



Comparison the Performance of Four Catalyst Types in the Catalytic Dehydration of Ethanol

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ABSTRACT

The dehydration of ethyl alcohol in atmospheric isothermal vapor phase to produce both ethylene and ether was studied in fixed bed reactor (2.54 cm inside diameter and 110 cm height). Two temperature ranges were used according to catalyst type, these are 250-350 °C for both alumina and zeolites (4A and 5A) and 90-120 °C for resin, besides weight ratio of catalyst to molar flow rate (W/FA) from 38 to 116.6 (gcat.hr/gmol) was selected to test the conversion, yield, selectivity and rate of reaction of products for each catalyst. Comparative study between catalysts was made and it was clearly found that alumina gives higher conversion than other catalysts (98% at 350 °C and W/F=116.6 gcat.hr/gmole), also the study shows longer deactivation time of resin in comparison to deactivation time of alumina and zeolites. Also it was clearly shown that ether can benefit from the large cage of catalyst for formation. The present work is concerned with catalytic dehydration of ethanol in vapor phase to produce diethyl ether and/or ethylene in packed bed reactor which is mainly directed to study the most effective parameters such as temperature of reaction, liquid hourly space time (residence time) and reaction time. Four different catalysts such as alumina, 4A zeolite, 5A zeolite and cation resin are used.

Keywords: Dehydration, Ethyl alcohol, Atmospheric pressure, Isothermal vapor pressure, Catalyst, Alumina, Zeolites, Resin

1. Introduction

During the past few decades, solid acid catalysts replaced most of their homogeneous counterparts in industrial scale. Acid catalyzed reactions increase environmental accountability of chemical companies and the always-present drive for more efficient processes is the major driving forces behind this transition. The two main advantages of solid acid catalysis in this respect are the ease of separation of the solid catalysts from the reaction mixture and the fact that their selectivity and activity are often much better compared to that of homogeneous acid

catalysts (Tanabe & Holderich, 1999). Both these aspects will lead to a reduction in the amount of waste produced thus moving closer to the ultimate goal of zero waste production. Cation exchange resins play key, although not exclusive, roles in this rapidly growing area (Harmer & Qun, 2001). Catalysts have been used commercially for more than a century from the deacon and contact process for sulfuric acid, used in the late 1800s to the latest FCC processes for petrochemical cracking. In 1901 Grigorieff rediscovered the catalytic dehydrations action of alumina on alcohols (Charubala, 2004). This induced Ipatieff to investigate systematically the catalytic dehydration in addition to the dehydrogenation, which he was already studying at that time (Ipatieff, 1902).

This work induced again various studies by Sabatier, Senderens, and Mailhe in the first decennium of this century (Winfield, 1960). Synthetic zeolites are alternative for the dehydration of alcohols (Birk & Yue, 1982), but most studies on alcohols dehydration have been conducted over alumina, from other hand zeolite catalysis and its interpretation has made much exciting progress in the past decade (Yue & Olaofe, 1984).

Ion exchange resin is the other important solid catalyst that is used in dehydration processes, and the processes using ion exchange resin as catalysts represent important examples of solid acid catalysis (Charubala, 2004). The present work is concerned with catalytic dehydration of ethanol in vapor phase to produce diethyl ether and/or ethylene in packed bed reactor, using Alumina, 4A zeolite, 5A zeolite and cation resin are used.

In catalytic dehydration of ethanol that two principal overall reactions occur simultaneously for ether and ethylene formations where the first occurs predominantly at low temperature, the second occurs at higher temperature as shown in Eq. 1 and Eq. 2 (Thomas & Ullah., 1988) and (Hughes, 1984):



2. Experimental Work

Experiments are directed to study the effect of temperature of reaction and liquid hourly space velocity on the reaction.

2.1 Materials:

Absolute ethanol (99.9% of purity), ethanol was used as feedstock and nitrogen was used as a carrier gas, and to purge off the gases from all the system Physical properties of materials are listed in Table (1).

Table 1: Physical properties of the materials

Property	Ethanol	Nitrogen
Molecular Formula	CH ₃ CH ₂ OH	N ₂
Molecular Weight	46.07	28.02
Specific Gravity	0.789	0.808
Melting Point (oC)	-112	-209.86
Boiling Point (oC)	78.4	-195.8

2.2 Catalysts:

Four types of commercial catalysts were used in this study. Three of their (alumina, 4A and 5A zeolite) are purchased from local bazaar while the resin was supplied from Beiji Refinery; the specifications of the first three catalysts are tabulated in Table (2) while the properties of resin are listed below.

2.2.1 Resin physical properties:

Type: Sulfonated copolymer of styrene and divinylbenzene in the acid form.

Ionic form: H⁺ R-SO₃⁻

Capacity min. (eq/l): 1.8

Sp.gr: 1.18

Mesh size: 16-50 (0.3-1.2 mm)

Surface area: 96 m²/ gm

Porosity: 0.67

Table 2: Physical properties of catalysts

Catalyst No.	Type	Structure	Particle density (kg/ m ³)	Surface area (m ² /gm)	Porosity	Shape	Size (m) x 10 ⁻³
(1)	γ -alumina	Al ₂ O ₃	1057	201	0.745	Sphere	5
(2)	Zeolite (4A)	Na ₁₂ Al ₁₂ Si ₂₄ O ₄₈ 27H ₂ O	740	10	0.33	Cylinder	6 x 2.5
(3)	Zeolite (5A)	0.7CaO.0.3Na ₂ O.Al ₂ O ₃ .2SiO ₂ .4.5H ₂ O	914	5	0.107	Cylinder	7 x 2.5

2.3 Experimental rig

The experimental rig of this study is shown schematically in Fig.1. The rig mainly consists of the following sections:

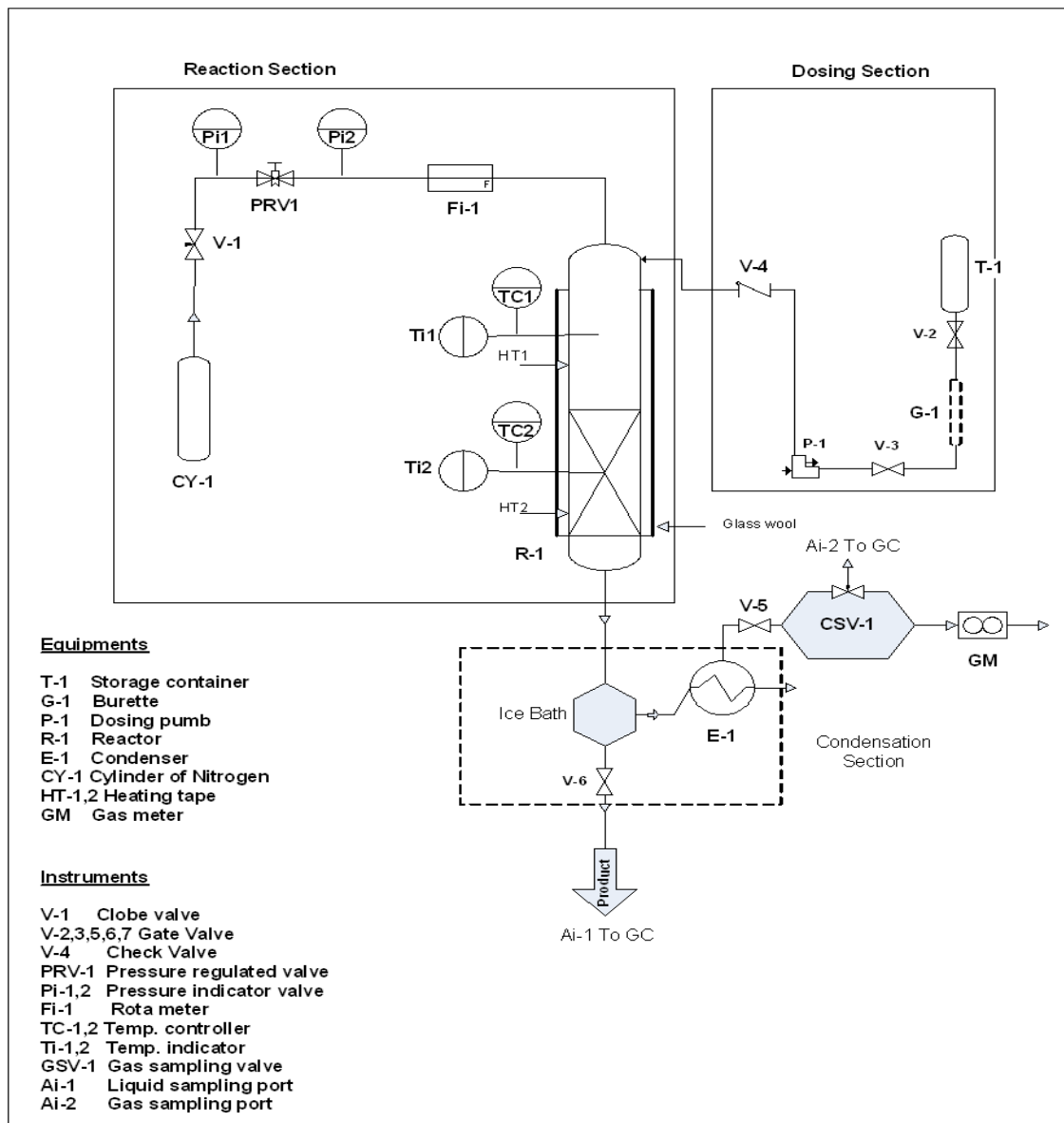


Fig.1. Schematic Diagram of the experimental rig.

Feeding- dosing section consist of feed container made of Pyrex glass of 1 liter capaciturette to observe and assess the flow rate of ethyl alcohol, and dosing pump. Three valves are installed in this section. Two gate valves before and after

Evaporation- reaction section consists of a rotameter which is used to observe and assess the flow rate of nitrogen prior to entering the reactor. The reactor consists of two regions, the upper region that incorporates to 50cm, is regarded as an evaporating section, which is filled with glass beads of 0.3-0.4cm diameter. The second region is filled with pellets of the catalyst and some of glass beads in order to support the catalyst bed.

The reactor is provided with single electric heating winding of nichrome wire and is designed to give a maximum reactor temperature of 600°C. Power was supplied to the heating element by means of a variable voltage regulator. Temperature measurement inside the catalytic pellet made by using thermocouple (TIC) which well was extended from the top of the reactor is to maintain constant temperature in the reactor. It consists of digital indicator type (k) sensor.

In order to condensate the vapors out coming from the reactor, round bottom flask is used surrounded by an ice bath. Double- pipe condenser is also used, connected with the flask to get a good condensation.

2.4 Experimental procedure and test method:

The dehydration of ethanol to produce ethylene and diethyl ether was carried out in vapor phase as described below:

- a. In the beginning nitrogen was used in order to purge off the air from the system and in order to insure a good temperature distribution in the reactor.
- b. After reaching the desired temperature then the Nitrogen valve was adjusted to the requested flow rate. A pre specified flow rate of ethanol was set on, vaporization of ethanol occurred in the evaporating section of the reactor.
- c. The ethanol vapor reached over the catalyst bed of the specified temperature, and flow rate. The vapor products passed throughout pipe condensers. The condensed vapor and gases were fed to gas meter to dissolve traces of reactants and products.
- d. All samples were taken double for analysis so that the amount of products could be determined.
- e. The catalytic reaction was carried out at a temperature depending on catalyst, (250-350 °C) for alumina and zeolite and (90-120 °C)for resin, and tabs 40 gm (i.e. about 7cm high) of catalyst in all types and fed flow rate about 0.02-0.061 L/hr or W/F =38-116.6 (g cat. hr/ gmol).
- f. The separation and analysis of the vapor product into their components were carried out using gas-liquid chromatography (shemadzu- 9A). A (parapak Q) stainless steel column with an outside diameter of (3.17mm) and length of 3m was used. The GLC column was connected to thermal conductivity detector (TCD); the hydrogen was used as a carrier gas.

- g. Yield was defined as the moles of ethylene and/or ether to moles of ethanol fed. The selectivity is defined as the moles of desired product to moles of undesired product, that means selectivity of ethylene equals moles of ethylene produced to moles of ether produced (So = moles ethylene / moles ether).

3. Results and discussion

3.1 Effect of duration time on the activity of catalysts:

Activity of the four tested catalyst was measured at 120 °C for cation resin and 350 °C for other catalysts (alumina, zeolite 5A and zeolite 4A). Other conditions were kept constant, W = 40gm of catalyst and (W/F) = 116.6 gcat.hr/gmol. The activity test was lasted for 5 hr for all catalysts.

As shown on Fig.2, the conversion of ethyl alcohol shows slows declination in activity for alumina and also for both types of zeolites. This slows decreasing of activity was mainly attributed to coke deposition. This observation is in good agreement with that of other workers (Thomas & Ullah., 1988; Bryant & Kranich, 1967) respectively over alumina and zeolites. In outrange to the mentioned catalysts, cation resin shows good stability within the 5 tested hours. This observation is consistent with Robert (Robert & Lennart, 1962) who justifies that deactivation of the same resin over a month of continuous operation is found negligible.

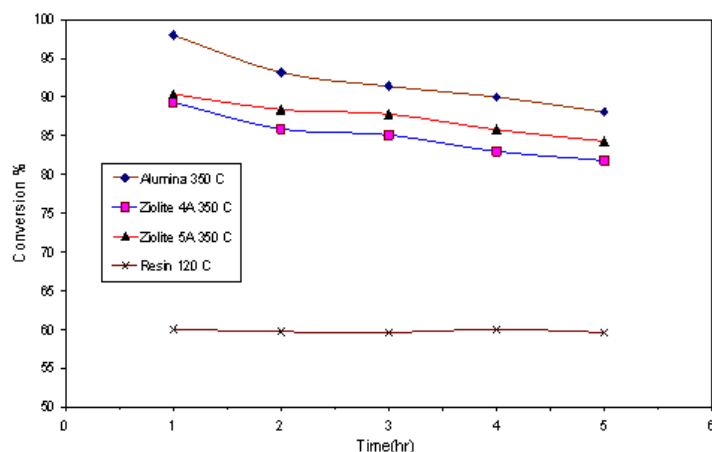


Fig.2. Effect of duration time to conversion of many type of catalyst (W/F=1)

3.2 Effect of residence time (W/F):

The effect of ratio catalyst weight to flow rate of ethyl alcohol (W/F) was studied at different temperatures and 40g of catalyst for the four different catalysts. Fig.3 shows the effect of W/F on ethanol conversion using 40 g of alumina and different temperatures (250,275,300 and 350 °C). It seems that higher ethanol converts with increasing W/F. Also at higher temperature higher conversion of ethanol was noticed. These increases are attributed to the resulting increase in contact time of the reactant. At temperature 350 °C the curve shows a concave characteristic

which indicate a negative reaction order. These observation were also noticed by (Yoshinori S., N. C., & E, 1985), while at lower temperature curves it converts from concave to convex with higher W/F. Figures (4) to (6) show the effect of W/F and temperature on conversion of ethanol using both types of zeolites (4A, 5A) and resin respectively. Same changes have been noticed for all catalysts with higher conversion have occurred at higher W/F and higher temperature. However, there is no negativity of reaction order as already shown for alumina.

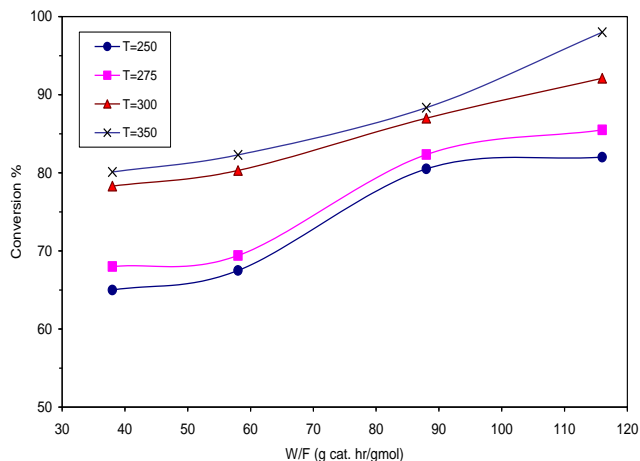


Fig.3. Effect of W/F on ethanol conversion over Alumina catalyst (w=40g).

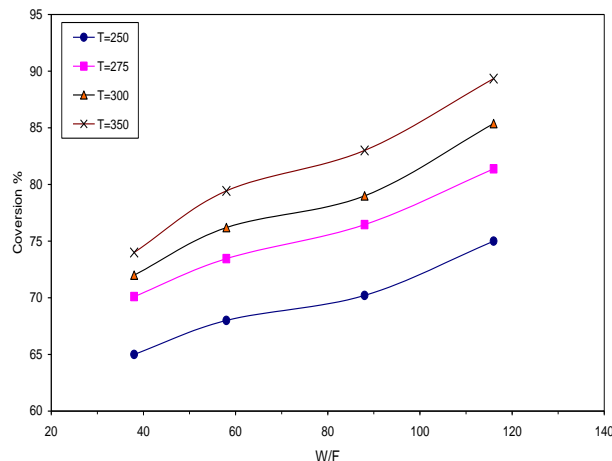


Fig.4. effect of ethanol conversion over Zeolite 4A Catalyst (W=40g)

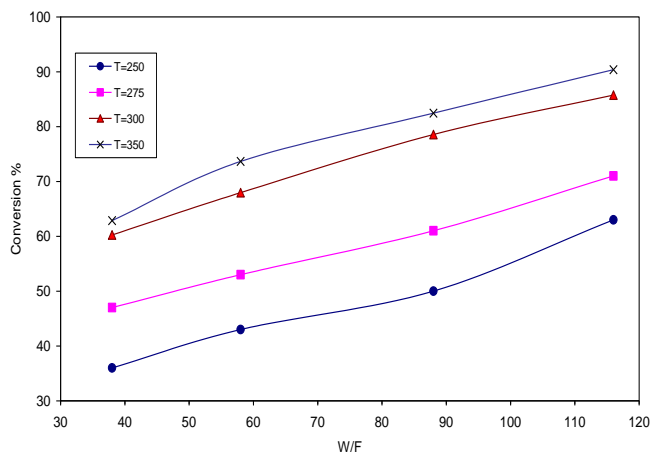


Fig.5. Effect of W/F on methanol conversion over Resin catalyst (w=40g)

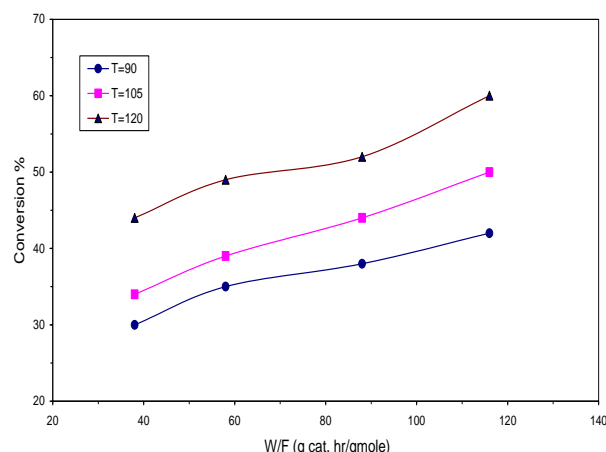


Fig.6. Effect of W/F on methanol conversion over Zeolite 5A catalyst (W=40g)

3.3 Effect of temperature

3.3.1 Effect of temperature on ethanol conversion:

The effect of temperature on conversion of ethanol in dehydration reaction was studied over all catalysts. Fig.3 shows the relationship between conversion and temperature in the range (250-350 °C) at different values of W/F over alumina. This figure shows that conversion increases with increasing temperature at constant W/F to maximum value 98% at 350 °C and (W/F = 116.6). Figures (4-6) show the similar relationship over (zeolite 4A, 5A and resin) catalysts respectively, but at different ranges of temperature according to resin. Similar behaviors are noticed on the other catalysts which reached maximum value of conversion of 90.37 %, 89.34% at 350 °C and W/F = 116.6 for zeolite 5A and zeolite 4A respectively, and 60% at 120 °C and W/F = 116.6 for resin. Fig.7 shows the comparison of ethanol conversion between the four catalysts used, this figure shows alumina catalyst has higher conversion but resin has lower conversion and the zeolites are between them.

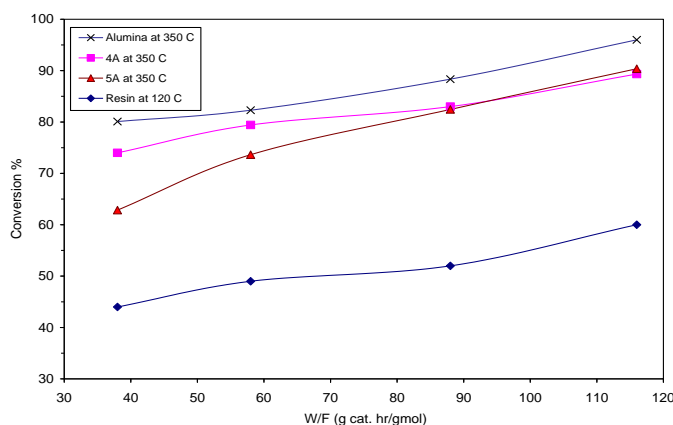


Fig.7. Comparison of ethanol conversion between the four catalysts used

3.3.2 Effect of temperature on yield and selectivity:

The effects of temperature on ether yield are shown in Figures (8-11) for alumina, zeolite 5A, zeolite 4A and resin catalysts respectively. These figures show increasing yield which reaches a maximum of 60.14%, 4.48%, 4.07% and 26.0% for alumina, zeolite 5A, zeolite 4A and resin respectively.

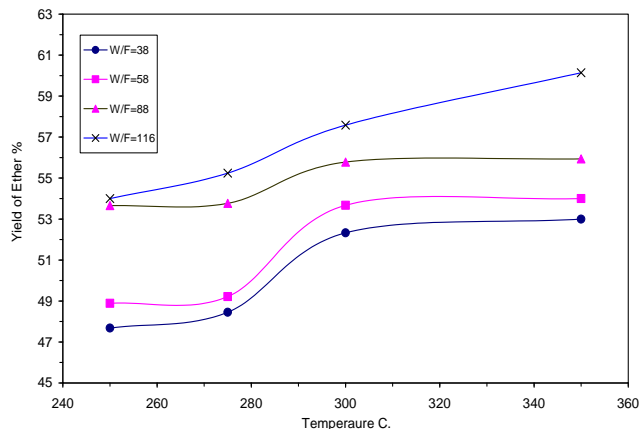


Fig.8. Effect of temperature on ether yield over alumina catalyst (W/F = 116.6).

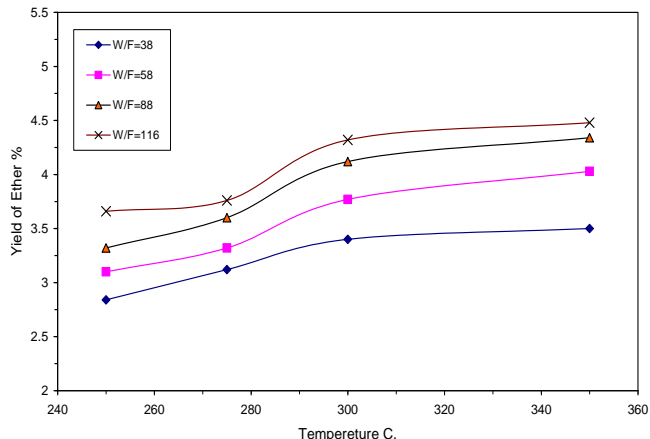


Fig.9. Effect of temperature on ether yield over zeolite 5A catalyst (W/F = 116.6).

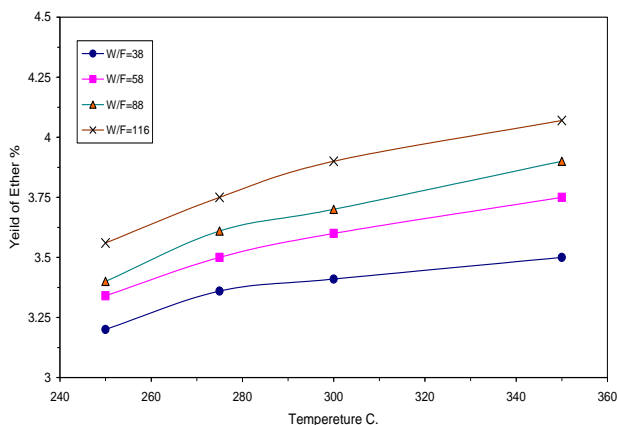


Fig.10. Effect of temperature on ether yield over zeolite 4A catalyst (W/F = 116.6).

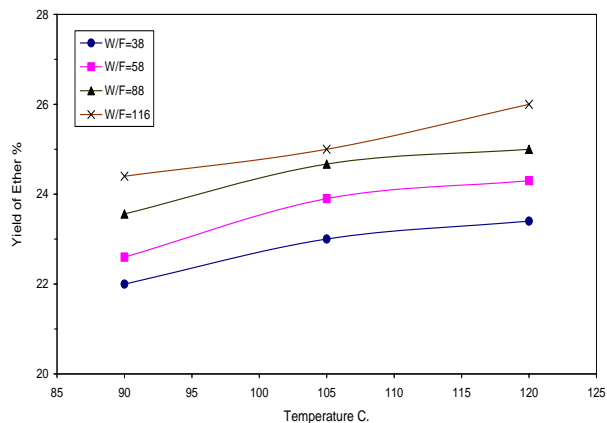


Fig.11. Effect of temperature on ether yield over Resin catalyst (W/F = 116.6).

The effect of temperature on yield of ethylene is shown in Figures (12-15). It is clear from these figures that yield of ethylene increases with increasing temperatures reaching a maximum of 14.14%, 51.61% and 51.3% at temperature 350 C° and W/F = 116.6 for alumina, zeolite 5A and zeolite 4A respectively, and 16.8% of temperature 120 C° and W/F = 116.6 over resin catalyst. Figures show that alumina is the most active catalyst for ether formation, and the next most active catalyst for ether formation is the Resin, and for ethylene formation is zeolite 5A and zeolite 4A.

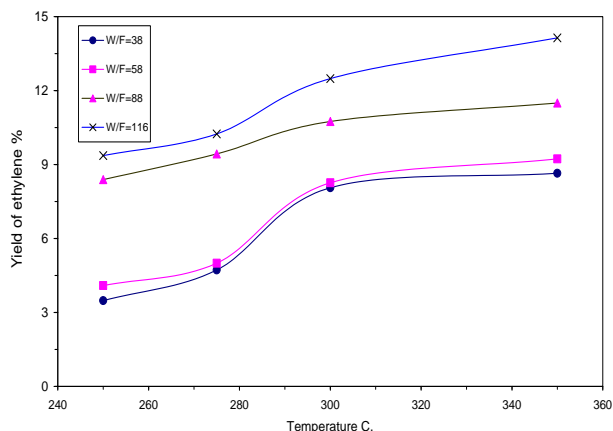


Fig.12. Effect of temperature on ethylene yield over alumina catalyst (W/F = 116.6).

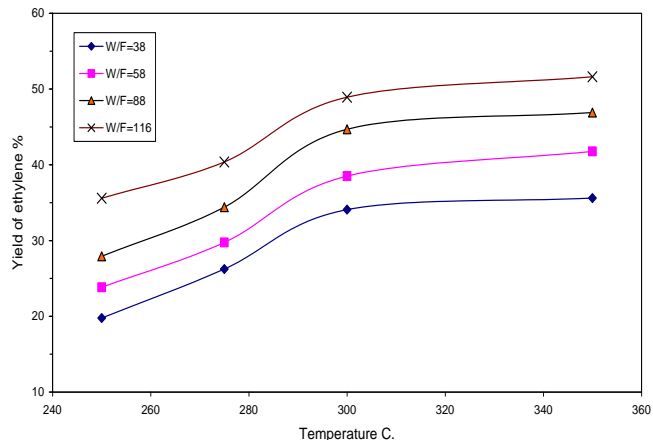


Fig.13. Effect of temperature on ethylene yield over zeolite 5A catalyst (W/F = 116.6).

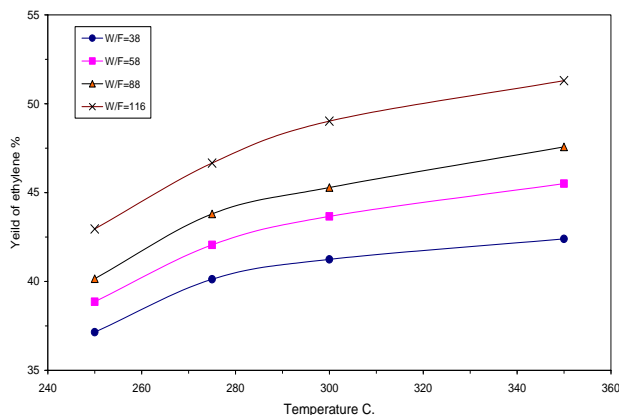


Fig.14. Effect of temperature on ethylene yield over zeolite 4A catalyst (W/F = 116.6).

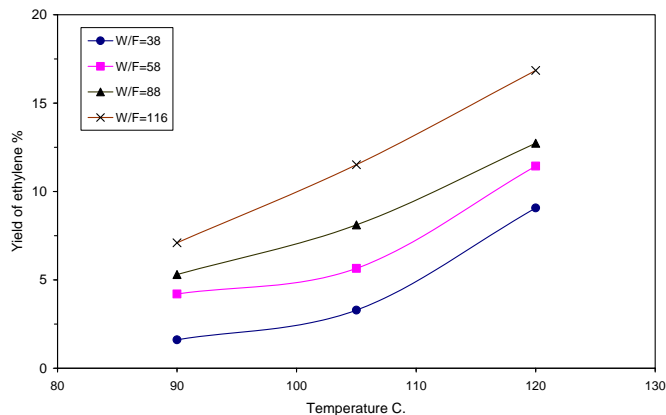


Fig.15. Effect of temperature on ethylene yield over Resin catalyst (W/F = 116.6).

This is consistent with the fact that ether formation would benefit from the large cage structure of alumina and resin, ethylene, on the other hand, would be able to move in the small zeolite cages nearly as freely as in the larger structure. The significance of pore geometry is most clearly shown by the selectivity results. The highest selectivity of ethylene (mole of ethylene produced/ mole of ether produced) is shown by the smallest pore zeolite catalysts that are clear in figures (16-19), apparently it is difficult for the carbon-oxygen chain to line up in the ether configuration and to escape from the small pore.

On the other hand the large-cage structure of the resin lends itself to about the same freedom of motion as in alumina, ether formation is not inhibited. This leads to smaller values of the ethylene selectivity ratio as shown in figures (16, 19) for alumina and resin.

Practically in every case, the selectivity increases with increasing temperature. These are the most likely results predominantly from the shift in the equilibrium constant in the dehydration reaction. Higher temperatures favor the increasing formation of ethylene from ether. It should be noted, however, that selectivity in resin catalyst is more sensitive to temperature than in the other catalysts. All above data are listed in Appendix (C), Table (C-2-5) in (Hadi, 2007).

Ether selectivity versus temperature absolutely shows inverse results from that shown in ethylene selectivity. In ether, the selectivity decreases with increasing temperature in all cases. These results are in good agreement with experimental data in (Tanabe & Holderich, 1999), (Yue & Olaofe, 1984) and (Robert & Lennart, 1962)].

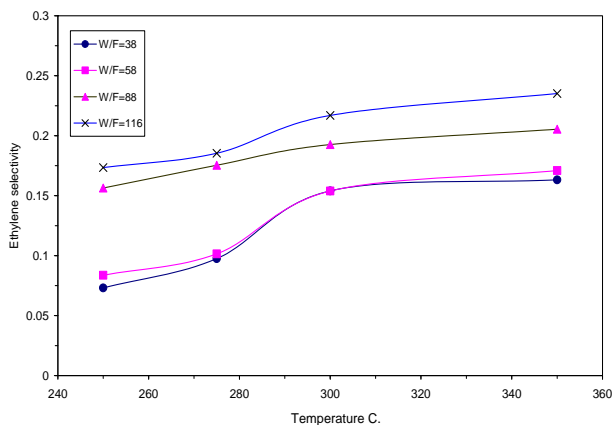


Fig.16. Effect of temperature on ethylene selectivity over alumina catalyst

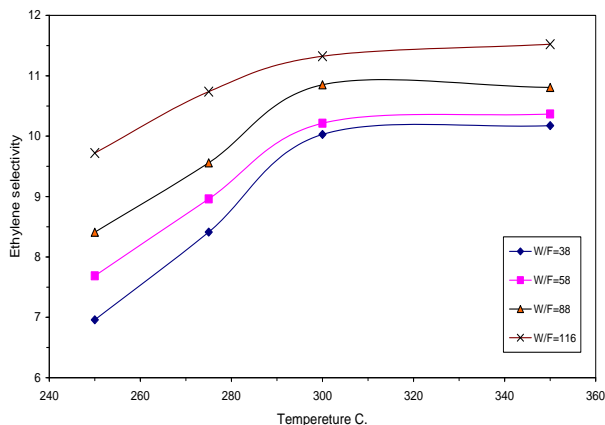


Fig.17. Effect of temperature on ethylene selectivity over zeolite 5A catalyst

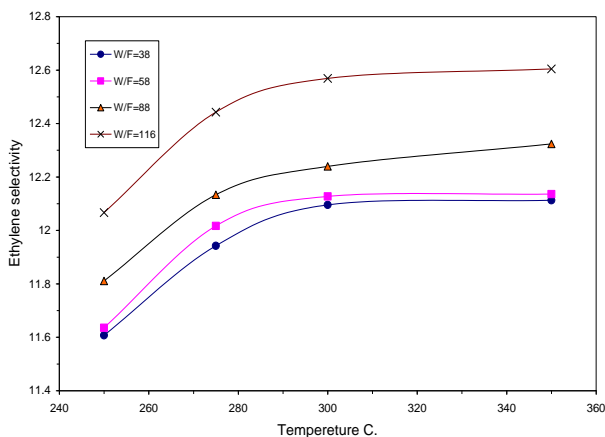


Fig.18. Effect of temperature on ethylene selectivity over zeolite 4A catalyst

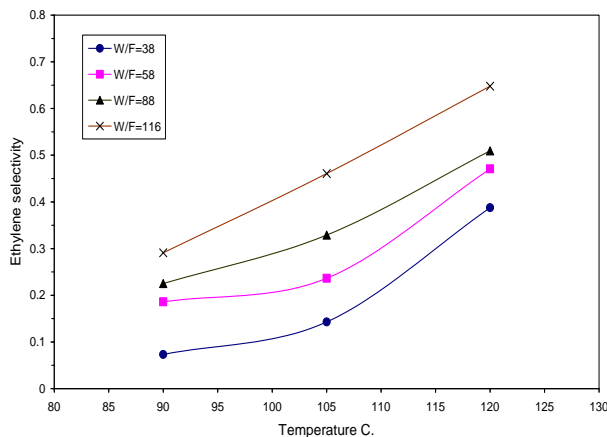


Fig.19. Effect of temperature on ethylene selectivity over Resin catalyst

3.3.3 Effect of temperature and W/F on the rate of dehydration reaction:

Product analysis showed none of side products are produced in these reactions, then the rate of ethanol consumption, ethylene and ether rate formation were calculated based on material balances. Figures (20-23) show the relationship between ethanol reaction rate ($-r_A$) versus temperature over the fourth catalysts. Figures show rate of reaction increases with increasing temperature in all cases.

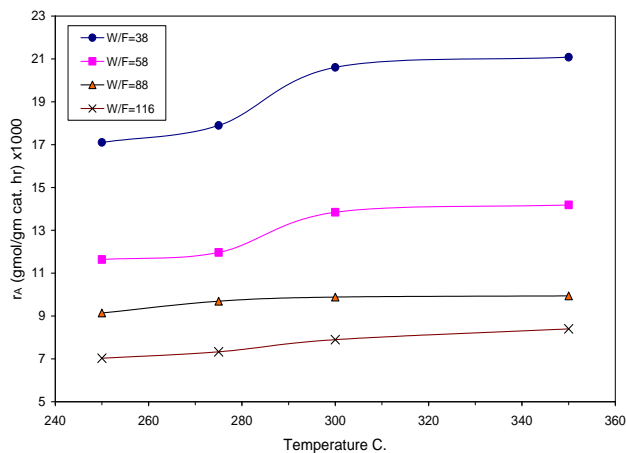


Fig.20 Effect of temperature on ethanol reaction rate over alumina catalyst

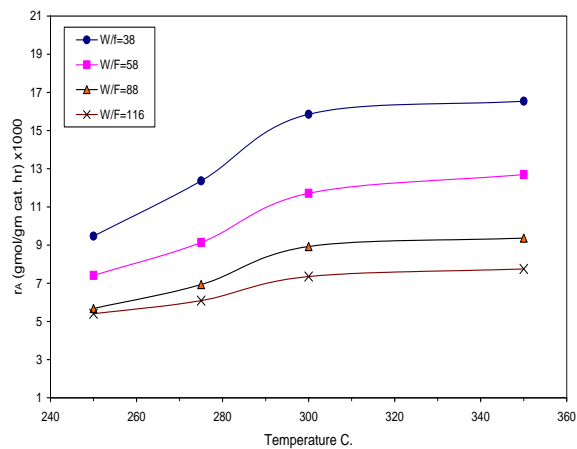


Fig.21 Effect of temperature on ethanol reaction rate over zeolite 5A catalyst

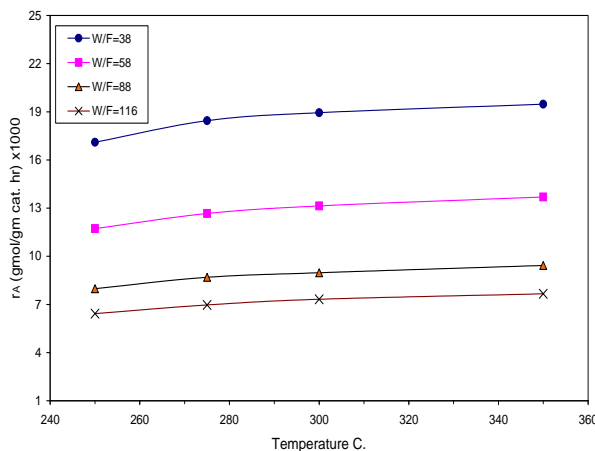


Fig.22. Effect of temperature on ethanol reaction rate over zeolite 4A catalyst

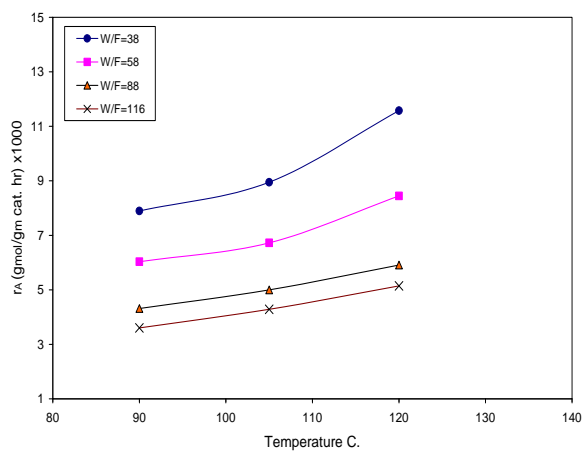


Fig.23. Effect of temperature on ethanol reaction rate over Resin catalyst

4. Conclusions

From this study, the following conclusions are made:

Both ethylene and ether are formed when ethanol is dehydrated over alumina, zeolite 4A, zeolite 5A and resin as catalysts.

Rate of deactivation of the resin catalyst with time is lower than the other used catalysts types.

The maximum conversion for ethanol dehydration is: 98% at reaction temperature 350 oC, W/F 116.6 gcat.hr/ gmol over alumina catalyst.

Ether needs large cage to be produced.

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