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CATALYTIC ACTIVITY OF THE 1:1:1 Zn, Cr AND Fe MIXED OXIDE: MECHANISTIC STUDY OF THE KETONIZATION OF ACETIC ACID

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ABSTRACT

The catalytic activity of a ternary oxide mixture of Zn, Cr and Fe in 1:1:1 atomic concentration has been studied using ketonization of acetic acid. The Arrhenius plot for the reaction shows a break around 673 K indicating the dependence of the reaction mechanism on temperature. Electrical conductance measurement also shows a change in the electronic nature of the catalyst around 673 K. The utilization of dehydration and dehydrogenation active sites of the catalyst for the ketonization process is established by the mutual effect of isopropyl alcohol and acetic acid on each others reaction on the catalyst. Competitive reaction study shows that ketonization follows Langmuir-Hinshelwood mechanism where as esterification follows Rideal-Eley mechanism. Product inhibition studies and infrared spectral studies show that the reaction is between two adsorbed acetate ions above 673 K and between one adsorbed acetate ion and an adsorbed acyl carbonium ion below 673 K.

INTRODUCTION

Acetic acid undergoes ketonization over transition metal oxides such as ZnO [1],Cr_2O_3 [2] and Fe_2O_3 [3]. It has been shown that both on Cr_2O_3 and Fe_2O_3, the activation energy of the reaction depends on the temperature at which the reaction is carried out [2,3]. The ketonization on Fe_2O_3 below 673 K is suggested to be a surface reaction involving the interaction of two adsorbed molecules of acetic acid, one of them being in the form of ketene. Above 673 K the reaction takes place through salt formation. Due to the change in electronic character of Cr_2O_3 at a temperature around 673 K,different mechanisms are postulated above and below

673 K. Above 673 K Cr_2O_3 is n-type and the rate determining step is the formation of the carbonium ion and below 673 K it is p-type and the rate determining step is the formation of acetate. The present investigation is an attempt to understand the mechanism of ketonization on the ternary oxide mixture of Zn,Cr and Fe in a 1:1:1 atomic concentration. This mixture calcined at 873 K is found to be more active than any of the binary and ternary combinations. Since the study of this reaction at various partial pressures did not enable the determination of the order of the reaction, the technique of competitive reaction is tried to elucidate the mechanism [4].

EXPERIMENTAL

The ternary oxide catalyst was prepared by the slurry method described by Batist and Derkinderan [5]. Recrystallized $Fe(NO_3)_3.9H_2O$ (SM,LR), $Cr(NO_3)_3.9H_2O$ (Reachim,AR) and ZnO (M and B) were used for the preparation of the catalyst.$Fe(OH)_3$ and $Cr(OH)_3$ were obtained by precipitation from nitrate solutions by the slow addition of ammonia (BDH,AR) keeping the system stirred. A ZnO paste made with distilled water was added to the mixture of $Fe(OH)_3$ and $Cr(OH)_3$ and the mixture was heated for 4 hours on a water bath keeping the whole mass stirred vigorously. After the reaction, the solid was filtered, dried overnight at 383 K and then calcined at 873 K for 4 hours. X-ray analysis of the catalyst was done using Mo-K_α radiation with a Philips generator PW 1140 unit. Electrical conductivity of the pellatised catalyst was measured by means of two probe conductivity set up using Keithley electrometer 610 B. The IR spectrum of the adsorbed species on the catalyst was recorded with a Perkin-Elmer 257 spectrometer using KBr as a solvent. Acetic acid (BDH,AR) was used as such without further purification. Isopropyl alcohol (BDH,AR) was purified by refluxing with fresly burnt quicklime for 4 to 6 hours followed by distillation [6]. Methyl alcohol (BDH,AR) was refluxed with 10% NaOH solution for about 6 hours followed by distillation [6]. The middle fraction of the distillates were used after checking their purity by chromatography. Acetone (BDH,AR) was used without further purification. CO_2 and N_2 used in the product inhibition study and partial pressure study respectively were supplied by the Indian Oxygen Company Ltd. The catalytic reaction was studied in a fixed bed flow type reactor at

1 atmosphere pressure with 0.15 s contact time. Complete coverage of the surface with the acid at 1 atmosphere pressure at the maximum temperature of the reaction was confirmed by partial pressure studies. The catalyst was regenerated after every run of the reaction by heating at 773 K in CO_2 free of oxygen. The reaction was carried out with 1.5 ml(weighing 1.51 g) of powdered catalyst of uniform grain size (maximum size = 25 μ) in a tubular reactor. It was verified that there was no diffusion control. Material balance was checked for the reaction in the entire range of temperature. Liquid products formed were analysed by Gas Chromatography using a Carbowax 20 M column. The acetic acid reacted was determined by direct titration with NaOH solution. The amount of ester formed was determined by first titrating a known amount of the liquid product with NaOH to determine the unreacted acid then refluxing a known weight of the product with excess alkali to hydrolyse the ester and back titrating the excess alkali. From the titre values the amount of ester formed was calculated. The gaseous products such as CO_2 and propylene were analysed using KOH and bromine water respectively in an Orsat gas analyser.

RESULTS

X-ray studies show that the mixed oxide of Zn,Cr and Fe in their atomic ratio 1:1:1 calcined at 873 K is a multiphasic system ($ZnFe_2O_4$-major, $ZnCrFeO_4$-minor, Cr_2O_3-very little, Fe_3O_4-very little, Fe_2O_3-very little). The Arrhenius plot for the ketonization reaction on this system in the temperature range 613 K to 733 K gives two lines with different slopes instead of a single straight line (Fig. 1). The discontinuity in the Arrhenius plot occurs around 673 K. Thus the mechanistic study of the reaction above and below 673 K is undertaken. The activation energy of acetone formation below 673 K is found to be 159 kJ mol^{-1} while it is 59 kJ mol^{-1} above 673 K. The pre-exponential factor A is found to be 3.9×10^{4} millimoles h^{-1} and 3.2×10^{8} millimoles h^{-1} at temperatures above and below 673 K respectively. The electrical conductance measurements made for the catalyst pellet (Diameter + the pellet = 1.44 cm and Thickness + the pellet = 2.63 mm) in He,O_2 and acetic acid atmospheres are given in Figure 2.

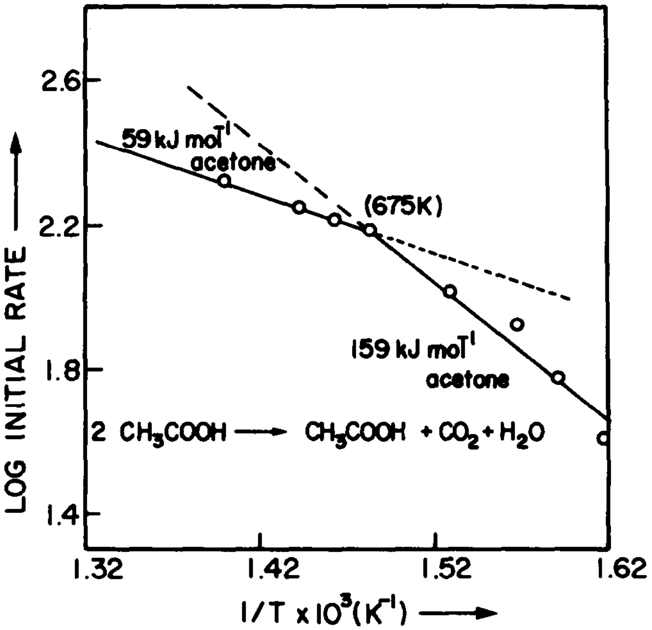

Fig. 1. Arrhenius plot for the ketonization of acetic acid.

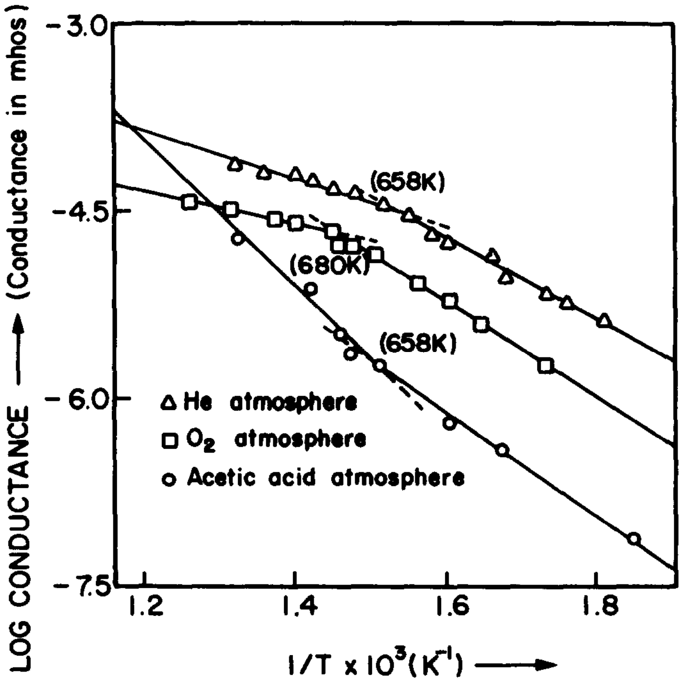

Fig. 2. Variation of conductivity with temperature.

Breaks are observed in the plots of log.electrical conductance versus 1/T around 673 K. The partial pressure of acetic acid was varied by mixing it with an inert diluent nitrogen, to study the effect of partial pressure of acetic acid on the reaction. Straight lines are obtained for both first order expression (1/rate versus 1/P) and the second order expression ($1/(\text{rate})^{1/2}$ versus 1/P) (Fig. 3).

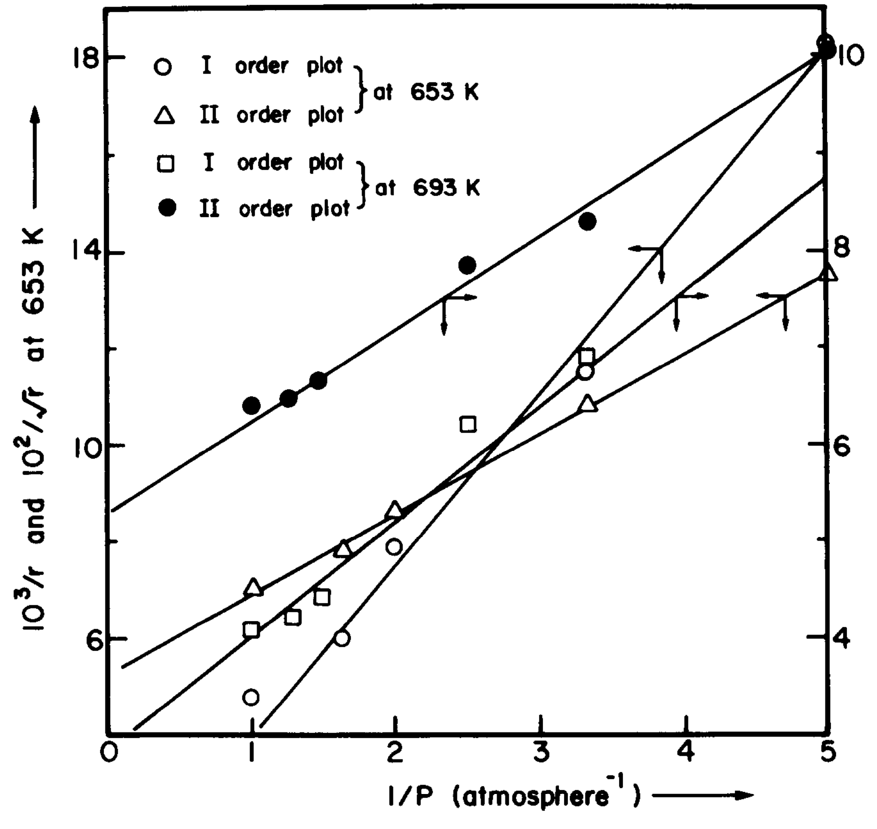

Fig. 3. Plot for the verification of the order of the reaction.

Partial pressure study with mixtures of acetic acid and isopropyl alcohol of various compositions with a total pressure of 1 atmosphere were carried out. Figures 4 and 5 represent the mutual effect of isopropyl alcohol and acetic acid on each other's reaction at 653 K and 693 K.

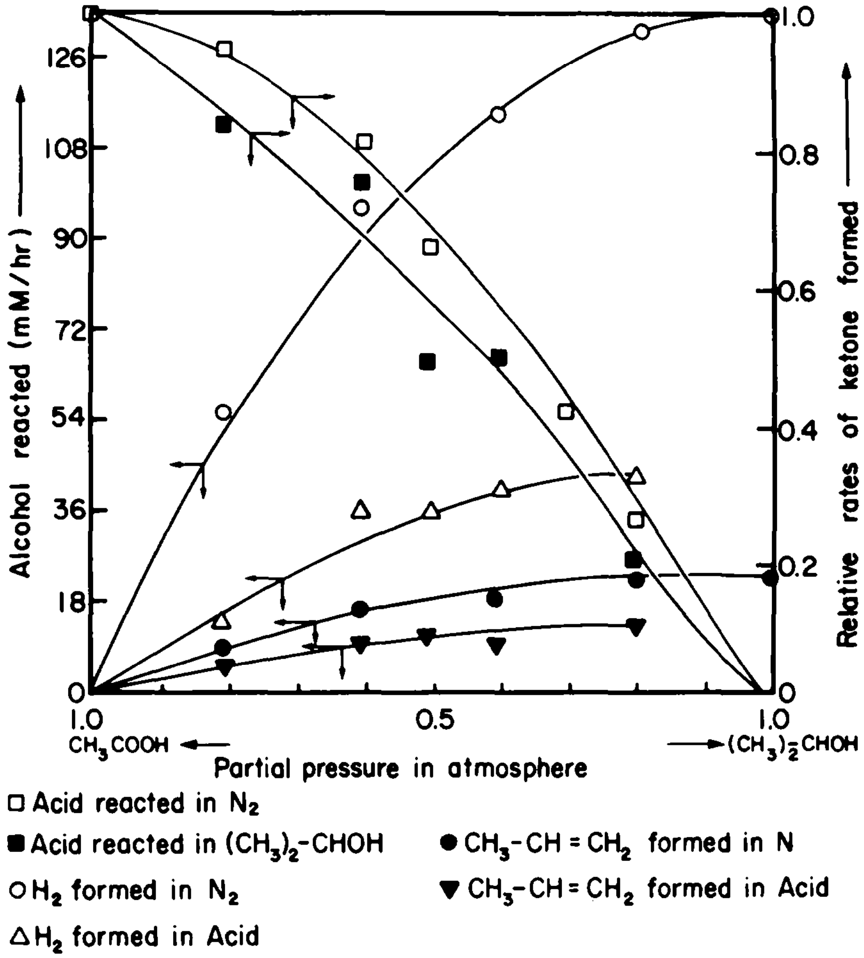

Fig. 4. Mutual effect of acetic acid and isopropanol on their reactions at 653 K.

Mixtures of acetic acid and methyl alcohol were allowed to react on the catalyst where ketonization and esterification formed the competing reactions. In Figure 6 the relative velocities of the ketonization and esterification are plotted as a function of composition of acetic acid and methanol in the feed.

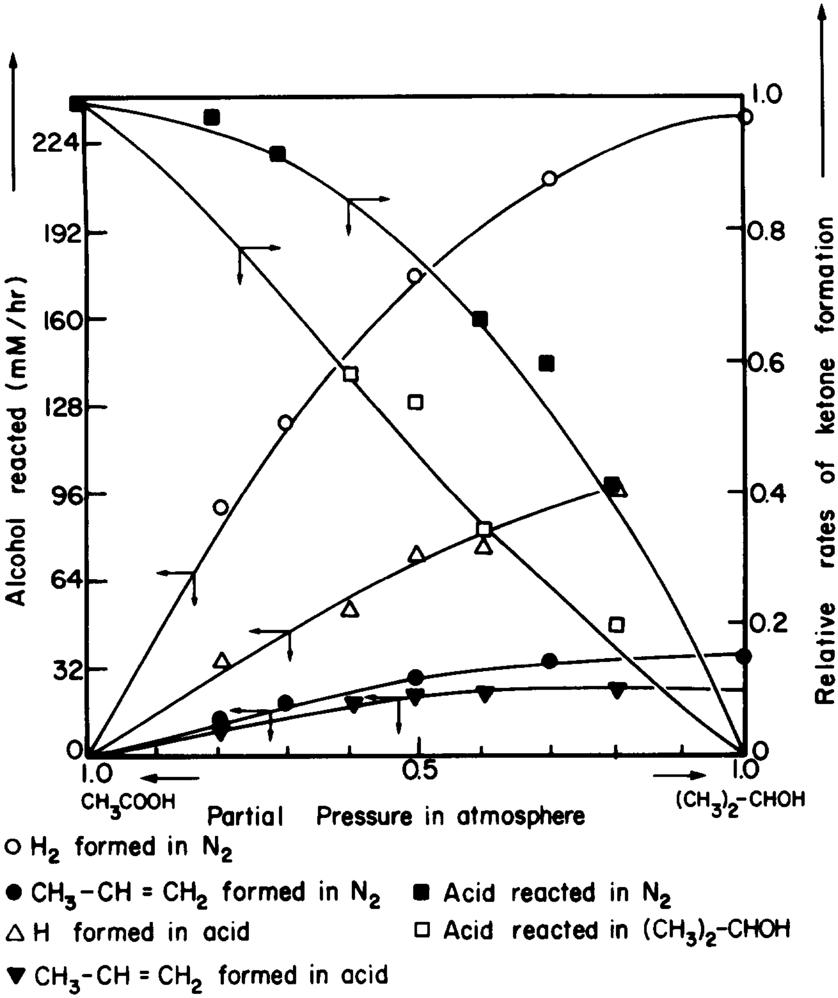

Fig. 5. Mutual effect of acetic acid and isopropanol on their reactions at 693 K.

The ratio of the relative adsorption coefficients of acid and alcohol (b_{ac}/b_{al}) is calculated from the partial pressures at which the rate of esterification is maximum [4]. If the Langmuir-Hinshellwood mechanism (L-H) is operative for the esterification, the condition for the maximum rate is

$$b_{ac}/b_{al} = P_{al}/P_{ac}.$$

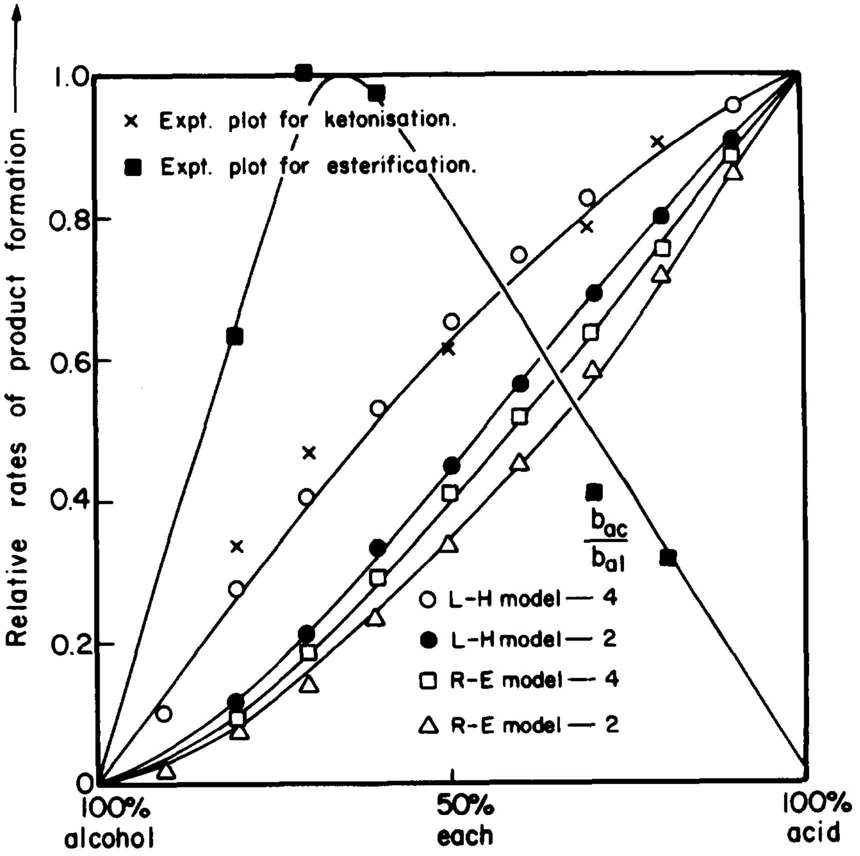

Fig. 6. Relative rates of formation of acetone and methyl acetate at 693 K for mixtures of acetic acid and methanol.

Similarly if the Rideal-Eley (R-E) mechanism is operative the condition for maximum rate is

$b_{ac}/b_{al} = [P_{al}/P_{ac}]^2.$

Thus two values of the adsorption coefficient ratio are obtained. Using these values, one can calculate theoretical curves for the ketonization for both L-H and R-E mechanisms.

$$\text{rate}_{ket} = k_{ket} \left(\frac{b_{ac} \cdot b_{al}}{b_{ac}P_{ac} + b_{al}P_{al}}\right)^2 \quad \text{———[L-H]}$$

$$\text{rate}_{ket} = k_{ket} \left(\frac{b_{ac}.P_{ac}^{2}}{b_{ac}P_{ac} + b_{al}P_{al}}\right) \qquad \text{———[R-E]}$$

Thus four theoretical curves are constructed which are represented in Figure 6. Figures 7 and 8 represent the results of the ketonization of acetic acid in the presence of various products as well as the inert diluent nitrogen at 653 K and 693 K. The infrared spectrum of the catalyst was taken after conducting the reaction and cooling it in inert atmosphere.

It showed only one broad peak at 1550 cm^{-1} corresponding to carboxylate species [8].

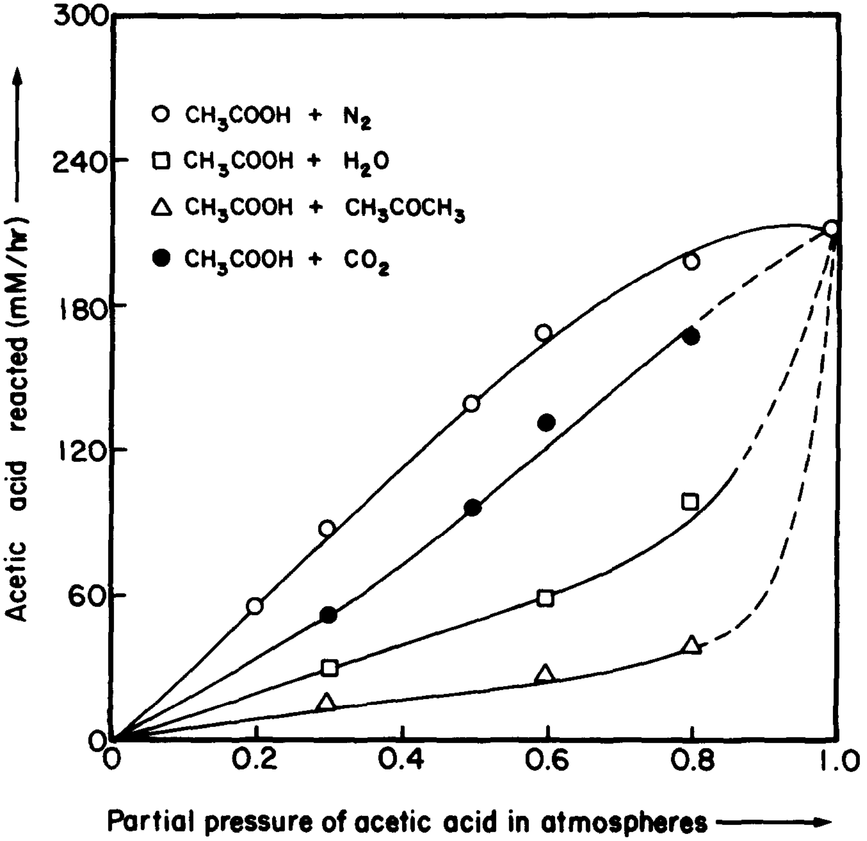

Fig. 7. Influence of products on the ketonization of acetic acid at 653 K.

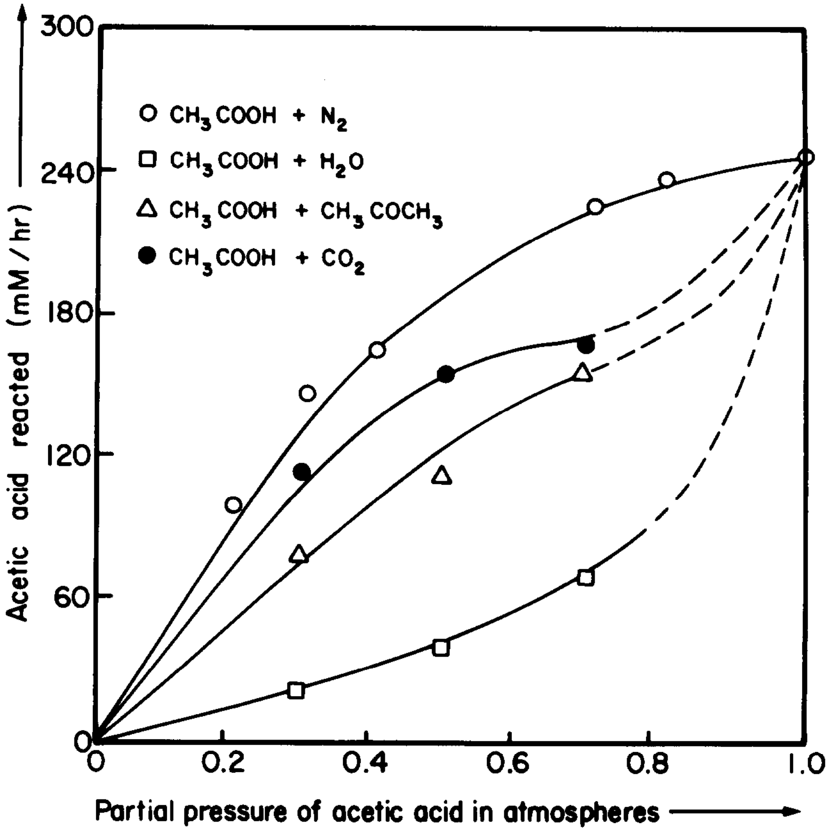

Fig. 8. Influence of products on the ketonization of acetic acid at 693 K.

DISCUSSION

The break in the Arrhenius plot observed around 673 K (Fig. 1) indicates that the mechanism of ketonization is not the same above and below this temperature. Since the rates of ketonization of acetic acid above 673 K are found to be less than what one should expect if the Arrhenius equation is obeyed, one may suspect that the break may be due to surface unsaturation. But partial pressure studies of acetic acid with nitrogen show that the surface is saturated at high partial pressures approaching 1 atmosphere acid even at a temperature of 693 K (Fig. 8). Thus the surface unsaturation is not likely to be the cause for the discontinuity in the Arrhenius plot. Similar break obtained in the plot of log conductivity versus 1/T around 673 K shows that there is a change in the electronic nature of the catalyst around this temperature (Fig. 2). Since conductivity is found to be less in the presence of oxygen than in the presence of He, the overall behavior of the catalyst is n-type above and below 673 K.

The inhibition of the ketonization of acetic acid by isopropanol and the supression of both dehydration and dehydrogenation of isopropanol by acetic acid above and below 673 K brings out the importance of the utilization of both dehydration and dehydrogenation sites of the catalyst for the ketonization reaction (Figs. 4 and 5).

Figure 6 shows that the experimental results for the ketonization of acetic acid at 693 K are found to lie on the L.H. plot for a value of $b_{ac}/b_{al}=4$ which corresponds to the R.E. mechanism for esterification. So one may conclude that ketonization above 673 K follows L.H. mechanism. The technique of competitive reaction could not be used at 653 K since the relative adsorption coefficients of alcohol and acid were not of the suitable magnitude to permit a clear distinction between the two mechanisms [9].

Figures 7 and 8 show that all the products inhibit the reaction. The extent of supression of ketonization by products above 673 K is in the order water>acetone>CO_2 and below 673 K inhibition is in the order acetone>water>CO_2. Thus with the product inhibition studies, one can consider that above 673 K the reaction takes place through the formation of acetate intermediate. Water can inhibit more than acetone because water can reverse the salt formation by hydrolysing the salt while acetone cannot compete for the surface in the same manner as water [10]. Below 673 K the possible intermediate is an acyl carbonium ion. The observation of the IR band at 1550 cm^{-1} can be accounted since the acyl corbonium ion adsorbed on the oxygen atom of the surface is not distinguishable from the acetate ion adsorbed on the metallic site. The reaction mechanism can be thus schematically represented as in Figures 9a and 9b.

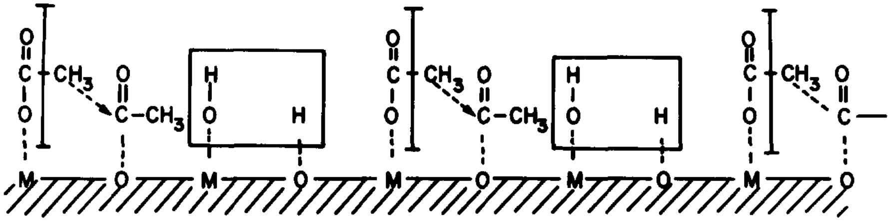

Fig. 9 (a) Mechanism of ketonisation of Acetic acid below 673 K.

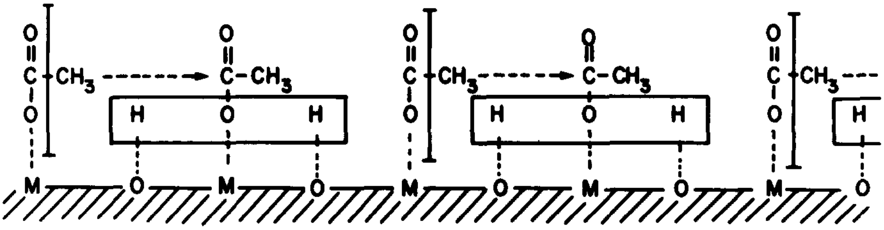

Fig. 9 (b) Mechanism of ketonisation of Acetic acid above 673 K.

CONCLUSION

The mechanism of the ketonization reaction on the mixed oxide of Zn, Cr and Fe (1:1:1) depends upon the electronic nature of the catalyst which depends largely on the temperature. The ketonization above 673 K is found to follow Langmuir-Hinshellwood mechanism through the carboxylate ion intermediate whereas the ketonization below 673 K is through the interaction between an acyl carbonium ion and a carboxylate ion. The proposed mechanism for ketonization of acetic acid is in agreement with the mechanism proposed on Fe_2O_3 and Cr_2O_3. In the case of Cr_2O_3 the acetate intermediate is postulated below 673 K whereas in mixed oxide system the reaction through the carboxylate intermediate occurs above 673 K. The catalytic activity of the mixed oxide system is greater than that of the the component oxides.

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