcohol was important and at low partial pressures a high S_{ct} was found, where a higher surface coverage is likely, when compared to a higher partial pressure. When there is lesser surface coverage at high pressures, then chances of secondary pressures being operative cannot be ruled out. Knözinger *et al.* (*10*) suggest that a monolayer coverage is indicated even at 1 atm pressure by the zero-order kinetics. It has also been mentioned that olefin isomerization did not proceed under these reaction conditions.

There have been many reports on 2-butanol dehydration (*2*, *5*, *11–13*) over various catalysts. All these assuredly point out that the product distribution was primary and no isomerization was operative. All the values differ in quantity, e.g., 1-butene concentration values vary from nil (*11*) to 44% (*2*). It is felt that a comparison of these various observations may not be valid as the catalyst preparations and hence characteristics of the catalysts and reaction conditions were quite different.

In the present study, only one set of catalysts, prepared in a single batch and characterized fully, is taken up for comparison.

Mention must be made regarding the study by Kibby *et al.* (*14*) in elucidating the mode of elimination operative over alumina by the use of deuterated butanol. From the studies carried out in this laboratory (*6*), it was evident that the elimination proceeded by the anti mode over alumina. The various aspects of sodium doping and its effect on acidity–basicity properties have been discussed.

EXPERIMENTAL

The reactions were carried out in a conventional flow-type reactor. The details regarding the preparations and properties of these catalysts are discussed in our earlier paper (*6*).

TABLE 1

Dehydration of Butanol over Pure, Na-Doped Al_2O_3 and ThO_2 Samples[a]

Catalyst	Percentage conversion	Product distribution			$\frac{\text{1-Butene}}{\text{2-butene}}$	*cis*/*trans*
		1-Butene	*cis*-2-Butene	*trans*-2-Butene		
γ-Al_2O_3	60	23	63	14	0.3	4.50
γ-Al_2O_3 + 10% v/v piperidine	14	25	61	14	0.33	4.35
γ-Al_2O_3 + 0.12% Na^+	50	28	59	13	0.39	4.55
γ-Al_2O_3 + 0.19% Na^+	38	34	54	12	0.52	4.50
γ-Al_2O_3 + 0.41% Na^+	30	36	52	12	0.56	4.33
γ-Al_2O_3 + 0.68% Na^+	23	42	48	10	0.73	4.80
γ-Al_2O_3 + 1.11% Na^+	15	45	45.5	9.5	0.83	4.80
γ-Al_2O_3 + 2.22% Na^+	Nil	—	—	—	—	—
Thoria	19.0	92	4.0	4.0	11.5	1.0

[a] Flow rate, 18 ml/hr; weight of catalyst, 1 g. Reaction temperature: Alumina, 300°C; thoria, 350°C.

TABLE 2

Dehydration of *threo*-3-Methyl-2-Pentanol[a]

Catalyst	Percentage conversion	Product distribution[b]				*cis*/*trans*
		2-E-1-B	3-M-1-P	3-Me-2-P *cis*	3-Me-2-P *trans*	
γ-Al_2O_3	64	16.0	3.5	61.5	19.0	3.24
γ-Al_2O_3 + piperidine (10% v/v)	31	19.0	3.5	62.0	15.5	4.0
γ-Al_2O_3 + 1.11% Na^+	24	28.0	6.0	51.0	15.0	3.40
Thoria	8	88.0	—	2	10.0	0.20

[a] Flow rate, 18 ml/hr; weight of catalyst, 1 g. Reaction temperature: Alumina, 300°C; thoria, 350°.

[b] 2-E-1-B, 2-ethyl-1-butene; 3-M-1-P, 3-methyl-1-pentene; 3-M-2-P *cis*, 3-methyl-*cis*-2-pentene; 3-M-2-P *trans*, 3-methyl-*trans*-2-pentene.

RESULTS AND DISCUSSION

The study of dehydration of 2-butanol over pure and sodium-doped alumina catalyst samples revealed that the S_{12} increased with increasing amount of dopant (Table 1). It was seen that sodium doping decreased the Brønsted acidity and increased the basicity of the alumina catalyst. Pure alumina, the most acidic of all the catalysts used, provides products, by a concerted pathway from an E1-like transition state, resulting in obtention of more of the internal olefin. With sodium-doped alumina samples, due to an increase in basicity, the transition state shifts to an E1CB-like one and this changes the selectivity. During a carbanion-like transition state, the hydrogen atom, which is more acidic, is preferentially extracted, which results in more of the terminal olefin in these reactions.

Studies conducted with *threo*-3-methyl-2-pentanol (Table 2) showed that the mode of elimination remained anti. Both alumina and sodium-doped alumina samples provided more *cis*-3-methyl-2-pentene, consistent with an anti elimination pathway.

There were reports suggesting a modification of catalysts, structure, and stabilization of alumina spinel by doping (*15*, *16*).

TABLE 3

Effect of Na Content on Surface Area using Aluminum Hydroxide Slurry

S No.	Catalyst description	Surface area (BET) (m^2/g)
1	γ-Al_2O_3 + 0.38% Na^+	215.5
2	γ-Al_2O_3 + 0.42% Na^+	200.2
3	γ-Al_2O_3 + 0.44% Na^+	198.4
4	γ-Al_2O_3 + 1.41% Na^+	174.9
5	γ-Al_2O_3 + 1.67% Na^+	82.2
6	γ-Al_2O_3 + 1.76% Na^+	60.5

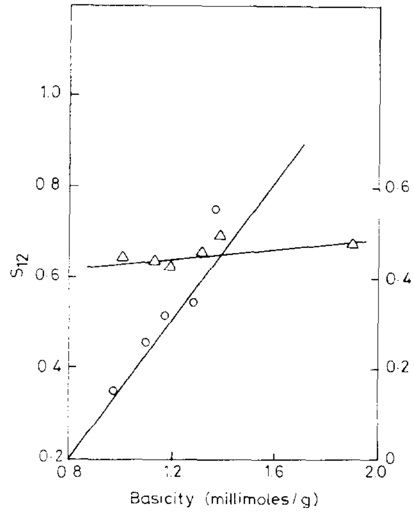

FIG. 1. Selectivities S_{12} and S_{ct} vs basicity, from trichloroacetic acid adsorption method. ○, S_{12}; △, S_{ct}.

Two procedures were used for doping the alumina samples with sodium ions. When sodium doping was carried out using aluminum hydroxide slurry and then calcined further, an amorphous solid resulted. When precalcined alumina was used, no such phenomenon was observed, as evidenced by X-ray studies. An important observation concerning the cataysts prepared by the former method is that there was significant change in the surface area—decrease with increasing sodium content (Table 3). Only the latter method was used for preparing the catalysts for dehydration studies.

The anti elimination and *cis* preference have been explained by Knözinger *et al.* (*11*) to occur via an inclination of the molecule on the surface with the bulky substituents kept away from the surface of the catalyst, to minimize substituent–surface interaction. It can be seen that S_{12} was higher for alumina catalyst samples having higher percentages of sodium ions (Fig. 1). The S_{ct} remained constant (around 4.5) and the sodium doping did not affect the selectivity for the *cis* or *trans* isomer. 1-Butene isomerization was tried under similar conditions, but no appreciable reaction was noticed under the reaction conditions. Though S_{12} increased with increasing basicity, it did not exceed the value 1.0 under these conditions. The limitation was due to the fact that a catalyst containing 2.2% sodium ions was not dehydrating at all, though the basicity of this catalyst was very high (*16*) (Table 4). Hence it was not possible to correlate S_{12} with basicity of sodium-doped alumina and thoria samples, though the same method was used for measurement of basicity of these samples.

TABLE 4

Basicity and Pure, Sodium-Doped Alumina Samples and Thoria Sample

Catalyst	Basicity (mmoles/g)[a]	Percentage dehydration
γ-Al_2O_3	0.98	60.5
γ-Al_2O_3[b] 2.2% Na^+	2.00	nil
Thoria	2.70	19.2

[a] Trichloroacetic acid adsorption method.

[b] Taken from Ref. (*16*).

The difference between sodium poisoning and piperidine poisoning can be seen from Table 1. When piperidine was used in the reaction, the 1-butene concentration was not altered much and thus the nitrogen base had just arrested the secondary isomerization process by poisoning the stronger acid sites. In contrast to this, sodium impregnation altered the catalyst fundamentally, resulting in a different selectivity for this catalyst.

We would like to mention that, even if a phase modification of the catalyst has occurred due to sodium doping (not detected by X-ray studies), the same selectivity S_{ct} was obtained for these reactions, while the syn process occurring over thoria has provided $S_{ct} = 1.0$ and $S_{12} = 12.0$.

It can be seen from Table 5 that alkali ion poisoning only decreased the activity of the catalyst, not affecting the *cis*/*trans* ratio. Piperidine poisoning and sodium ion poisoning decrease the activity of the catalyst, and neither alters the mode of elimination. It can be seen that in the case of ben-

TABLE 5

Effect of Alkali and Piperidine Poisoning of Alumina

Catalyst	Substrate	*cis*/*trans*	$\frac{\text{1-olefin}}{\text{2-olefin}}$
γ-Al_2O_3	2-Butanol	4.5	0.3
γ-Al_2O_3 + piperidine (10% v/v)		4.4	0.33
γ-Al_2O_3 + 1.11% Na		4.7	0.83
Thoria		1.0	12.00
γ-Al_2O_3	Benzylmethyl carbinol	1.8	0.35
γ-Al_2O_3 + piperidine (10% v/v)		3.5	0.50
γ-Al_2O_3 + 1.11% Na^+		3.5	0.45
Thoria		0.1	0.30

zylmethylcarbinol, the *cis/trans* ratio has remained the same for alumina (piperidine poisoning arresting secondary isomerization) and sodium-doped alumina, while in case of thoria, the ratio has become 0.1.

It appears that steric factors decide the *cis/trans* ratio, but still the mode of elimination also seems to have a part in this. When the mode is anti the steric interaction between the substituents and the surface is crucial and hence provides more of the *cis*-olefin. But when the mode is syn, the substituents are already kept away from the surface and the steric strain between the substituents is the deciding factor and this leads to more of the *trans*-olefin in the product.

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