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Author(s)	JEWUR, S. S.; KURIACOSE, J. C.
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INFLUENCE OF PRODUCTS AND PRETREATMENTS ON THE KETONISATION OF ACETIC ACID OVER IRON OXIDE

By

S. S. JEWUR*) and J. C. KURIACOSE*)

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Abstract

With a view to understand the mechanistic details of the ketonisation of acetic acid on iron oxide the influence of products on the rate of the reaction was studied at different temperatures. Inhibition of the ketonisation due to water is greater than that due to carbon dioxide and acetone at all temperatures. The extent of catalytic dehydration and dehydrogenation of alcohols and the ketonisation of acetic acid was also studied on catalysts reduced to different degrees. The results suggest the necessity of dehydrogenation as well as dehydration activities of the catalyst for the ketonisation reaction.

Introduction

From a survey of the literature it is found that the ketonisation reactions of fatty acids over metal oxides have been suggested to proceed through the formation of a salt[1~5] or through the interaction between two adsorbed species not amounting to a salt[6]. The mechanistic route taken by the reaction seems to depend on the nature of the oxide catalyst. The properties of a catalyst could be altered by doping, subjecting it to heat treatment, supporting the catalyst etc. Such techniques have been used for quite a few reactions[7~11]. An alternate method suggested is the temporary doping effect resulting from an interaction of a reagent that is added to the substrate and functions during the period of the reaction[12]. The latter method of enhancing the activity of catalysts have been demonstrated in the decomposition of ethyl alcohol on chromia[13], the influence of acetic acid on the dual activity of chromia[12,14,15], and the influence of products on the catalytic activity of ZnO–Al_2O_3 for the dehydrogenation of isopropanol[16]. From these studies it was concluded that the selectivity as well as the mechanism of a catalytic reaction could be altered by the use of suitable reagents along

*) Department of Chemistry, Indian Institute of Technology, Madras 600036, India.

with the substrates. The present work is an attempt to study the influence of the products of the ketonisation of acetic acid on a Fe_2O_3 catalyst with a view to understand the effect of the products on the activity of the catalysts and the mechanism of the ketonisation seaction.

Experimental

Ferric oxide was prepared from $FeCl_3 \cdot 6H_2O$(SM, LR). A 10 percent solution of ammonia was added to a 0.55 N solution of the salt to precipitate Fe(III) as ferric hydroxide which was washed free of chloride ions. The solid was dried at 120°C for 15 hours to obtain the oxide. The oxide was crushed to coarse crystallites and baked at 500°C for 5 hours. The baked catalyst was found to be α-ferric oxide (haematite) by X-ray analysis. Catalysts containing different proportions of ferrous and ferric iron were prepared by controlled reduction of the oxide in hydrogen at 450°C. Pure dry hydrogen was passed over ferric oxide for different periods of time following which the catalysts were cooled to room temperature in an atmosphere of nitrogen and then subjected to chemical analysis. The volume of the same weight of the catalyst reduced to different extents differed very little and so a constant weight of one gram was used for the catalytic reaction. Each lot of the catalyst was used only for a single run since it is difficult to restore their original composition by regeneration.

Acetic acid (BDH, LR) used in the reaction was purified by distillation after refluxing it with potassium permanganate (15 gm per litre) and acetic anhydride (30 mℓ per litre). Isopropyl alcohol (BDH, AR) and acetone (BDH, AR) were found to be chromatographically pure and hence used as such. Tertiary butyl alcohol (BDH, LR) was dried and distilled over clean pellets of sodium. Nitrogen, hydrogen and carbon dioxide used were found to be chromatographically pure and the traces of moisture were removed by passing them through towers packed with anhydrous calcium chloride.

Catalytic reactions were studied in a differential tubular flow reactor operating at atmospheric pressure, mercury being used to displace the reactant from a feeder into the reactor[17]. The conversion of acetic acid was followed by titrating the unreacted acid against standard alkali. The liquid products were condensed in a cold trap and analysed by vapour phase chromatograpy using a carbowax column. Hydrogen was used as a carrier gas and the column was maintained at a temperature (10～15°C) above the boiling point of the highest boiling liquid in the mixture to be analysed. Propylene and isobutylene formed from dehydration of isopropyl alcohol and tertiary butyl alcohol respectively, were estimated by the Orsat gas

analyser using bromine water prepared by dissolving Br_2 in a saturated solution of KBr for absorbing the olefins.

Results and Discussion

Influence of products on the ketonisation of acetic acid

There has been a pronounced increase in the rate of ketonisation of acetic acid on ferric oxide with increase in temperature around 400°C giving rise to a lower activation barrier for the reaction[18] above 400°C. Further, the study of the influence of alcohols on the ketonisation reaction revealed a temperature dependence of the mechanism of the ketonisation reaction[19].

Therefore, with a view to understand the influence of products on the kinetics of the conversion of acetic acid, studies were made at 375 and

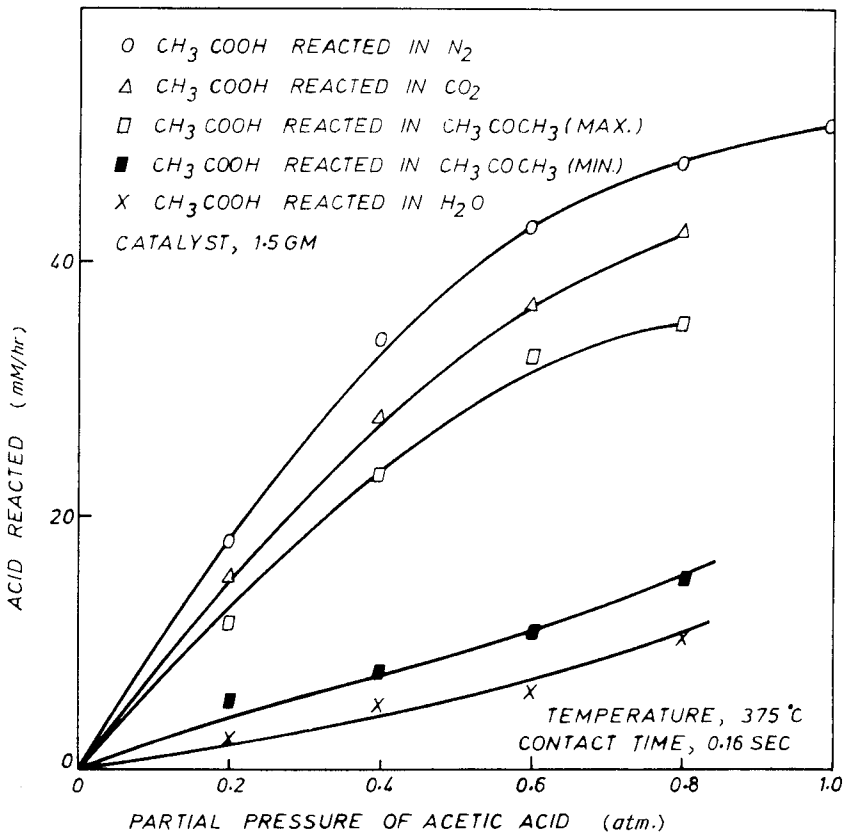


Fig. 1. Influence of products on the ketonisation of acetic acid on air pretreated catalyst.

440°C mixing various proportions of acetone, carbon dioxide and water, separately with acetic acid. For comparison, the ketonisation was also carried out in the presence of nitrogen as a diluent.

The treatment of the catalyst with isopropyl alcohol for 15 minutes at 500°C was found to increase the activity of the catalyst. The influence of products both on isopropyl alcohol pretreated catalysts and air pretreated catalysts exhibit a number of points of differences in their inhibitive effects at 375°C as seen in Figs. 1 and 2.

Water suppresses the reaction more strongly in both the cases compared to acetone and carbon dioxide. But from Table 1, it is quite clear that the amount of inhibition of the ketonisation reaction due to water on an air pretreadet catalyst is more compared to that on an isopropyl alcohol pretreated

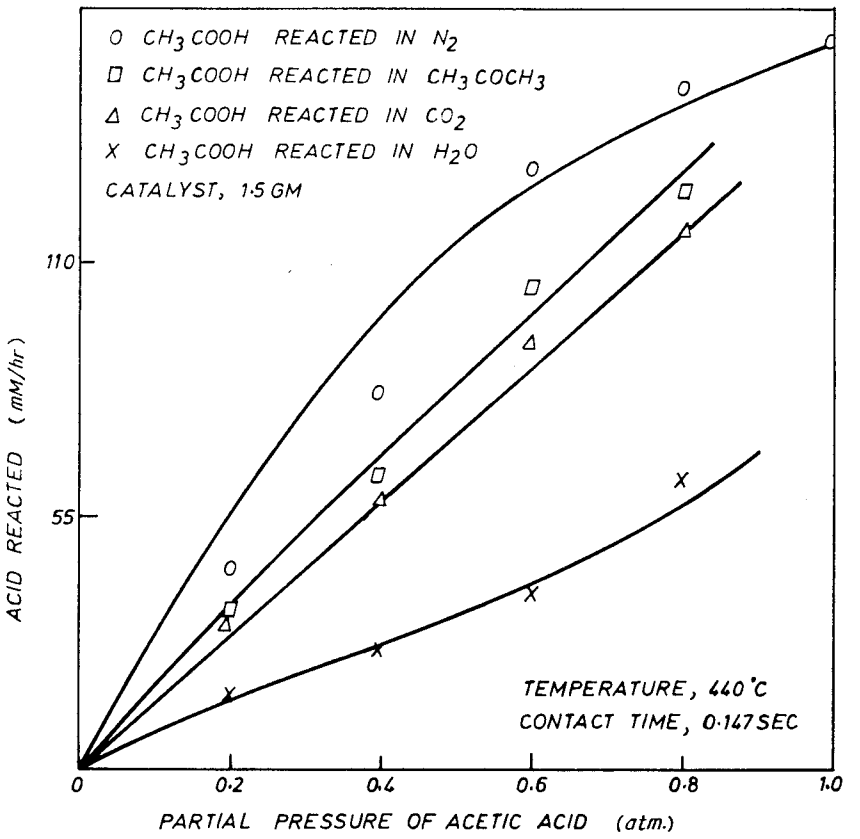


Fig. 2. Influence of products on the ketonisation of acetic acid on isopropyl alcohol pretreated catalyst.

TABLE 1 Comparison of the relative amount of inhibition of ketonisation due to water on air pretreated and isopropyl alcohol pretreated catalysts

Partial pressure of CH_3COOH (atms.)	Partial pressure of H_2O or N_2 (atms.)	The ratio of mM acetone per hour in H_2O to that in N_2 on air pretreated catalyst	The ratio of mM acetone per hour in H_2O to that in N_2 on isopropyl alcohol pretreated catalyst
0.2	0.8	0.1444	0.2667
0.4	0.6	0.1471	0.2232
0.6	0.4	0.1395	0.2500
0.8	0.2	0.2084	0.3462

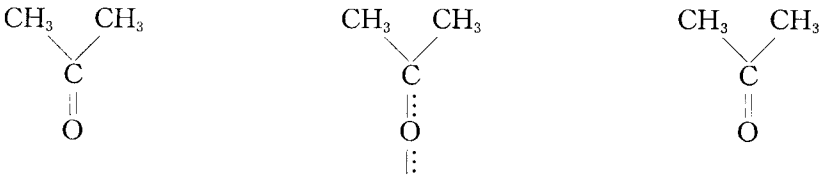
one. The general trend of suppression of ketonisation due to products at 375°C is in the order: water>acetone>carbon dioxide. BLYHOLDER and RICHARDSON[20] have investigated the dissociative chemisorption of water and hydrogen sulphide on α–Fe_2O_3 by IR spectroscopy. Water was found to be dissociatively adsorbed to from OH^- ion and a proton which reacts with a surface O^{2-} ion to produce another OH^- ion. The hydroxide ions formed by the chemisorption of water are presumed to occupy the surface lattice positions which are in the first coordination shell of a Fe^{3+} ion. The strong inhibition of the reaction by water may be attributed to the possibility that water gets dissociatively adsorbed into two OH^- ions on ferric oxide, thereby blocking the sites for the ketonisation reaction compared to a surface that has undergone a little reduction. On a slightly reduced surface this inhibition may be less because of the lower chemisorption of water as a consequence of the absence of surface oxide ions.

Acetone exhibited a variation in its inhibitive effect, the inhibition increased with time on an air pretreated catalyst. The time required to

TABLE 2 Inhibition of ketonisation of acetic acid by acetone

Partial pressure of CH_3COOH (atms.)	Partial pressure of CH_3COCH_3 (atms.)	Rate of formation of acetone (max.) (mM/hr)	Rate of formation of acetone (min.) (mM/hr)	Time during which the minimum activity is attained (min.)
0.2	0.8	15	6	1
0.4	0.6	24	10	3
0.6	0.4	40	15	5
0.8	0.2	50	20	9
0.9	0.1	60	32	15

attain the minimum steady state rate for conversion of acetic acid varied inversely with partial pressure of acetone. The results are tabulated in Table 2. Adsorption of acetone on ferric oxide is a donor process[21]. Ferric oxide is a semiconductor in which the density and the nature of current carriers is known to change when it is subjected to slight oxidation or reduction[22]. Acetone will be strongly held on an oxidised catalyst because of the lower concentration of electrons on such a catalyst. The adsorption and desorption of acetone may be visualised as represented below :



$Fe^{3+}O^{2-}$ $Fe^{2+}O^{2-}$ $Fe^{3+}O^{2-}$

a. before adsorption b. adsorbed state c. after desorption

If Fe^{2+} in b is surrounded by Fe^{3+} ions, there would be immediate delocalisation of electron charge from Fe^{2+} to Fe^{3+}, resulting in acetone being held strongly to the surface. Thus the desorption of acetone becomes difficult. In the presence of Fe^{2+}, in the vicinity of the point of adsorption, the desorption of acetone becomes easier. Hence the lesser amount of inhibition due to acetone on an isopropyl alcohol pretreated catalyst. The time required for the surface saturation of the catalyst with acetone will increase with decrease in partial pressure of acetone. This is reflected in the inverse relationship observed for the time required to attain the steady state of ketonisation as a function of partial pressure of acetone.

The extent of suppression of ketonisation by products at 440°C is in the order : water>carbon dioxide>acetone as shown in Fig. 3. The effect of products on the rate of ketonisation seems to be less inspite of the higher conversion. Carbon dioxide hinders the reaction to a greater extent than acetone whereas the reverse is true at 375°C. The adsorption of carbon dioxide at 440°C is stronger compared to that of acetone, probably because of the temperature dependence of the surface properties of the catalyst and a favourable heat of adsorption for carbon dioxide.

Influence of pretreatment on the activity of ferric oxide catalyst

The change in the activity pattern of ferric oxide subjected to various pretreatments was determined for the ketonisation of acetic acid at atmospheric pressure. The results of these experiments are given in Table 3.

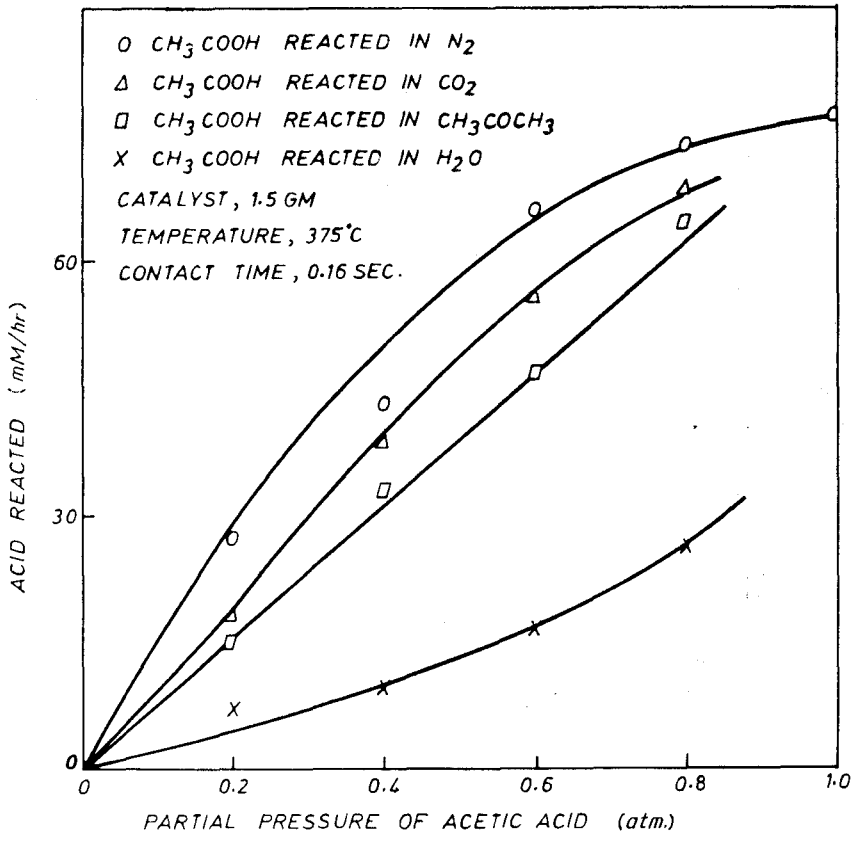


Fig. 3. Influence of products on the ketonisation of acetic acid on air pretreated catalyst.

TABLE 3 Conversion of acetic acid on iron oxide subjected to different pretreatments

Type of pretreatment	Condition of pretreatment	Percentage conversion of acetic acid
Hydrogen	500°C, 15 min.	26.3
Isopropyl alcohol	500°C, 15 min.	19.2
Fresh catalyst	—	13.6
Air	500°C, 2 hrs.	10.5
Oxygen	500°C, 2 hrs.	6.7

It is clear from the results that the oxidation of the catalyst brings down the ketonisation activity whereas reduction increases it. The catalyst was

found to undergo transformation from haematite (α-Fe_2O_3) to magnetite (Fe_3O_4) during the ketonisation at temperatures above 390°C. The results of these observations are recorded in Table 4.

It was therefore thought interesting to follow the activity of the catalyst with the extent of reduction. Hence the catalyst batches containing different proportions of ferrous and ferric iron were prepared by controlled reduction as described earlier. The amounts of Fe^{2+} and Fe^{3+} estimated in a known weight of the catalyst enabled the computation of the mole percent of Fe_3O_4, Fe_2O_3 and free iron present in each batch of the catalyst. The mole percent of free iron, α-Fe_2O_3 and Fe_3O_4 for the reduced catalyst obtained in different batches along with the phases detected by XRD is presented in Table 5.

Studies on the decomposition of isopropyl alcohol and tertiary butyl alcohol were also made along with those on the ketonisation of acetic acid

TABLE 4 Temperature dependence of reduction of α-Fe_2O_3 to Fe_3O_4 in presence of acetic acid

Temperature of ketonisation (°C)	Percentage conversion of α-Fe_2O_3 to Fe_3O_4	Phases detected by XRD
360	0.000	α-Fe_2O_3
375	0.000	α-Fe_2O_3
390	0.825	α-Fe_2O_3
400	3.185	α-Fe_2O_3
420	6.925	α-Fe_2O_3, Fe_3O_4
440	17.270	α-Fe_2O_3, Fe_3O_4

Feed rate = 0.525 mole/hour. Duration of ketonisation = 15 min.

TABLE 5 Chemical compositions of the different phases present in various batches of the catalyst

Catalyst Batch	Time of reduction (hrs.)	Chemical composition (mole percent)			Phases detected by XRD
		Fe	Fe_3O_4	Fe_2O_3	
A	0.0	—	—	100	α-Fe_2O_3
B	0.5	—	27.36	72.68	α-Fe_2O_3, Fe_3O_4
C	1.5	—	55.12	44.88	α-Fe_2O_3, Fe_3O_4
D	2.5	—	79.72	20.28	α-Fe_2O_3, Fe_3O_4
E	3.5	1.86	96.27	1.87	— Fe_3O_4
F	4.5	13.65	86.35	—	— Fe_3O_4, α-Fe

Temperature of reduction = 450°C, volume of hydrogen pased per minute = 50 mℓ.

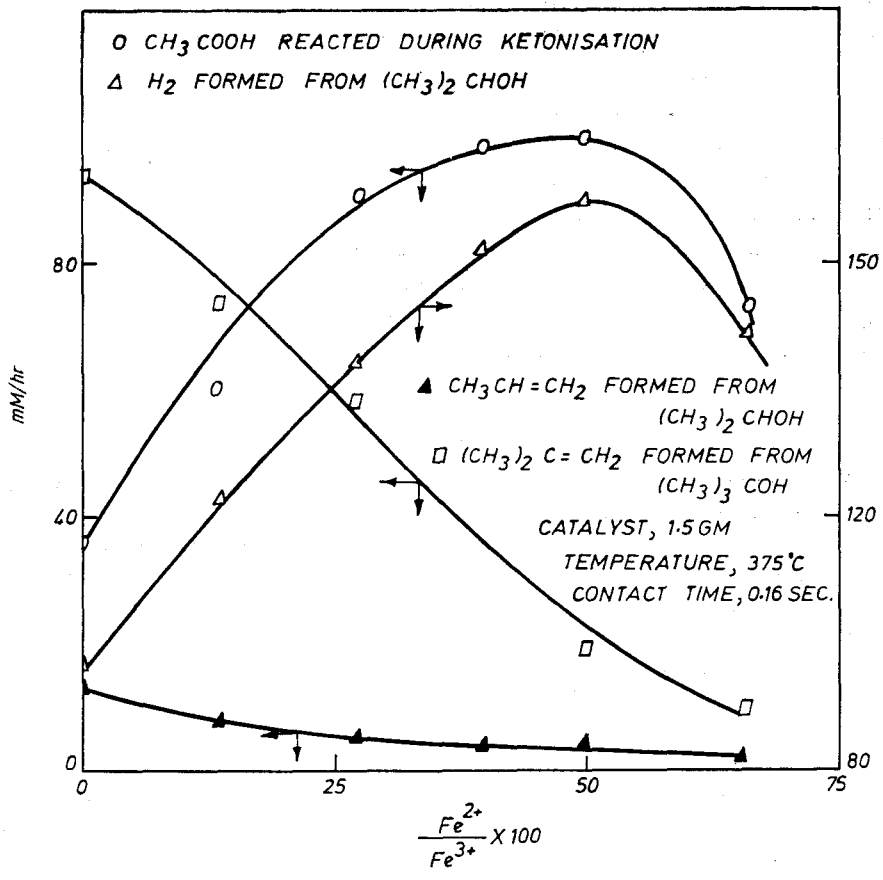


Fig. 4. Activity of the reduced catalyst for various reactions.

using the catalysts obtained from different batches at 375°C. The results of all these runs are presented in Fig. 4.

Dehydrogenation of isopropyl alcohol was found to increase steadily with the extent of reduction of ferric oxide and showed the maximum rate in the region where the catalyst phase was completely Fe_3O_4, while dehydration decreased simultaneously. The reduction of the catalyst may increase the basicity while the acidic centres may be getting destroyed. Moreover, the rate of dehydration of tertiary butyl alcohol on a catalyst reduced to the Fe_3O_4 stage decreased approximately to half of its original rate on the unreduced catalyst. Fe_3O_4 is more active for dehydrogenation but less efficient for dehydration than Fe_2O_3. The rate of ketonisation of acetic acid was also found to be maximum near a composition of the catalyst

corresponding to Fe_3O_4 and fell sharply with increase in free iron in the system. The presence of free iron renders the catalyst inefficient for ketonisation as well as for the decomposition of alcohols.

One may conclude that the inhibition of the ketonisation due to water is greater compared to carbon dioxide and acetone at all temperatures. The dissociative adsorption of water as two OH^- ions might poison the activity of the catalyst thereby hindering the reaction. The rate studies of the reactions of alcohols and acetic acid separately on reduced catalysts reveal the necessity of dehydrogenation as well as dehydration activities of the catalyst for the ketonisation. An excess of dehydration sites are found to decrease the ketonisation activity of the catalyst.

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