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NOTES

The Bifunctional Nature of Cu–Al$_2$O$_3$ Catalysts in the Conversion of Ethanol to Ethyl Acetate*

NOMENCLATURE

K_{p_1}, K_{p_2}	Equilibrium constants for reactions (1) and (2), respectively
p_E, p_A, p_H, p_R	partial pressures of the subscripted components (atm)
P_t	total pressure (atm)
x_E	conversion of ethanol to products (moles ethanol converted)/(moles ethanol fed)
x_A	specific conversion of ethanol to acetaldehyde (moles acetaldehyde formed)/(moles ethanol fed)
x_R	specific conversion of ethanol to ethyl acetate (2 × moles ethyl acetate formed)/(moles ethanol fed)
E, A, R, H	subscripts for ethanol, acetaldehyde, ethyl acetate and hydrogen.

The direct catalytic conversion of ethanol to ethyl acetate over promoted and supported copper catalysts has been studied in detail by Dolgov, Koton and Siderov (*1*) and Dolgov and Nizovkina (*2*):

$$2C_2H_5OH = 2CH_3CHO + 2H_2, \qquad (1)$$

$$2CH_3CHO = CH_3COOC_2H_5, \qquad (2)$$

$$2C_2H_5OH = CH_3COOC_2H_5 + 2H_2. \qquad (3)$$

During a further study of this direct esterification (*3*), we have examined (*4*)

a. the exposure of metallic copper surface on the Cu–Al$_2$O$_3$–carbon catalyst by the N$_2$O-reaction method and
b. the distribution of Cu, Al and C in the surface layer by means of X-ray microscan (electron probe microanalysis, EPMA).

The present paper reports the results of experiments undertaken to elucidate the bifunctional nature of the catalyst in the direct esterification reaction.

The flow reactor used in the present studies has been described elsewhere (*3*, *5*). Unless otherwise specified the catalyst used was Cu–20% Al$_2$O$_3$ supported on activated coconut shell charcoal, the preparation of which has been previously described (*4*). This catalyst had a BET surface area of 560 m^2/g, particle size about 2 mm, Cu/Al atomic ratio 3.2, and specific copper surface area 28 m^2/g catalyst or 280 m^2/g Cu (*4*).

1. *Mechanical Mixture of Catalyst Components*

The simplest direct method for testing the cooperative action of catalyst components consists of a comparison of conversion results between experiments where catalyst particles of only component X (copper in this case), only of component Y (alumina), and where a loose mixture of the same amounts of X and Y particles have been placed in the reaction zone, under otherwise similar contact conditions. Polystep action is then indicated if the extent of reaction in the latter case is seen to exceed the sum of the conversions in the

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* This forms a part of the PhD thesis of J. P., Andhra University, India, 1970.

two single-component catalyst runs. Weisz and Swegler (*6*) and Hindin, Weller and Mills (*7*) employed such mechanical mixtures to demonstrate the dual functional characteristics of platinum–acidic oxide catalysts in hydrocarbon reactions. In the present work, the catalytic activities of the following were determined under identical conditions:

a. Copper on carbon carrier (25 ml catalyst)

b. Copper on carbon (25 ml) followed by alumina on carbon (25 ml), the two layers being separated by glass wool,

c. a physial mixture of the components of (b), and

d. the coprecipitated normal catalyst, $Cu–Al_2O_3$–carbon.

2. Effect of Acetaldehyde on the Catalyst

Dolgov and Nizovkina (*2*) reported that acetaldehyde, an intermediate in the conversion of ethanol to ethyl acetate, is a poison to the catalyst. In the light of the findings on the bifunctional nature of the catalyst, the poisoning effect of acetaldehyde on the catalyst was of special interest.

The glass reactor was charged with 30 g catalyst and reduced in a stream of H_2 for 6 hr at 300°C. Ethanol was then fed into the reactor at 10 ml/hr with a microfeed pump. After the catalyst had attained constant activity at 275°C, a sample of the product was collected in a receiver cooled in liquid nitrogen and analyzed by gas chromatography. Ethanol flow was stopped, the catalyst was flushed with H_2 for 15 min, 2.5 ml pure acetaldehyde was fed into the reactor from an ice-cooled burette at 10 ml/hr, the catalyst again purged with H_2 for 15 min, ethanol feed was resumed and, after attaining the steady state, a product sample was collected and analyzed. The uncondensed gas was collected over saturated brine. On analysis it was found to be practically H_2 only. In this way the activity of the catalyst exposed to various amounts of acetaldehyde was determined.

3. Poisoning by H_2S

Hydrogen sulfide is a strong poison to metallic catalysts. Poisoning studies were carried out with H_2S to compare its action on the catalyst with that of acetaldehyde. The reactor was charged with 30 g catalyst and the catalyst was reduced for 6 hr at 300°C. Ethanol was then fed into the reactor at 10 ml/hr. After the catalyst had attained constant activity at 275°C, a sample of the product was collected and analyzed. Pure ethanol feed was then stopped, and ethanol containing dissolved H_2S (0.49 g H_2S/liter ethanol) was then pumped into the reactor at 10 ml/hr, maintaining the catalyst at 275°C. The product samples were analyzed at different intervals to follow the effects of the progressive poisoning of the catalyst.

The result of mechanical mixing of the active components of the catalyst is shown in Table 1. When copper alone is used as catalyst, the main product is acetaldehyde,

TABLE 1
BIFUNCTIONAL NATURE OF $Cu–Al_2O_3$ CATALYSTS IN THE CONVERSION OF ETHANOL TO ETHYL ACETATE[a]

		Composition of liquid product (%)				
No.	Catalyst	EtOH	AcH	AcOEt	EtOEt	Unknown
1	Cu	66.8	12.6	4.5	—	16.1
2	Cu followed by Al_2O_3	56.5	10.9	3.0	18.6	11
3	Cu + Al_2O_3 physical mixt.	53.0	30.0	12.6	4.4	—
4	$Cu–Al_2O_3$ coprecipitated	44	30	26	—	—

[a] Continuous flow system; temp 275°C.

but a small quantity of ethyl acetate is also produced. When copper and alumina layers, separated from each other, are used as catalyst, the acetaldehyde and ester yields are not much changed, but the ethanol does form some diethyl ether on the alumina at this temperature (275°C). When the copper and alumina layers are mixed, appreciably higher amounts of both acetaldehyde and ethyl acetate are formed, the ether formation is drastically reduced and the unknown component of the product is suppressed. Finally, the normal coprecipitated copper–alumina catalyst gives a still higher yield of the ester and suppresses the ether and the unknown component. These results indicate that while dehydrogenation occurs on the metal active sites (Type A), the Cu-alumina co-sites (Type B) [as characterized by Sinfelt (*8*)] are the major active sites for the production of ethyl acetate.

Another interesting feature of the results in Table 1 is that when copper and alumina are in close proximity, they influence the catalytic property of each other, as seen in the suppression of the unwanted side products. Alumina is a well-known catalyst for converting ethanol to diethyl ether in this temperature region (275°C), but even this is substantially decreased for the mechanical mixture and appears to be totally suppressed in the case of the coprecipitated catalyst. Such striking effects on the composition of reaction products are well known in the case of bifunctional Pt–alumina catalysts in hydrocarbon reactions [Weisz and Prater (*9*)].

Figure 1 shows the effect of pretreatment of poisoning of the catalyst with increasing amounts of pure acetaldehyde. The amount of acetaldehyde released as a result of decrease in ethyl acetate formation is greater than the decrease to be expected from decreasing ethanol conversion. Hence an overall increase in acetaldehyde is observed. The equilibrium constants K_{p_1} and K_{p_2} for reactions (1) and (2), respectively, were calculated according to:

$$K_{p_1} = \frac{p_A \cdot p_H}{p_E} = \frac{x_E \cdot x_A}{(1 + x_A + 0.5x_R)(1 - x_E)} \cdot P_t$$

$$K_{p_2} = \frac{p_R}{p_A^2} = \frac{0.5x_R(1 + x_A + 0.5x_R)}{x_A^2} \cdot \frac{1}{P_t}$$

The values of K_{p_1} at the different experimental points starting from the fresh catalyst (not subjected to acetaldehyde treatment) and going in the direction of treatment of catalyst with increased amounts of pure acetaldehyde are: 0.27, 0.25, 0.26, 0.24, 0.26, 0.25 (thermodynamic value is 0.29). The corresponding values of K_{p_2} are: 4.21, 3.27, 1.29, 0.82, 0.35, 0.33 (thermodynamic value is 7.15). These values show that reaction (1) is in equilibrium and remains practically unaffected on poisoning the catalyst with acetaldehyde while the equilibrium

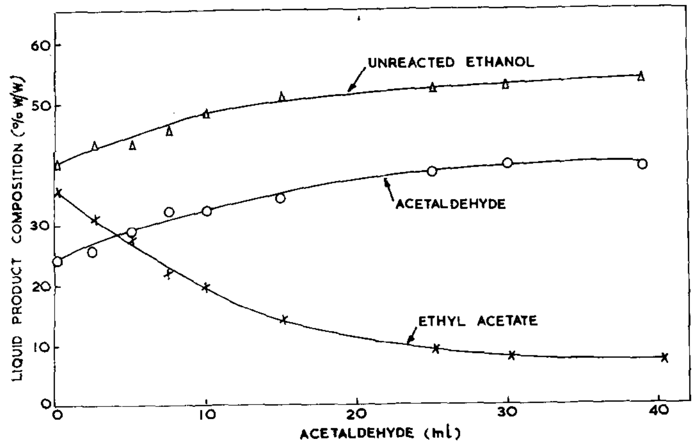

FIG. 1. Effect of acetaldehyde as a catalyst poison at 275°C.

of reaction (2) is increasingly shifted to the left.

In gravimetric studies of the catalyst under reaction conditions we have shown (*10*) the beneficial influence of hydrogen circulation on the catalyst: in a H_2–ethanol vapor system at 275°C the weight of the catalyst remains practically unchanged, while in a N_2–ethanol vapor system the catalyst weight increases steadily. Obviously, H_2 scavenges the catalyst surface of all potentially polymerizable reaction products and gives the catalyst long life. The poisoning effect of acetaldehyde on the catalyst may be due to the slow condensation or polymerization of it into resinous products or coke precursors. Such reactions preferentially take place on the acidic sites of alumina. Hence the deterioration of Type B co-sites is only to be expected.

The almost specific effect of acetaldehyde as a poison to the catalyst in relation to the two reactions can be seen in comparison with the results obtained by poisoning the catalyst with H_2S. The results obtained in the latter case are shown in Fig. 2 and represent typical poisoning curves as discussed by Maxted (*11*). The concentration profiles are typical of the effect of space velocity on a consecutive two-step reaction. With increasing poisoning time, the poisoned zone on the catalyst bed increases and consequently the reaction time on the clean (unpoisoned) catalyst decreases since the flow rate of the feed is maintained constant. During the first 6 hr of poisoning time, reaction (1) remains in equilibrium while beyond that the equilibrium is shifted rapidly to the left. The fact that the catalyst does not exhibit any dehydrating properties at the end of the experiment indicates that copper and alumina are both poisoned.

Conclusions

The conversion of ethanol to ethyl acetate on a $Cu–Al_2O_3$–carbon catalyst proceeds in two steps: the dehydrogenation of ethanol to acetaldehyde on the copper sites followed by the condensation of two molecules of the aldehyde to form the ester on the $Cu–Al_2O_3$ co-sites. On pretreating with acetaldehyde the activity of the catalyst deteriorates although the co-sites are affected more severely. Poisoning by H_2S affects the activity of the catalyst towards both reactions. The

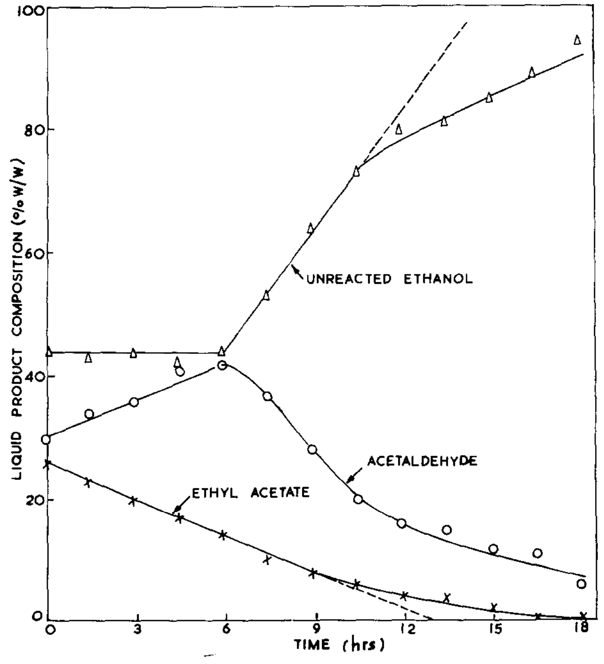

Fig. 2. Effect of H_2S as a catalyst poison at 275°C.

unique feature of the composite copper-alumina catalyst is that it suppresses the formation of side products, notably that of ether on alumina.

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X-Ray Diffraction Study of Nickel Ion Migration in Y-Zeolite

In a previous paper (*1*) it was shown by X-ray crystal structure analysis that cations in copper-exchanged Y-type zeolites may change positions when various reagents were added. In this paper we have studied by the same method the behavior of nickel ions in a $Ni_{14}Na_{23}Y$ zeolite heated at different temperatures or submitted to the action of different reagents (pyridine, NO and NH_3).

The Linde NaY starting material was ion exchanged in the conventional way with a $NiSO_4$ solution. Chemical analysis for Al^{3+}, Ni^{2+} and Na^+ showed the unit cell composition to be $Ni_{14}\ Na_{23}\ H_5\ Al_{56}\ Si_{136}\ O_{384}$. Samples I–IV were dehydrated respectively at 140, 200, 300 and 600°C, by heating in oxygen for 12 hr and subsequent evacuation (10^{-5} Torr) for the same time. Seven other samples were obtained on addition of reagents to dehydrated samples. The treatment conditions for each sample are given in Table 1.

The experimental techniques and resolution methods used for crystal structure analysis have already been described in previous papers (*1*, *2*). Atomic parameters of framework and extra-framework atoms were refined using 232 structure factors corresponding to 126 diffraction lines. No attempt has been made to locate the Ni^{2+} ions and reagent molecules occupying the supercages.

The cubic unit cell constants and nickel population of hexagonal prisms for all samples are given in Table 1.