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CATALYTIC DEHYDRATION REACTION OF ETHANOL OVER TRANSITION METAL CATALYSTS

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ABSTRACT

Ethylene is the essential material for producing oxygenates, which are used as gasoline additives designed to enhance the octane number. Due to the dramatic rise in the use of fuel oxygenates, catalytic dehydration of ethanol to produce ethylene was performed over transition metal catalysts (Fe_2O_3, CoO and NiO/clay). The reaction was carried out in a pulse microcatalytic reactor operated under atmospheric pressure at reaction temperature ranging between 250 to 400°C. The reaction products are mainly composed of diethyl ether, which formed at the lower reaction temperature, and ethylene that formed at the higher temperature, on using nickel and cobalt catalysts. Meanwhile, on using iron catalyst, ethylene is formed at the lower and higher reaction temperatures.

KEYWORDS: Dehydration, ethanol, ethylene, transition metal catalysts, bentonite clay material

1. INTRODUCTION

Due to problems with environmental pollution expanding reliance on imported sources of petrochemicals feedstock and undervalued agricultural commodities increasing attention to possiblities for using fermentation products as alternative feedstock for the synthesis of higher value of chemical and fuel oxygenates.

The selective conversion of ethyl alcohol to ethylene in mildly acidic homogenous solution was first detected by Bondt et al., over 200 years ago [1].

The heterogenous catalysis of this reaction has been practiced before the turn of the 20th century on the industrial scale by passing ethanol vapours under atmospheric

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pressure over γ– Al_2O_3 and/or supported acid catalyst at 395°C [2]. Zeolite allow a more systematic study of the selective production of ethylene from ethanol [3-7]. The dehydration of the biomass-derived ethanol was carried out over H-ZSM5 to produce ethylene [8]. Ion-exchange resin was also used as a catalyst for this synthesis [9].

Literature survey reveals that, ethanol dehydration is persumed over synthetic supports (alumina, zeolite and or resin). This study deals with the production of ethylene from ethanol via dehydration reaction using oxide transition metal catalysts (Fe_2O_3, CoO and NiO/bentonite-clay).

2. EXPERIMENTAL

Transition metal "iron-, cobalt- and nickel" catalysts were previously prepared by the incorporation of the fresh prepared corresponding metal hydroxide precipitate into the activated-bentonite clay material [10]. The catalysts are calcined in presence of a stream of dry air at ~ 300°C for iron- and nickel-catalysts and at ~ 200°C for the cobalt one.

Infrared spectroscopic analysis has been studied to follow the changes that occurred upon the impregnation of transition metal cations into the bentonite silicate structure. The analysis was carried out using Varian Fourier Transformer infrared apparatus.

2.1 Catalysts Activity

Ethanol conversion is taken as a model reaction for measuring the catalytic activity of the prepared catalysts towards dehydration reaction. The catalytic dehydration reaction of ethanol was performed in a pulse microcatalytic reactor operated under atmospheric pressure, at reaction temperature ranging from 250 to 400°C. The microreactor was charged with 500 mg of the dried catalyst, before carrying out any reaction, the catalyst was activated at 200°C for two hours in a stream of the hydrogen carrier gas and then brought to the required temperature. A 2 µl dose

of ethanol was injected into the hydrogen stream flowing continuously down the catalyst bed at a rate of 40 ml/min. Products stream was immediately analyzed when passing through the gas chromatographic column directly attached to the microreactor. The column was packed with chromosorb W60-80 mesh size loaded with 15% squalane mentained at temperature of 50°C.

3. RESULTS AND DISCUSSION

From the chromatographic analysis data, it is clear that, the dehydration of ethanol practically leads to diethyl ether and ethylene formation. The activity of the prepared catalysts becomes almost constant as judged from the analysis after less than 10 pulses at about 15 minutes intervals. Accordingly, the average of conversion after 10 injections was taken as the catalyst activity at the corresponding temperature. The data are included in Table 1 and plotted graphically in Fig. 1(a-c).

On using cobalt oxide/bentonite catalyst, data in Fig. 1(a) reveals that, the dehydration of ethanol to produce ethylene begins at reaction temperature 250°C with a low value of ~ 4.7% as compared with the produced diethyl ether ~ 95.3%. On raising the reaction temperature, the yield of ethylene increases and diethyl ether shows the reverse. In other words, the response curves for ethylene and diethyl ether reaction products are intersected at a critical reaction temperature of 325°C , after that "ethylene" was gradually increased in its yield as "diethyl ether " was decreased.

Nickel oxide catalyst behaves the same normal route like that obtained on cobalt catalyst. The intersection point of the ethylene and diethyl ether on curve is also at ~ 325°C, Fig. 1(b), after this temperature, ethylene is sharply increased to reach 98.3% which accompanied with gradual decrement in diethyl ether until reached 1.7%at the higher reaction temperature 400°C.

Table. 1. Effect of Reaction Temperatures on the Converted Products of Ethanol Dehydration on Using Transition Matal Catalysts.

	CoO/ bentonite catalysts						
	Reaction Temperature, °C						
	250	275	300	325	350	375	400
Total conversion (mol %)	100	100	100	100	100	100	100
Converted products							
Ethylene	4.7	12	27	50	67	72	77
Diethylether	95.3	88	73	50	33	28	23
Polymer products	--	--	--	--	--	--	--
	NiO/ bentonite Catalyst						
Total conversion (mol %)	100	100	100	100	100	100	100
Converted products							
Ethylene	3	10	20	45	84	97	98
Diethylether	97	90	80	55	16	3	2
Polymer products	--	--	--	--	--	--	--
	Fe_2O_3/ bentonite Catalyst						
Total conversion (mol %)	100	100	100	100	100	100	100
Converted products							
Ethylene	23	42	59	66	73	85	88
Diethylether	77	58	41	34	27	15	4.2
Polymer products	--	--	--	--	--	--	7.8

On using iron oxide catalyst, the dehydration of ethanol, behaves a contrary route as compared with the cobalt and nickel catalysts, which is a direct low-temperature route to ethylene formation, the ethylene converted product is formed at the lower reaction temperature "250°C" with a remarkable value ~ 23%, the intersection point of ethylene and diethyl ether curves are at a lower reaction temperature of ~ 280°C, after this temperature, ethylene is gradually increased until reachs its maximum value of ~88% at 400°C, in addition polymer products of ~ 7.8%, (Table 1) are formed. Concurrently, the dehydration of ethanol to diethyl ether shows the reverse, by means that, it decreases as the reaction temperature increases until reachs its lower value ~ 4% at 400°C, Fig. 1(c). Thus from the previous results, it can be summarized that:-

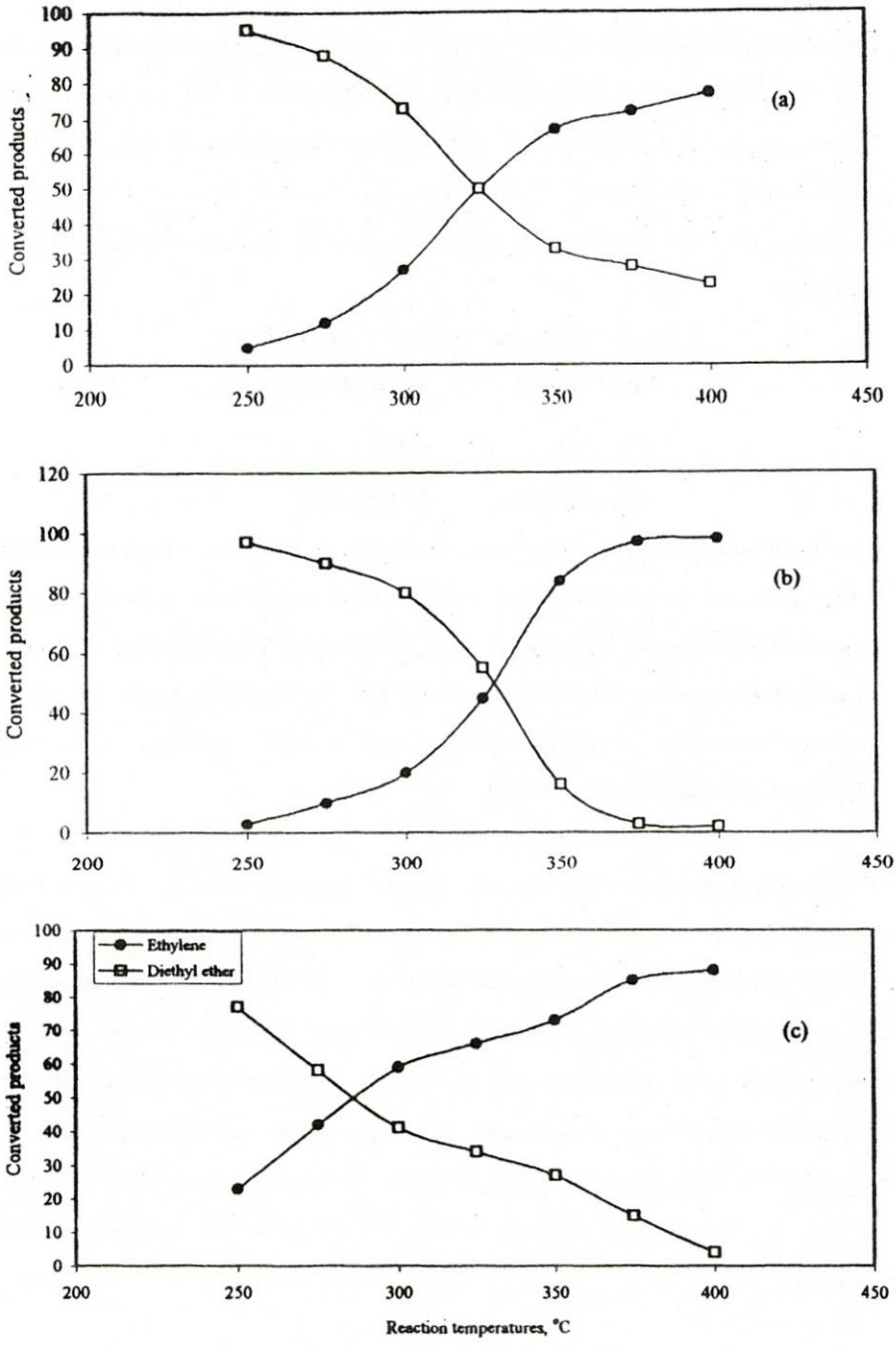

Fig. 1. Effect of reaction temperatures on the conversion of ethanol over: (a) CoO (b) NiO and (c) Fe_2O_3 /bentonite catalysts.

The dehydration of ethanol to ethylene occurred at high reaction temperature, meanwhile the diethyl ether formation is obtained at a lower one on using cobalt and nickel catalysts. This behavior may be explained upon that:- the intermolecular dehydration of ethanol (needs 2 moles) to form diethyl ether, requires a lower energy than the intramolecular dehydration of ethanol to from ethylene

$$C_2H_5OH + C_2H_5OH = C_2H_5O\,C_2H_5 + H_2O$$

Ethylalcohol Diethylether

$$C_2H_5OH = C_2H_4 + H_2O$$

Ethylalcohol Ethylene

- The formation of ethylene dehydrated product with a relatively high value at the lower reaction temperature, that happened on using iron catalyst, can be explained according to Krossner et al.'s [11] proposal that, the water molecules produced during the dehydration of ethanol, facilitate the hydration of the Brönsted acid sites including supported iron catalyst forming dimeric water (H_3O^+) or tetrameric water ($H_5O_2^+$) ...

The simultaneous forming of dimeric water is the preferred state of larger water clusters within higher surface coverage (4-atoms). The dimeric water clusters have also a unique effect on the carbenium transition state which shielding the carbenium ion from nucleophilic attack by another adsorbed ethanol molecule, thus allowing the competing β-elimination reaction to prevail (Fig. 2). The efficiency of this shielding effect increases with the size of the water cluster. At lower reaction temperature, the shielding effect is also enhanced while at higher temperature, this cluster is much smaller and the number of bridging protons increases which directed ethylene formation [12]

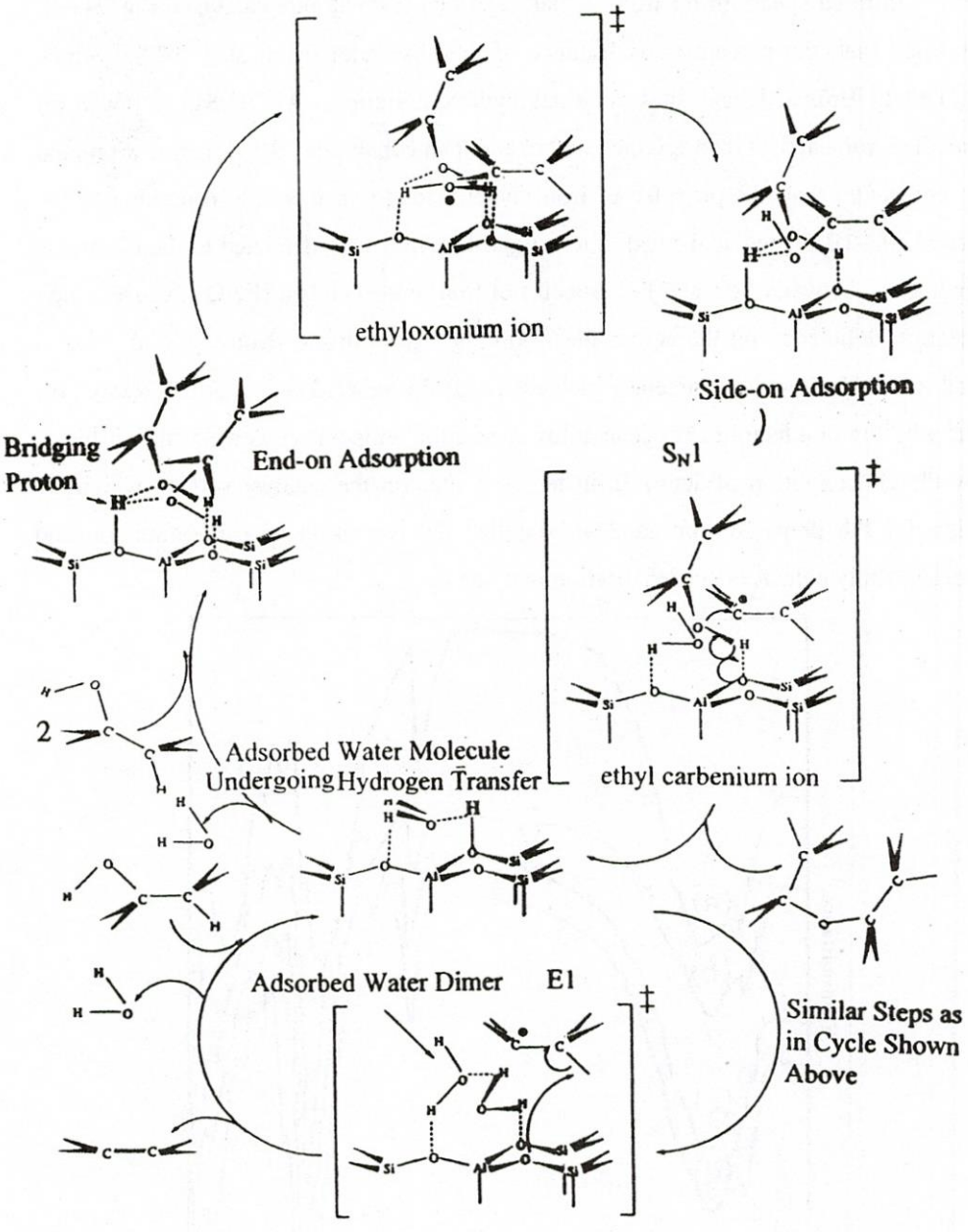

Fig. 2. Reaction Mechanism of Ethanol Dehydration.

Infrared spectrum for iron-, cobalt- and nickel-/bentonite catalysts, Fig. 3(a-c), clarified that, the percent transimittance of the absorption band at 3618cm^{-1} which related to Brõnsted acid sites (internal hydroxyl group... Al-OH-Si) is lower for calcined iron catalyst than calcined nickel and than cobalt ones. However, it is rational to conjecture that, the presence of iron nuclei leads to an increase in number of the active sites (Brõnsted acid sites). Such suggestion may also if related to the electronic interaction between Fe^{2+} and Fe^{3+} species of iron oxide catalyst (Fe_2O_3), cause a high electron deficiency on the active sites, borning a new strong Brõnsted acid sites, in addition to the bentonite lamella which act as a Brõnsted acid sites. For this reason, the dehydration of ethanol to ethylene at lower reaction temperature is well fairly affected by the concentration of active Brõnsted acid sites on the catalyst surface which are high for the prepared iron catalyst, stabilize the formation of carbenium ion and consequently enhances the dehydration reaction.

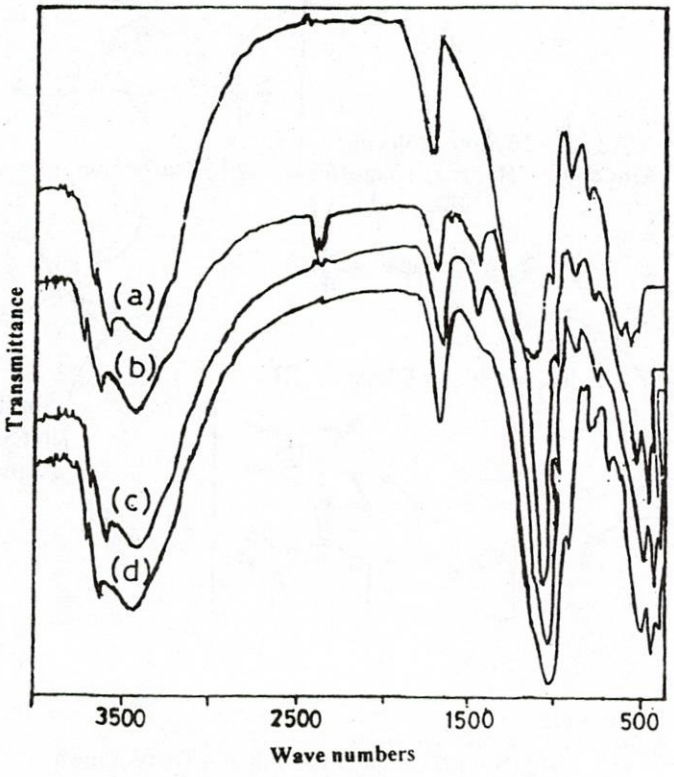

Fig. 3. Infrared spectra.

3.1 Kinetic Measurements

It was interesting to compare the kinetics of dehydration reaction of ethanol over the three studied catalysts to evaluate the catalysts activities under atmospheric pressure to find out their proper application.

Therefore, the data (Table 1) obtained were treated kinetically by means of Bassett Hobgood kinetic Eq. (1), [13] for pulse system, where the overall reaction constant:

$$Kk = \frac{Fo}{273\,RW} \ln \frac{1}{1-x} \qquad (1)$$

where,

x = mole degree of conversion

R = universal gas constant

Fo= corrected flow rate of gas carrier

w = weight of catalyst

Plotting of log ln 1/1-x against 1/T, verifying Arrhenius relation, straight lines were obtained and the activation energies were determined from the slop of these straight lines. Arrhenius plots were graphically represented in Fig. 4.

From the figure, it was clear that Arrhenius plots were divided into two regions, the high reaction temperature range "diffusion region" and the lower range " Kinetic region". The reaction rate temperature coefficient (γ) can be also calculated from vant Hoff's Eq. (2):

$$\frac{K_2}{K_1} = \gamma \frac{T_2 - T_1}{10} \qquad (2)$$

The calculated activation energies and temperatures coefficient (γ) for both regions are summarized in Table 2.

Table 2. The Activation Energy and Temperature Coefficient (γ) for Ethylene Formation.

Catalysts	Activation Energy K.cal./mol			γ values	
	E. diffusion	E. kinetic	E. Mean*	Diffusion	Kinetic
CoO/bentonite	16.78	21.3	16.5	1.04	1.5
Ni/bentonite	19.12	21.6	21.3	1.08	1.45
Fe_2O_3/bentonite	9.12	15.46	9.29	1.12	1.38

* Obtained through regression analysis of data by means of statistical micro-computer, canon inc., Japan.

The variation in the activation energy for both regions either diffusion and or kinetic on using the different prepared catalysts can be explained on the basis of that: It is well known that, the increase of temperature by 10°C, increases the reaction rate constant by 3-4 times (γ = 3-4) for kinetic controlled reaction (kinetic zone), while increases only by about (1-2) times, γ = 1-2 for the diffusion controlled reaction (diffusion zone) which means small slope for the latter case in the Arrhenius plot and consequently a low activation energy [13].

Thus dehydration reaction of ethanol over the prepared catalysts has taken place in the diffusion region as indicated also by γ values (Table 2).

3.2 Reaction Mechanism

The reaction mechanism for ethanol dehydration involving simultaneous ethylene and diethyl ether formation (Fig. 2). Two ethanol molecules are assumed to coadsorb end – on (perpendicular to catalyst surface) onto the Brõnsted acid and the adjacent Lewis basic bridging hydroxyl sites via a strong by hydrogen bonding [14], one of these two molecules is probably more weakly adsorbed allowing for reorientation [15]. Therefore, a transition state is formed involving a partially rotated ethyloxinum ion which eventually decomposes back into two adsorbed ethanol

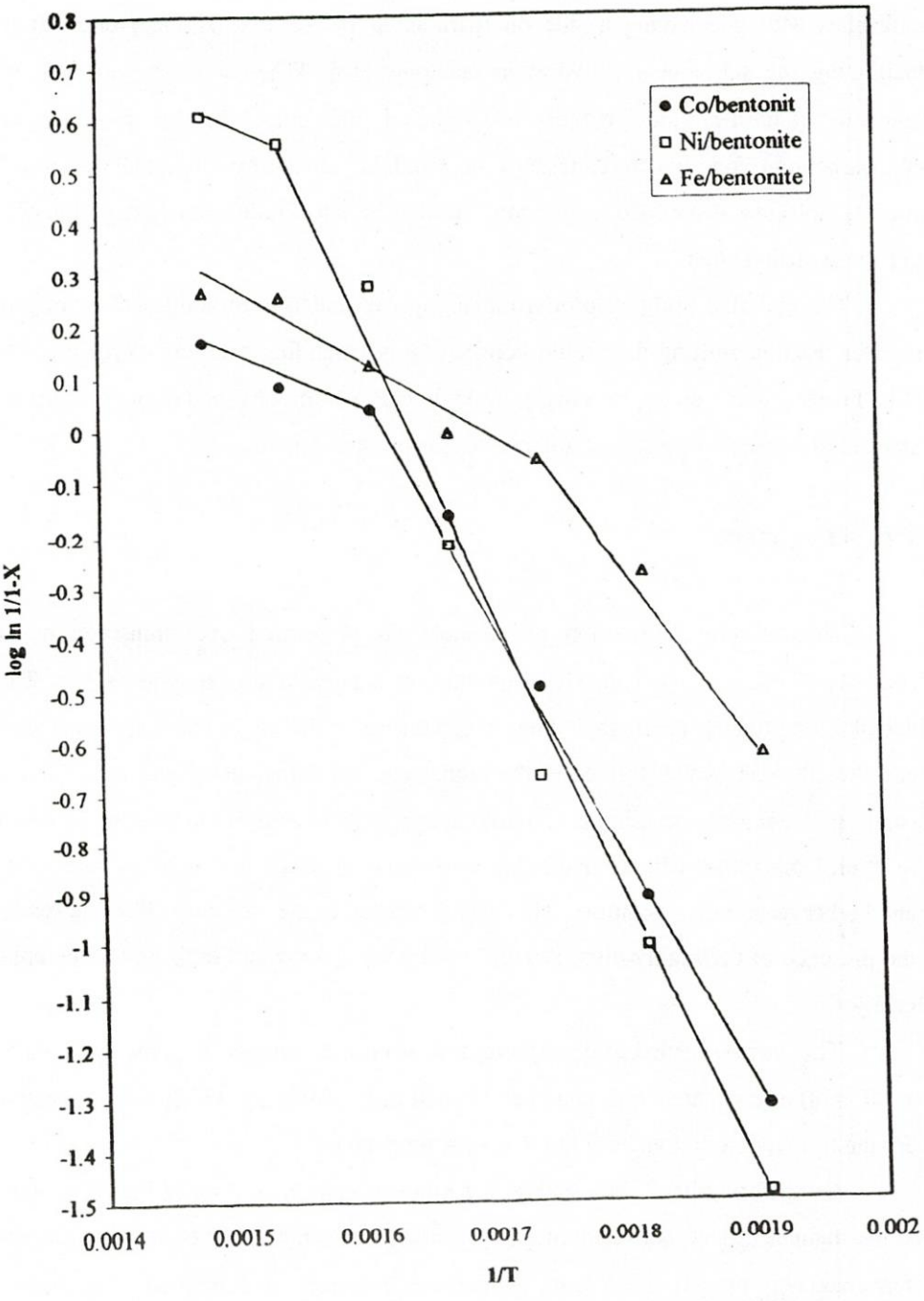

Fig. 4. Arrhenius plots for ethanol dehydration.

molecules with one having a side on (parallel to the catalyst surface) orientation facilitating the subsequent dehydration reactions [16]. When a water molecule is released from the side on adsorbed ethanol molecule, thereby forming an ethylcarbenium ion, which undergoes nucleophilic attack by the other adsorbed ethanol molecule. A diethyloxonium ion is produced and simultaneously deprotonated to release diethyl ether.

The hydrated bridging proton remaining can undergo an additional hydrogen transfer reaction shifting the proton between the surrounding bridging oxygen atoms [11]. Further, it can either, become more hydrated to form adsorbed dimeric water or an ethanol molecule coadsorbed and ethylene is produced again.

4. CONCLUSION

The dehydration reaction of ethanol was performed over transition metal catalysts, "Fe_2O_3/, CoO/ and NiO/bentonite" in a pulse microcatalytic reactor. The dehydration products are diethyl ether, which formed at the lower reaction temperature and the ethylene, which formed at the higher one, on using nickel and cobalt oxide catalysts. Meanwhile on using iron oxide catalyst, ethylene begins to form at the lower reaction temperature with a remarkable amount i.e. ethylene is formed at both lower and higher reaction temperatures. This may be related to the shielding effect caused by the presence of the highly dispersed Brõnsted acid sites on and onto Fe_2O_3/bentonite catalyst.

The energy needed to desorp ethylene from iron catalyst is a low value (9.12 k.cal. mol) as compared with nickel and cobalt ones (Table 2), which is an indication for the formation of ethylene at low reaction temperature.

On the other hand, iron species are more strongly incorporated between silica-silica lamella sheets in bentonite clay structure, which related to the highest ferromagnetic properties of iron, where the existence of unpaired electrons on individual iron species delocalized and participate in the formation of a conduct band

within the bentonite lamella. This fact is confirmed by differential scanning calorimetry analysis data [10].

Consequently, iron catalyst is riched with dispersed active sites, whatever the surface and lamella of iron catalyst is crowded by the converted products which competite each other facilitating its desorption at a lower activation energy value.

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تفاعل النزع الحفزى للماء من الكحول الأثيلى بواسطة حفازات العناصر الانتقالية

تـم تحضـير الأثيلين بالنزع الحفزى للماء من الأيثانول باستخدم العوامل الحفازة المكونة من العناصـر الأنتقالية مثل أكاسيد الحديد (III)- الكوبلت (II) – النيكل (II) المحملة على الطفلة المحلية المنشطة، وقد أجرى التفاعل باستخدام جهاز معملى تحت الضغط الجوى المعتاد وعند درجات حرارة تتراوح ما بين ٢٥٠ م الى ٤٠٠ م وأسفرت النتائج أنه عند درجات الحرارة المنخفضة يتكون مركب ثـنائى ايـثيل ايثر، وعند درجات الحرارة العالية وفى وجود عاملى الكوبلت والنيكل يتكون الأيثلين، باستخدام الحديد كعامل حفاز يتكون الأثيلين عند درجات الحرارة المنخفضة والمرتفعة على حد سواء، وعـليه يتضح أن استخدام الطفلة المحلية كمادة حاملة للعامل الحفاز يعطى نتائج إيجابية عالية لانتاج الايثيلين اذا قورنت بمثيلتها الغير محلية.