Dehydrogenating Behaviour of 4f Metal Oxides in Decomposition of Butanols

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The kinetic parameters for 1- and 2-butanol dehydrogenation over La_2O_3, CeO_2, Pr_6O_{11}, Sm_2O_3, Eu_2O_3, Dy_2O_3, Ho_2O_3, and Yb_2O_3 are reported. The selectivity of these oxides for the dehydrogenation–dehydration of the alcohols is discussed with reference to the fractional selectivity S_F, where $S_F = 100 \cdot r_{H_2}/(r_{H_2} + r_{H_2O})$. No definite pattern of S_F is found in the series of 4f oxides studied, but several trends of S_F are observed, depending on the selected alcohol or temperature. These results show the limitations of S_F in establishing direct correlations between the catalytic behaviour of metal oxides and their chemical constitution. This is particularly noticeable in the case of lanthanide oxides, because of the gradual variation of their properties throughout the series.

INTRODUCTION

Establishing simple relationships between the chemical constitution of metal oxides and their catalytic selectivity for dehydrogenation–dehydration reactions is a subject which has often been reported in the literature (1). On account of the regular changes that the general properties of 4f oxides show throughout the whole series (2), these oxides may be considered very appropriate for discussing the possible existence of correlations such as those mentioned above.

Selectivity has frequently been investigated using formic acid decomposition. We selected this reaction in order to investigate the factors pertaining to the selectivity of 3d metal oxides (3). Nevertheless, the interaction of lanthanide oxides with formic acid gives a bulk formate, the decomposition of which takes place through the corresponding dioxomonocarbonate (4). Therefore, an alternative test reaction, namely, alcohol decomposition, has been selected. A study of the selectivity of 4f oxides in the dehydration of butanols has been previously reported (5), and here we report on dehydrogenation.

METHODS

Catalysts and alcohols. The 4f sesquioxides were obtained by calcining in air, at 873 K, the hydroxides prepared by precipitation with ammonia from the corresponding nitrate solutions. According to our X-ray diffraction and pore size distribution studies, all the sesquioxides were cubic, C-type structure, and no microporosity has been found in the catalysts (6). Also, the interaction of Yb_2O_3 with several alcohols, as well as its hydration and carbonation, has been studied by ir spectroscopy (7).

In order to distinguish these oxides from the commercial ones, series I, formerly studied, they will be termed series II catalysts.

The alcohols used in this work were 1-butanol and 2-butanol, Merck A.R. grade without further purification.

Catalytic activity. The flow reactor employed here has been described elsewhere (6). Under our operating conditions the reaction rate was independent of the alcohol pressure and the catalytic activity measurements were carried out at low conversion in order to prevent secondary reactions. Likewise, diffusion phenomena

were avoided.

TPD system. The special temperature-programmed desorption (TPD) system used in this paper is described elsewhere (*8*). In this experimental device, which operates at normal pressure, quantitative analysis of the evolved gases is carried out by mass spectrometry. Furthermore, the system allows the preparation *in situ* of the corresponding adsorbed phases. Treatments of the oxides under conditions similar to those operating in our catalytic flow reactor were possible.

RESULTS AND DISCUSSION

From catalytic activity measurements corresponding to 1- and 2-butanol dehydrogenation on 4*f* oxides, the kinetic parameters, activation energy E_a and preexponential factor A, have been calculated. These parameters are reported in Table 1.

The analysis of the data of Table 1 demonstrates that throughout the selected series of oxides no definite sequence of the kinetic parameters exists. On the other hand, when we plot $\log A$ vs E_a (Fig. 1), a linear relationship like that previously reported for formic acid dehydrogenation over 3*d* metal oxides (*3*) is found. Parameters corresponding to the dehydrogenation of ethanol and 2-propanol, reported else-
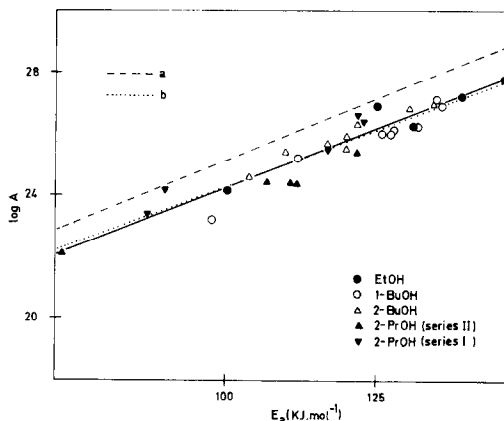

FIG. 1. E_a vs $\log A$ for dehydrogenation of alcohols on 4*f* oxides. Data corresponding to the dehydration of 1- and 2-butanol over these oxides are also included in the straight lines a and b (*5*).

where (*9*), have also been included in Fig. 1. These data were obtained from commercial 4*f* oxides, the series I catalysts.

Table 2 shows the characteristic parameters, slope *e* and intercept *B*, as well as the isokinetic temperature β, associated with the above linear relationship (*10*). The analogous parameters for the dehydration of these alcohols on the same catalysts (*5*) are also included in Table 2. The kinetic parameters for the dehydration of 1-butanol and 2-butanol to *cis*- and *trans*-2-butenes lie on straight line b, whereas line a corresponds to 1-butene formation from 2-butanol. Both lines a and b are plotted in Fig. 1.

TABLE 1

Kinetic Parameters for the Dehydrogenation of
1-Butanol and 2-Butanol on 4*f* Oxides

	1-BuOH		2-BuOH	
	$E_a{}^a$	A^b	$E_a{}^a$	A^b
La$_2$O$_3$	98	1.5×10^{23}	128	6.8×10^{26}
CeO$_2$	135	1.2×10^{27}	135	9.4×10^{26}
Pr$_6$O$_{11}$	136	8.0×10^{26}	122	1.9×10^{26}
Sm$_2$O$_3$	132	1.8×10^{26}	110	2.7×10^{25}
Eu$_2$O$_3$	126	9.0×10^{25}	120	7.9×10^{25}
Dy$_2$O$_3$	112	1.5×10^{25}	117	4.5×10^{25}
Ho$_2$O$_3$	128	1.2×10^{26}	104	3.9×10^{24}
Yb$_2$O$_3$	125	1.1×10^{26}	120	2.9×10^{25}

^{a} Activation energy in kJ mol^{-1}.
^{b} Preexponential factor in molec. $\cdot$ s^{-1} m^{-2}.

TABLE 2

Alcohol Decomposition on 4*f* Oxides; Characteristic Parameters Corresponding to the Linear Relationships Found between E_a and $\log A$

	e^a	B^b	$\sigma_e{}^c$	$\sigma_B{}^d$	β (K)
Dehydrogenation	0.077	16.49	5×10^{-5}	1.34	677
Dehydration^e					
a	0.080	17.14	1×10^{-3}	1.30	655
b	0.074	16.86	1×10^{-3}	1.56	712

^{a} Slope of the straight line.
^{b} Intercept of the straight line.
^{c} Standard deviation of the slope.
^{d} Standard deviation of the intercept.
^{e} Taken from Ref. (*5*).

Several authors have studied the alcohol dehydrogenation mechanism over polar catalysts. Some of them have suggested, from experimental and theoretical studies (*11–14*), that alkoxide species are intermediates, the decomposition of which would control the reaction rate. Isotope effect studies carried out by Nondek and Sedláček (*13*) seem to confirm that the scission of the C_α–H bond must be involved in the rate-controlling step. However, Vinek *et al.* (*15*) have proposed a dehydrogenation mechanism on basic oxides which would have a first step similar to that shown by the ElcB dehydration mechanism. According to this, the first step of the dehydrogenation reactions would imply the breaking of a C_β–H bond. A rather similar mechanism has recently been suggested by Davis over india (*16*). By means of this mechanism, the authors (*15, 16*) try to explain the simultaneous observation of dehydrogenating activity and high 1-alkene formation (Hofmann preference) in the dehydration reaction.

Although lanthanide oxides are generally considered to be basic compounds, our results do not seem to confirm the hypothesis advanced by Vinek *et al.* (*15*). In effect, straight line a in Fig. 1 includes parameters corresponding to reactions that imply the elimination of a hydrogen atom from a –CH$_3$ group, whereas in the case of line b, the dehydration reaction involves a –CH$_2$– group. As already discussed (*5*), these results seem to indicate that the nature of the β-H determines the preexponential factor values, being greater when a methyl group participates in the elimination reaction. If the analogy between the dehydrogenation and dehydration mechanisms suggested in (*15, 16*) existed in our case, an effect similar to the one discussed above for the dehydration reaction ought to be observed. However, Fig. 1 shows the existence of a single straight line in the case of alcohol dehydrogenation.

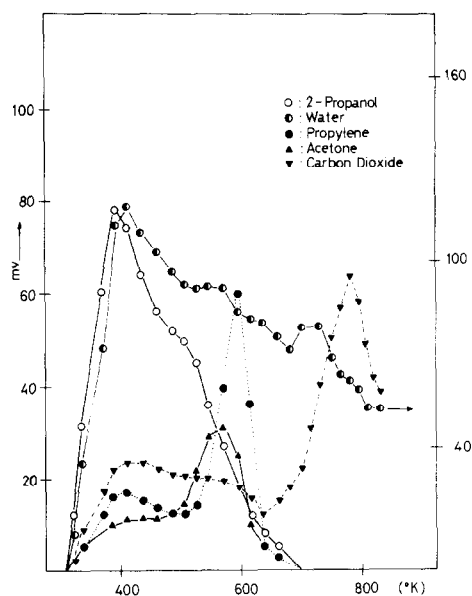Furthermore, the results of our TPD study of the system 2-propanol/Yb$_2$O$_3$,

FIG. 2. TPD–MS study of Yb$_2$O$_3$ after treatment with 2-propanol at 403 K.

summarized in Figs. 2 and 3, suggest that both dehydrogenation and dehydration reactions take place on different active cen-
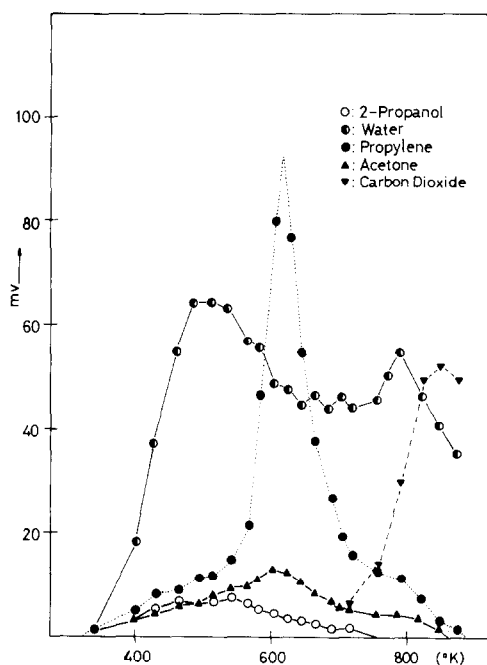

FIG. 3. TPD–MS study of Yb$_2$O$_3$ after treatment with 2-propanol at 723 K.

ters. These experiments, carried out in helium flow at a linear heating rate of 10 K min^{-1}, constitute a part of a larger study in which the influence of hydration and carbonation of 4f sesquioxides on their catalytic behaviour will be analysed. Therefore, only some aspects of the experiments will be discussed here.

Figures 2 and 3 account for the thermal evolution of the adsorbed phases prepared by interaction of Yb$_2$O$_3$ with a flow of 2-propanol (alcohol pressure 6.7 × 10^4 Pa) at two different temperatures, 403 and 723 K, respectively. After 2 h of treatment, the system was cooled in alcohol to 330–340 K. In both experiments the Yb$_2$O$_3$ was used without special pretreatment. According to these figures, the preparation conditions of the adsorbed phases have an opposite effect on the surface dehydrogenation and dehydration reactions. From the data reported in Table 3 it can be observed that the amounts of propylene and acetone desorbed after treatment at 403 K (Fig. 2) are similar. On the contrary, if the interaction alcohol–oxide takes place at 723 K, the alkene formation is enhanced, whereas the amount of acetone decreases. In order to confirm the origin of the desorbed acetone, we have carried out parallel experiments in which the evolution of hydrogen was studied. Analogous desorption spectra have been found for both hydrogen and acetone, which strongly suggests that this latter product may be ascribed to the dehydrogenation reaction. The different nature of the dehydrogenation and dehydration ac-

TABLE 3

TPD–MS Study of the System 2-Propanol/Yb$_2$O$_3$; Amounts of Evolved Acetone and Propylene

Treatment temperature (K)	Molecule · nm^{-2}	
	Propylene	Acetone
403	0.26	0.27
723	0.41	0.13

tive centers has been previously reported (17).

On the other hand, our ir spectroscopy study of the interaction of ethanol, 2-propanol, and 2-methyl-2-propanol with ytterbia (7, 18) demonstrates the existence of the corresponding alkoxide species on the oxide surface. Therefore, a mechanism such as that suggested by Kibby and Hall (11) and by Nondek and Sedláček (13) could operate in the case of alcohol dehydrogenation over 4f oxides.

In order to analyse the possible existence of simple relationships between the chemical constitution of catalysts and their selectivity towards dehydrogenation–dehydration of alcohols, the definition of fractional selectivity proposed by IUPAC (19) has been used:

$$S_F = 100 \cdot r_{H_2}/(r_{H_2} + r_{H_2O}).$$

From the above equation, the kinetic parameters included in Table 1, and those pertaining to the dehydration reactions previously reported (5), we have calculated the S_F values shown in Fig. 4. For 2-butanol, the dehydration rate, r_{H_2O}, has been taken as the summation of the reaction rates corresponding to the formation of the three alkenes found, namely, 1-butene and the cis- and trans-2-butenes.

According to Fig. 4, no definite patterns of selectivity are found throughout the whole series of 4f oxides. This is particularly noticeable if we take into account that, as a consequence of the lanthanide contraction effect, properties such as the bulk basic character of sesquioxides steadily decrease from La$_2$O$_3$ to Lu$_2$O$_3$ (2).

Concerning the above figure, some other points may be noted:

(1) The temperature has a very important influence on the selectivity. Particularly, for 1-butanol decomposition on lanthana, S_F ranges from 75.8 at 573 K, to 5.5 at 773 K.

(2) For a specific alcohol, the effect of the temperature on the selectivity depends on the selected oxide. As a consequence, three
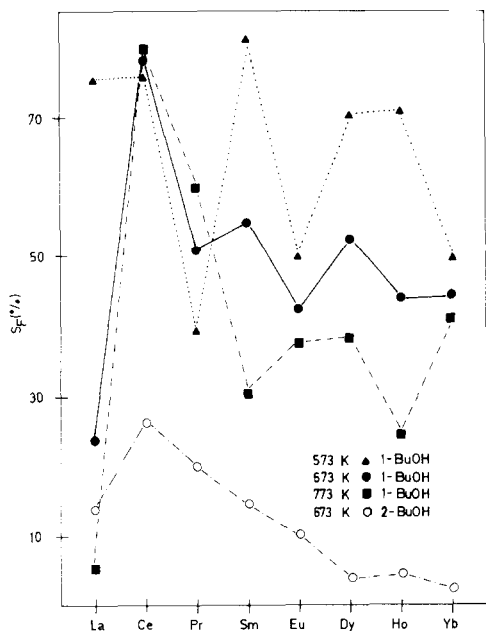
FIG. 4. Fractional selectivity data corresponding to dehydrogenation/dehydration of 1- and 2-butanol over 4f oxides at various temperatures.

different trends of selectivity are found throughout the series of oxides when the decomposition of 1-butanol is studied at 573, 673, and 773 K, respectively.

(3) At a single temperature, namely, 673 K in Fig. 4, the selectivity patterns for 1- and 2-butanol are also different, the lowest selectivity values corresponding to 2-butanol decomposition.

From these three points we may reach some general conclusions, the validity of which is not restricted by the mechanistic discussion previously carried out. First of all, fractional selectivity is a parameter of very limited validity for correlating catalytic behaviour and chemical constitution of oxides. It is apparent from our results that doubtful correlations may be obtained if S_F data corresponding to a single temperature or a restricted range of temperature are used (20). Likewise, our findings suggest that, from the former correlations, very different conclusions may be drawn depending on the selected alcohol. In short, without assuming either mechanistic

changes or some other kind of modification, conclusions strongly dependent on the selected alcohol or temperature may be reached from the correlations discussed above.

Regarding the 4f oxides studied here, our results may be related to the reported compensation effect. Thus, for 1-butanol decomposition, it can be seen from Table 2 and Fig. 1 that straight lines including dehydrogenation and dehydration kinetic parameters are approximately parallel and, therefore, their corresponding isokinetic temperatures are rather similar. So, in accordance with the known meaning of β (11), the selectivity values will decrease at increasing temperature if $E_a(H_2O) > E_a(H_2)$, becoming less than 50% around 675–700 K. The opposite will be true when $E_a(H_2O) < E_a(H_2)$.

In relation to the 2-butanol selectivity pattern, analogous comments could be applied. However, the dehydration rate is now the sum of three reaction rates, the kinetic parameters for 1-butene formation lying on straight line a. Accordingly, because the intercept B is greater in this case, we must expect lower selectivity values for 2-butanol decomposition. This is true for a wide range of temperatures. Therefore, the lower selectivity found seems to be related to the dehydration reaction, specifically to the higher preexponential factor that implies the elimination of a β-H from a methyl group. Nevertheless, this conclusion cannot be generalised under all conditions, since it is necessary to consider the simultaneous influence of the temperature through the activation energy. In fact, on lanthana the difference between the activation energy for both dehydrogenation and dehydration reactions of 1-butanol ($E_a(H_2O)$: 171 kJ mol^{-1} and $E_a(H_2)$: 98 kJ mol^{-1}) determines that at temperatures higher than 723 K the lowest selectivity values correspond to 1-butanol decomposition.

In summary, the present study emphasizes that fractional selectivity data obtained at only one temperature, or even at a

certain interval, are not appropriate to compare a series of catalysts. No simple pattern of $4f$ oxide selectivity in dehydrogenation–dehydration reactions is to be expected using S_F data. In spite of the difficulty in interpreting the compensation effect, if it exists, the corresponding intercept and isokinetic temperature may give more complete information about the behaviour of a series of catalysts.

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