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Conversion of Ethanol to Acetone over Promoted Iron Oxide Catalysis

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The transformation of ethanol to acetone was studied on promoted iron oxide catalysts. The catalysts were characterized by X-ray and BET surface area measurements. Of the various catalysts investigated, the ZnO-promoted iron oxide catalyst (1 : 1 ratio) showed the best activity and stability. Based on literature reports and experimental evidence, a tentative mechanism has been proposed for the formation of acetone from ethanol. © 1988 Academic Press, Inc.

INTRODUCTION

Industrially acetone is manufactured (*1*) either by the dehydrogenation of 2-propanol or as a by-product in the manufacture of phenol. In view of the fast dwindling of petroleum resources, agro-based methods of production are of current interest (*2–4*). The availability of renewable agricultural raw materials in plenty motivated us to examine the study of ethanol-based chemicals. Ethanol from fermentation of molasses could form an excellent feed stock for chemicals like acetone. This paper presents studies of the conversion of ethanol to acetone over promoted iron oxide catalysts and the catalyst texture. A tentative mechanism for the conversion has been proposed.

EXPERIMENTAL

Catalyst Preparation

Anhydrous $FeCl_3$ (65 g) was dissolved in distilled water (650 ml) and filtered. Into this solution, 27.4 g $CaCl_2 \cdot 2H_2O$ in 274 ml water was added. The pH of this solution was adjusted to 9–9.5 by adding 5% NaOH solution. The precipitated mixture of $Fe(OH)_3$ and $Ca(OH)_2$ was filtered, washed free of chloride ions, dried initially at 120°C, and later calcined at 450°C for 4 h. The catalyst was ground and sieved. Samples (50–100 mesh) were used for the experiments. Similarly, all other catalysts with different promoters were prepared.

Unpromoted iron oxide catalyst was prepared by the addition of sodium hydroxide solution to a solution of $FeCl_3$. In supported catalysts, the catalyst-to-support ratio 1 : 1 was maintained, e.g., in iron oxide–calcium oxide catalyst the ratio of $Fe_2O_3/CaO : SiO_2 = 1 : 1$.

The silica-supported catalyst was prepared by mixing hydroxides of Fe^{3+} and Ca^{2+} with the hydrogel of silica, which was in turn prepared by the addition of sodium silicate solution (with 5% SiO_2) to dilute H_2SO_4 and adjust to pH 7. Gellation was allowed for 4 h. Compositions of the catalysts used in this study were $Fe_2O_3 : CaO$ (1 : 1), $Fe_2O_3 : MnO$ (1 : 1), and $Fe_2O_3 : ZnO$ (1 : 1).

Apparatus and Experimental Techniques

The reactions were carried out in a flow-type reactor at 400–450°C. The reactants (ethanol and water in 1 : 9 molar ratio) were introduced by a dosing pump (normally at an LHSV of 2 with 20 ml catalyst of 50–100

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mesh) into the reactor through a preheater maintained at 300°C. The liquid products were condensed by circulating ice-cold water and the gaseous products were vented out. The products were analyzed by gas chromatography using a PEG-400 on Celite (80–120 mesh size), $\frac{1}{4}$ in. diameter, a 6-foot column, and a flame ionization detector.

The surface areas of the catalysts were determined by Sorptomatic (Carlo Erba Series 1800), applying the BET method with nitrogen as the adsorbate. The X-ray powder patterns of the catalyst were recorded using a D-500 Kristaloflex Siemens X-ray diffractometer. A copper target was used with a nickel filter. By dosing the reactants at a high flow rate (200 ml/h), the products were collected. Acetone and acetaldehyde were removed from the products by means of a high-vacuum pump. Then the products were extracted with ether and dried with sodium sulfate. Ether was evaporated and the products were analyzed for their carbonyl function using an FT-IR (Nicolet).

TABLE 1

Conversion of Ethanol

Sl. No.	Catalyst	Yield of acetone[a]
1.	$Fe_2O_3:CaO$ (1 : 1, mole ratio)	52[e]
2.	$Fe_2O_3:CaO$[b] (1 : 1, mole ratio)	15
3.	$Fe_2O_3:CaO$[c] (1 : 1, mole ratio)	34
4.	Fe_2O_3	39
5.	$Fe_2O_3:CaO$ (1 : 1, mole ratio)[d]	Trace
6.	$Fe_2O_3:MnO$ (1 : 1, mole ratio)	54
7.	$Fe_2O_3:ZnO$ (1 : 1, mole ratio)	51

Note. Temperature, 450°C; LHSV, 2; ethanol; H_2O, 1.9 molar ratio; Time on stream, 3 h.

[a] Weight percent based on ethanol.

[b] Reaction was carried at 350°C.

[c] Catalyst was supported on SiO_2.

[d] Ethanol : H_2O molar ratio is 1 : 2.

[e] This yield corresponds to a selectivity of 90%.

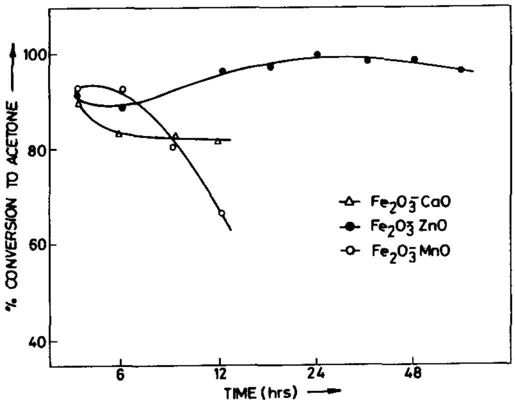


FIG. 1. Conversion of ethanol on promoted iron oxide catalysts.

RESULTS AND DISCUSSION

Results of the reaction of ethanol over various catalysts have been presented in Table 1. Iron oxide promoted with CaO, ZnO, or MnO showed better activity than unpromoted iron oxide. The promoters (CaO, ZnO, and MnO) themselves showed negligible activity. Iron oxide promoted with CaO supported on silica or alumina showed lower activity than unsupported catalyst. Results of the reaction of ethanol with water at two different ratios (1 : 2 and 1 : 9) are also shown in the Table 1. At lower water contents, the reaction gives rise to a more gaseous product consisting of CO_2, CO, and olefins. At higher water contents, the reaction becomes more selective toward the formation of acetone. It has been clearly established (*5*) that water tends to block some of the very active sites on the oxide surface. Thus, the higher selectivity at higher water contents is probably due to the fact that further reactions of acetone were retarded and also the olefin formation was suppressed. The maximum conversion with maximum selectivity (90%) was observed at 450°C (52% acetone, Table 1). At 350°C, the conversion of ethanol to acetone is less (15% acetone).

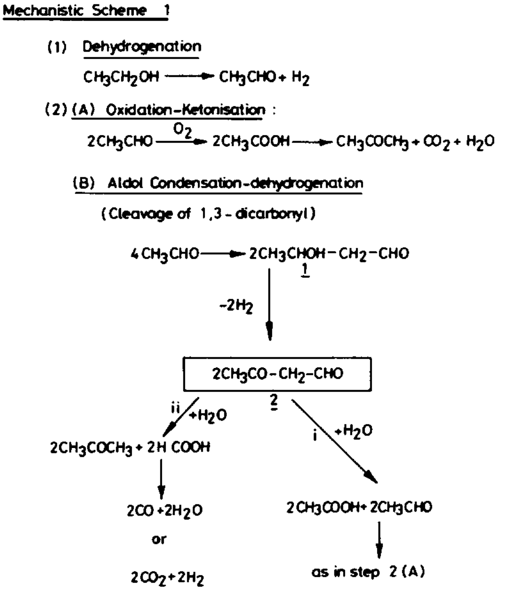
The conversions of ethanol over three different promoted iron oxide catalysts are shown in Fig. 1. All three promoted iron oxide catalysts showed high initial activity (time on stream, 3 h). However, MnO- and CaO-promoted catalysts were deactivated rapidly, whereas ZnO-promoted catalyst showed maximum stability (i.e., even after 54 h usage of ZnO-promoted iron oxide catalyst showed the activity to be at the same level as the initial activity). The mechanism of the formation of acetone from ethanol can probably be represented as shown in the Scheme 1. Iron oxide is best known as a dehydrogenation catalyst (*6*). Thus, the formation of acetaldehyde from ethanol is expected. Acetaldehyde, acetic acid, and formic acid were detected in trace amounts in the product when reaction was carried out at low temperatures. Also acetone was formed when a water solution of acetaldehyde was passed over Fe_2O_3–CaO catalyst. The formation of acetone from acetaldehyde could be due to one of the two routes (2A or 2B in Scheme 1) or to both.

In route 2A the acetaldehyde formed could be oxidized to acetic acid, which in turn could undergo ketonization resulting in acetone. Evidence for such reactions is available in the literature (*7, 8*). In view of the absence of oxygen from the reactant system, this route is likely to be insignificant. In route 2B, the acetaldehyde formed could undergo aldol condensation to butan-1-al-3-ol (**1**). Aldol condensation is facile over basic oxide catalysts (*9–11*). Then (**1**) could undergo dehydrogenation to butan-3-one-1-al (**2**). The 1,3-dicarbonyl compound (**2**) could undergo cleavage in one of two ways: (i) giving rise to acetic acid and acetaldehyde or (ii) giving rise to acetone and formic acid. This type of cleavage is known (*12*) to occur over basic oxide. The acetic acid could have ketonized to acetone. The formic acid formed in (ii) might have decomposed to CO_2, CO, and water. The presence of trace amounts of formic acid and acetic acid in the reaction mixture support the above routes.

TABLE 2

Sl. No.	Catalyst	Surface area (m^2/g)	Pore volume (cc/g)	Mean pore radius (Å)
1.	Fe_2O_3–CaO (Fresh)	76	0.25	46
2.	Fe_2O_3–CaO (Used)[a]	33	0.12	69
3.	Fe_2O_3–ZnO (Fresh)	111	0.25	45
4.	Fe_2O_3–ZnO (Used)[a]	45	0.26	114

[a] Used for 15 h.



SCHEME 1

FT-IR spectra of the intermediate product showed the ketonic peaks at 1717 and 1672 cm^{-1} (which are characteristic for the dicarbonyl group and its keto-enol tautomerism) and an intense peak at 1647 cm^{-1} (which indicates the presence of a double bond). These support the intermediate formation of the ketoaldehyde, **2**, as pictured in route 2B.

TEXTURE OF THE CATALYSTS

The surface area, total pore volume, and mean pore radius are measured before and after use of the catalysts and the results are presented in Table 2. The pore size distributions before and after use of the catalysts are shown in Figs. 2 and 3. From the results, it is clear that the total pore volume and the surface area drop by about 50% in calcium oxide-promoted iron oxide catalyst after the reaction, whereas in the case of zinc oxide-promoted iron oxide catalyst only surface area decreased by more than 50% but the total pore volume remained more or less the same. However, from Figs. 2 and 3 it is clear that there is a drastic change in the pore size distribution after the reaction in both catalysts. It seems that some of the smaller pores have widened and that the others might have collapsed. Such a widening of pores is known to occur in the presence of steam. Although the surface area dropped by about 50%, the decrease in the activity of calcium oxide-promoted iron oxide is only 25% (See Fig. 1). No such drop in the activity of zinc oxide-promoted iron oxide was observed. This observation clearly indicated that in this type of reaction, there was no specific relation between surface area and activity. The catalytic activities of the pores larger than 35 Å play an important role in this type of reaction. The drop in the activity of the spent Fe_2O_3–CaO catalyst could be due to the collapse of these pores as a result of sintering. However, more detailed studies are necessary to explain the promotional effect of the additives and the consequent enhancement of the stability of the catalyst.

The *d*-spacings and the relative intensities of the three catalysts (namely, Fe_2O_3–CaO, Fe_2O_3–MnO, and Fe_2O_3–ZnO) were calculated. All three catalysts have shown common *d*-spacings at 2.98, 2.54, and 1.48 Å, which are characteristic of γ-iron(III) oxide. It is worthwhile to mention (*13*) that *d*-spacings which are characteristic of free CaO, MnO, and ZnO are absent. It is likely that they might have formed a solid solution with Fe_2O_3, which is indicated by the additional peaks observed at other *d*-spacings in all the three samples.

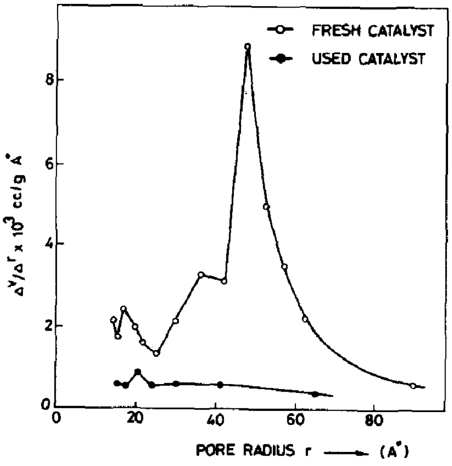


FIG. 2. Pore size distribution of Fe_2O_3–CaO.

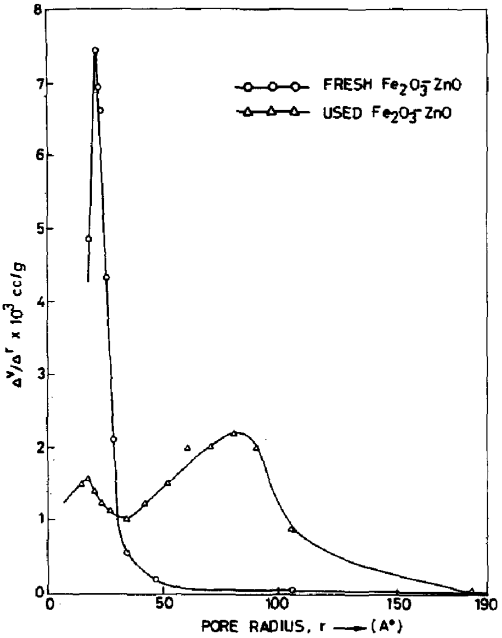


FIG. 3. Pore size distribution of Fe_2O_3–ZnO catalysts.

CONCLUSIONS

Among all three catalysts, Fe_2O_3–ZnO is the most efficient for the conversion of ethanol to acetone. This catalyst has also shown greater stability as well as high activity and selectivity.

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