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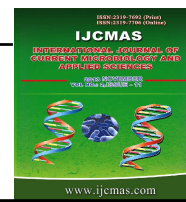


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## Original Research Article

# The kinetic study of catalytic esterification by nickel based catalyst promoted with different metal oxides as a catalyst

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## ABSTRACT

### Keywords

Preparation,  
XRD, IR,  
complexometric  
analysis,  
thermal analysis

The present work deal with the kinetics study of esterification of ethanol and butanol with acetic and valeric acid in presence of nickel metal promoted with CoO, Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> as a catalyst. The catalyst prepared by co-precipitation technique were subjected to complexometric analysis, X. ray diffractometer, IR absorption spectra, thermal analysis and surface area measurement through the adsorption - desorption isotherms.

## Introduction

Aluminum oxide is the most famous promoters for nickel (1) several publication were given in the literature which recommended the use of Ni/Al<sub>2</sub>O<sub>3</sub> as catalyst. Some of them recorded partial reduction of nickel in presence of aluminum oxide promoters. Systematic studies on Ni/Al<sub>2</sub>O<sub>3</sub> catalyst Armstrong and Hilditch (2). These are a lot of works (3) used Cr<sub>2</sub>O<sub>3</sub> as promotes for nickel in hydrogenation – dehydrogenation processes which founded as good promoters due to its high melting point, an indication for the efficiency of this catalyst for the hydrogenation – dehydrogenation esterifications processes was. given by Sadek , Taylor (4), wassel and Amira Different metal oxide promoters such as

CoO, Fe<sub>2</sub>O<sub>3</sub>, CuO, Mno and ZrO<sub>2</sub> for nickel catalyst to produce a binary one were tried.

The activity of these catalysts varies greatly not only according to the method of it is preparation, but also according to it is composition.

Esterification of benzyl alcohol with acetic acid catalyzed by amberlyst-15 (cation-exchange, resin) (5) was carried out in a batch reactor in the liquid phase in the temperature range from 328-359 C<sup>0</sup> and at 1 atm. The reaction rate increased with increase in catalyst concentration and reaction temperature. Resin particle size and stirrer speed had virtually no effect on

the rate under the experimental conditions. The rate data were correlated with a kinetic model based on homogeneous reaction. The apparent activation energy was found to be  $73.3\text{KJ mol}^{-1}$  for the formation of benzyl acetate. The use of a solid ion-exchange resin as catalyst was the following inherent advantages over catalysis effected by dissolved electrolytes for these reasons (a) the catalyst can be readily removed from the reaction product by decantation or filtration, (b) continuous operations in columns are possible, (c) the purity of the products is higher since side reactions can be completely eliminated, (d) it is possible to isolated the reactions intermediates; and (e) ion-exchange resists can discriminate between small and large molecules.

The effect of the amount catalyst as largely studied by many authors. Zaltan (6), gave a correlation between the quantity of catalyst and the rate of reaction. The rate of reaction was found to be reduced after attaining an optimal amount of catalyst. The esterification of alkyl alcohol with acetic in a batch stirred reactor catalyzed by cation exchange resin, showed that reaction was increased when increasing the catalyst amount up to a certain limit (7).

The same authors (8) determined the catalytic property of cobalt oxide supported with alumina ( $\text{CoO}/\text{Al}_2\text{O}_3$ ) for hydro-desulfurization with the aid of a micro-reactor plisse technique under chromatographic conditions. Attention was given to the effect of poisoning substances. The catalyst is fully activated by reduction sulfidation of the catalyst does not increase its activity. The role of the  $\text{CoO}$  in the catalyst remains obscure. Paryczak and co-workers (9) studied the influence of preparative conditions on

specific area and porosity of supported cobalt and on molybdenum catalysts; thus temperature, pH of precipitation roasting of Co-Mo were studied roasting temperature ( $400\text{C}^0$ ) and pH precipitation; ranged from 4.5 to 9 were found to have an essential influence on the properties of the catalyst.

Wassel and Amira studied the effect of sodium salts on the catalytic properties of Co – Mo oxide catalysts by introducing of  $\text{Na}_2\text{MoO}_4$ ,  $\text{NaCl}$  and  $\text{NaNO}_3$  in amounts containing more than 0.4 wt.% Na into Co- Mo oxide catalysts with Co : Mo atom ratio of 2.5 and 1.55 decreases the activity of the initial samples by a factor of about 9. The selectivity remains unchanged. The introducing of sodium into supported catalysts leads also to a decrease in selectivity. An explanation of the observed effects is proposed.

## **Materials and Methods**

### **Preparation**

Nickel supported with  $\text{Cr}_2\text{O}_3$ ,  $\text{CoO}$  and  $\text{Fe}_2\text{O}_3$  to obtain binary mixed catalyst, The catalysts were prepared by Co-precipitation of calculated amounts of the corresponding nickel, chromium, iron and cobalt nitrate solution by means of sodium carbonate solution at room temperature.

In order to ensure complete precipitation, one molar nitrate solutions of such elements were mixed together and added slowly to about 1.5 molar solution of sodium carbonate under continuous mixing. The precipitate was then washed by breaking up the filter cake in a small amount of bidistilled water and adding additional amount of about five liters bidistilled water and stirring up the whole mass in the precipitating vessel for one quarter to one half an hour.

The precipitate is then allowed to settle and then again sucked off on a Buchner funnel. The washing cycle was repeated until the catalyst becomes free from the impurities by reaching a constant conductivity reading as that of bidstilled water. The obtained material was then dried for twenty four hours at about 105C<sup>0</sup>. The dried materials was first claimed at 350 – 370 C<sup>0</sup> to decompose the metal carbonates into oxides and then sieved into 0.2- 0.4 mm diameter grain. Reduction of the claimed material was made by using hydrogen gas at about 320C<sup>0</sup>. The hydrogen flow rate was about 15 L / h. The obtained catalyst was stabilized before use against spontaneous oxidation in air by impregnation in distilled water and allowing slow oxidation to take place while water evaporate through slow heating up to 100°C.

It is advisable to refresh the catalyst before use by passing hydrogen gas at temperature of about 160°C for two hours. The thermal treatment of the catalyst of calcinations, reduction and stabilization was carried out using the arrangement shown in fig. (1)

The different compositions of the selected catalyst are shown in table -1.

### **Catalyst characterization**

#### **Complexometreic Analysis**

The percentage of metal in the prepared catalyst was determined complexometreically<sup>(11)</sup>. The sample was dissolved in the least amount of 2N /HCl and then evaporated to about one third of its initial volume. After cooling the solution which contains the metal caution was transferred quantitatively in to a

measuring flask, the metal ion concentration was determined by EDTA titration. The result of analysis given in table-2, which are in a good agreement with the proposed tentative composition.

#### **Infrared absorption spectra**

The IR spectra of the different catalysts under investigation were recommended by KBr disc technique using a Perkin-Elmer 1430 double beam spectrophotometer in the range 4000-200 cm<sup>-1</sup>, as shown in fig - 2.

#### **Thermal analysis**

Thermal method were based upon the measurement of the dynamic relationship between temperature and some property of the system such as mass, heat of reaction or volume.

The thermogravimetric analysis (T.G.A) of some representative catalysts as well as differential thermal analysis (D.T.A) were performed by shimadzu DT-40 apparatus in the temperature range 25 °C up to 500°C with 10°C/min heating rate using air as an atmosphere, as shown in fig -3.

#### **X-ray measurement**

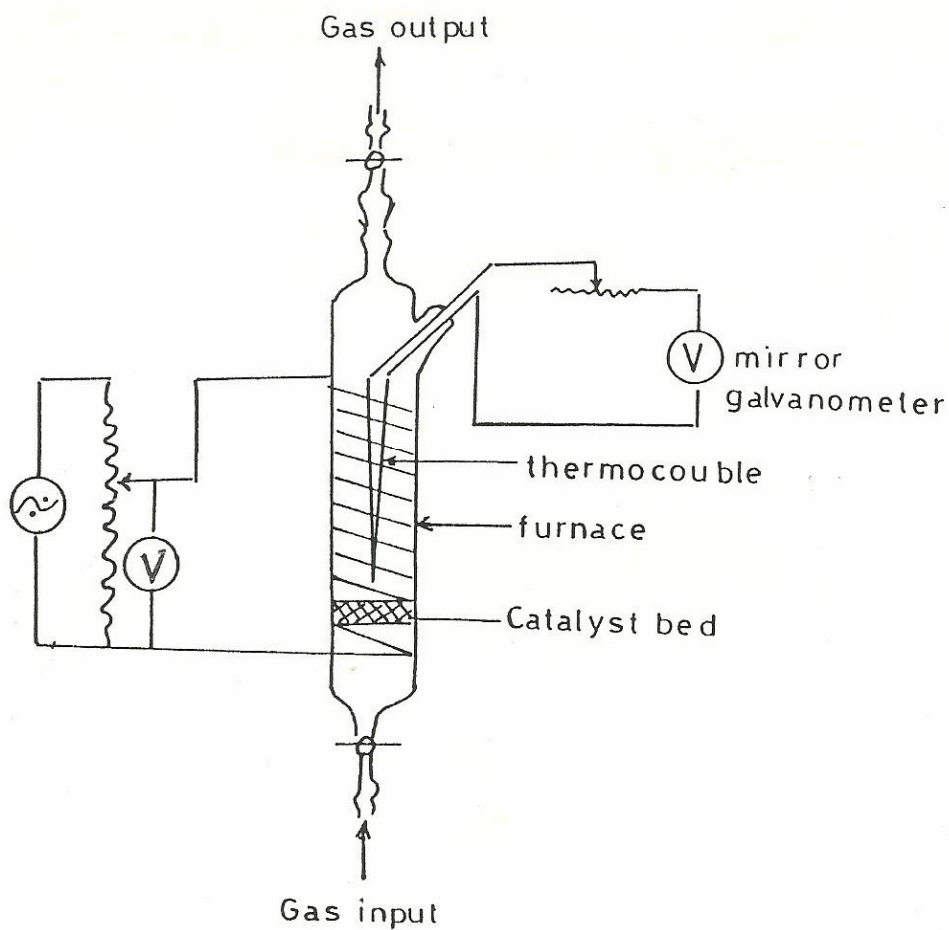
The XRD spectroscopy represents one of the most powerful tool available for rapid determination of the feature of samples such as mixed catalyst by a Philips diffractometer<sup>(13)</sup> type PW 1390.

The position of the resulting X-ray peaks was determined in terms of diffraction angle ( $\theta$ - value). It was then possible to estimate the distance between the different planes of the crystal (d-value), characteristics for crystalline materials, as shown in fig -4.

**Table.1** the catalytic composition of the selected catalyst

Catalyst	Composition mol %
NiCoO	80/ 20
	85/15
	90/10
NiCr <sub>2</sub> O <sub>3</sub>	80/20
	85/15
	90/10
NiFe <sub>2</sub> O <sub>3</sub>	80/20
	85/15
	90/10

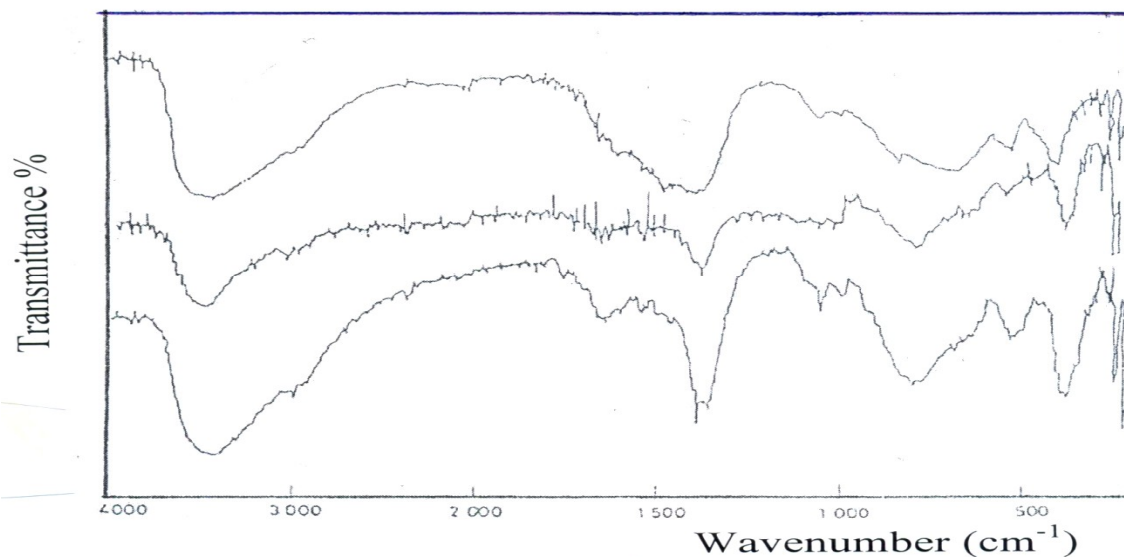
**Figure.1** The Arrangement used for thermal analysis of catalysts.



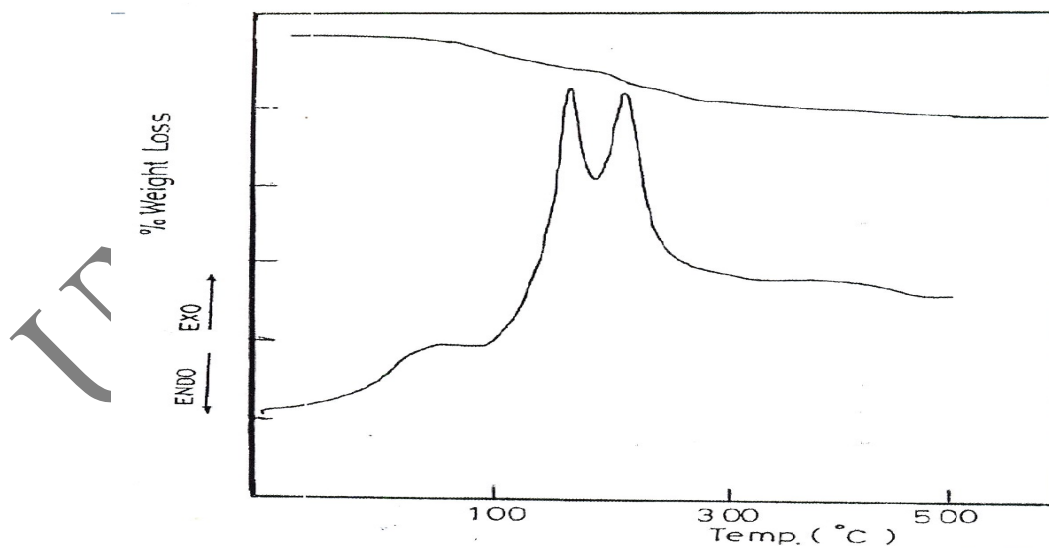
**Table.2** Complexometric Analysis of metal percent in some selected catalyst

Catalyst	Composition	Input metal %	Output metal %
1	Ni/CoCo <sub>3</sub>	80/20	79.63/19.21
2	Ni/Cr <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	80/20	79.73/19.32
3	Ni/Fe <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	80/2	79.82/20.02

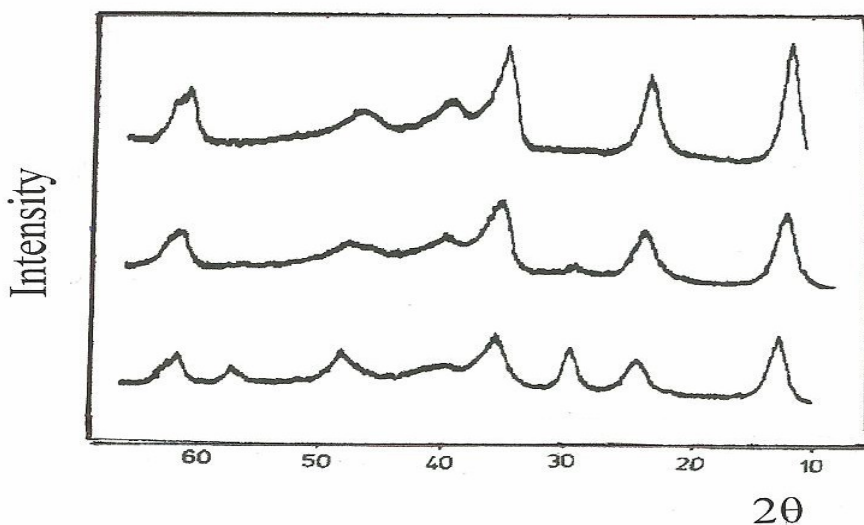
**Fig.2** IR Spectra of the selected metal oxide catalysts



**Fig.3** DTA and TG curve of selected catalysts



**Fig.4** X-ray diffraction pattern of selected catalysts



### Surface area

The specific surface area ( $\text{m}^2/\text{g}$ ) was determined by BET analysis<sup>(14)</sup> of  $\text{N}_2$  adsorption isotherm measured on the tested catalyst at liquid nitrogen temperature by using a conventional volumetric apparatus. Prior to exposure to the adsorptive molecules. The investigated catalysts were out-gassed at  $200^\circ\text{C}$  and  $10^{-5}$  torr for 3h. The adsorption-desorption isotherm is shown in fig -5, and the  $v_L$ -t plots in fig -6, and the surface area resulted in table -3.

### Results and Discussion

To ensure the composition of the produced end-product catalyst, different investigations were carried out:

The complexometric analysis of these samples given table-1, ensure that the weight loss during preparation not exceeds 2% .

Inspection of the D.T.A and T.G.A curves of some examined catalytic systems proved that phase transformation takes place during thermal treatment of the samples.

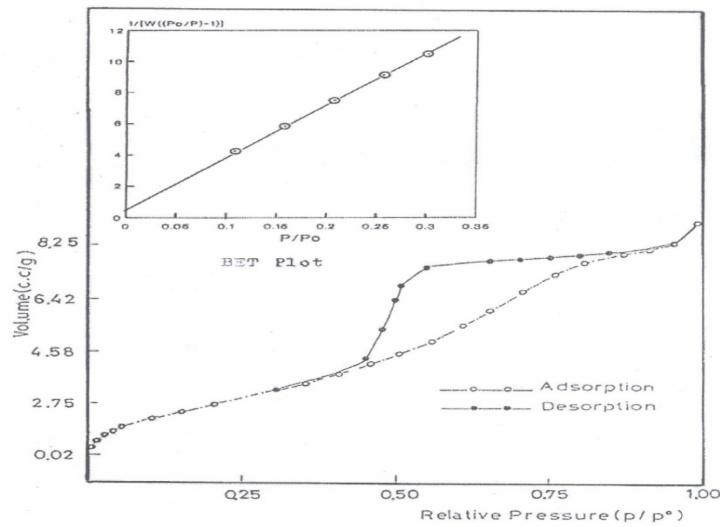
I.R spectro photometric investigation showed that the presence of a broad band at  $3600\text{-}3300\text{ cm}^{-1}$  of the OH group of the physically adsorbed water molecules. Another band at about  $1350\text{ cm}^{-1}$  of the  $\text{Cr}^{+3}\text{-O}^{-2}$  and two bands at about  $800, 530\text{ cm}^{-1}$  are due to presence of  $\text{Fe}^{+3}\text{-O}^{-2}$  and Co-O due to tetrahedral and octahedral complexes of nickel-metal stretching bond.

X-ray examination of some selected catalysts permitting study of the structural properties of the bulk catalytic systems which ensures the presence of NiO in the composition due to partial reduction of nickel throughout its thermal treatment.

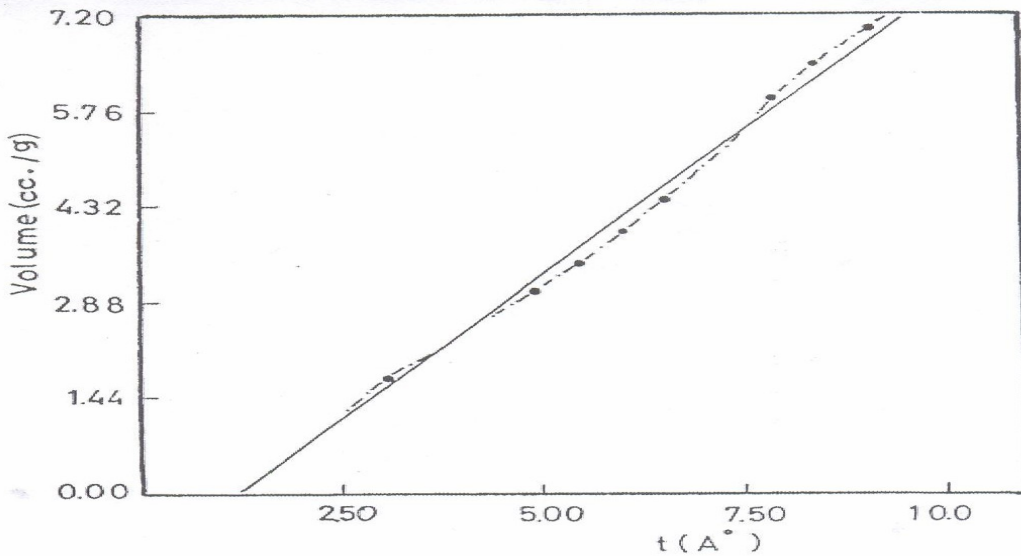
**Table.3**  $S_{BET}$  and  $S_t$  Results

Catalyst	Composition	Surface area $m^2/g$	
		$S_{BET}$	$S_t$
1	Ni/C <sub>2</sub> O <sub>3</sub>	52	52
2	Ni/Cr <sub>2</sub> O <sub>3</sub>	62.77	62.76
3	Ni/Fe <sub>2</sub> O <sub>3</sub>	61.30	61.29

**Fig.5** Adsorption – Desorption isotherm of N<sub>2</sub> at -196C<sup>0</sup> on catalyst



**Fig.6**  $V_L - t$  plots of N<sub>2</sub> adsorption on catalyst





**Table.4** Esterification of ethanol with acetic acid on mixed metal oxides of different temperatures

Metal oxides	Temp.C <sub>0</sub>	X <sub>Ac</sub>	K <sub>X</sub> 10 <sup>-4</sup> Exper	K <sub>X</sub> 10 <sup>-4</sup> theor	Ea cal mol <sup>-1</sup>	ΔH <sup>*</sup> cal mol <sup>-1</sup>	ΔS <sup>*</sup> cal mol <sup>-1</sup>	ΔG <sup>*</sup> .cal.mol <sup>-1</sup>
	50	0.83	8.001	8.135	6735.593	5432.121	54.354	23260.32
NI / CoO	55	0.84	9.501	9.501	6735.593	5412.251	54.354	23505.55
	60	0.87	11.198	11.072	6735.593	5396.355	54.288	23691.52
	50	0.74	5.868	5.877	6947.552	5644.080	54.324	23412.43
NI / Cr <sub>2</sub> O <sub>3</sub>	55	0.77	6.909	6.897	6947.552	6524.210	54.348	23732.05
	60	0.82	7.956	7.812	6947.552	5608.314	54.337	23919.93
	50	0.70	3.696	3.777	7174.482	5859.406	54.339	23466.04
NI / Fe <sub>2</sub> O <sub>3</sub>	55	0.75	4.441	4.471	7174.482	5840.036	54.341	23718.07
	60	0.79	5.234	5.266	7174.482	5820.166	54.369	23979.47

**Table.5** Esterification of Butanol with Acetic acid on mixed metal oxides of different temperatures

Metal oxides	Temp.C <sup>0</sup>	X <sub>Ac</sub>	K <sub>X</sub> 10 <sup>-4</sup> Exper	K <sub>X</sub> 10 <sup>-4</sup> theor	Ea cal mol <sup>-1</sup>	ΔH <sup>*</sup> cal mol <sup>-1</sup>	ΔS <sup>*</sup> cal mol <sup>-1</sup>	ΔG <sup>*</sup> cal.mol <sup>-1</sup>
	50	0.74	6.5956	6.2552	7096.42	5757.19	54.3778	24082.53
NI / CoO	55	0.81	8.0425	7.5290	7096.42	5733.34	54.3816	24386.26
	60	0.83	9.4244	9.7437	7096.42	5713.47	54.4363	2457.32
	50	0.69	3.7672	3.6590	7455.90	6116.67	54.4896	24479.69
NI / Cr <sub>2</sub> O <sub>3</sub>	55	0.74	4.5798	4.4333	7455.90	6092.82	54.4702	24776.11
	60	0.78	5.3239	5.1994	7455.90	6072.95	54.4812	25032.41
	50	0.60	2.0057	1.8826	7900.59	6561.35	54.0107	24762.99
NI / Fe <sub>2</sub> O <sub>3</sub>	55	0.64	2.4886	2.3139	7900.59	6537.51	54.9937	25057.31
	60	0.70	2.9992	2.7334	9700.59	6517.64	54.0119	25313.81

**Table.6** Esterification of Butanol with valeric acid on mixed metal oxides of different temperatures

Metal oxides	Temp.C <sup>0</sup>	X <sub>Ac</sub>	K <sub>X</sub> 10 <sup>-4</sup> Exper	K <sub>X</sub> 10 <sup>-4</sup> theor	Ea cal mol <sup>-1</sup>	ΔH <sup>*</sup> cal mol <sup>-1</sup>	ΔS <sup>*</sup> cal mol <sup>-1</sup>	ΔG <sup>*</sup> .cal.mol <sup>-1</sup>
	50	0.73	6.2458	6.2552	7096.42	5757.19	54.3778	24082.53
NI / CoO	55	0.80	7.6369	7.5290	7096.42	5733.34	54.3816	24386.26
	60	0.82	8.7543	9.7436	7096.42	5713.47	54.4363	2457.32
	50	0.61	3.5419	3.6570	7455.90	6116.67	54.4896	24479.69
NI / Cr <sub>2</sub> O <sub>3</sub>	55	0.7	4.3106	4.4333	7455.90	6092.82	54.4702	24776.11
	60	0.74	5.0845	5.1994	7455.90	6072.95	54.4812	25032.41
	50	0.58	2.2612	1.8826	7900.59	6561.35	54.0107	24762.99
NI / Fe <sub>2</sub> O <sub>3</sub>	55	0.64	2.8535	2.3139	7900.59	6537.51	54.9937	25057.31
	60	0.70	3.3882	2.7334	7900.59	6517.64	54.0119	25313.81

Examination of the surface area resulted in table (3) for the three examined catalytic system of nickel based catalyst promoted with CoO, Cr<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, refers to the Ni/ Cr<sub>2</sub>O<sub>3</sub> > Ni/Fe<sub>2</sub>O<sub>3</sub>> Ni/CoO but for catalytic activity the Ni/CoO> Ni/Cr<sub>2</sub>O<sub>3</sub>> Ni/Fe<sub>2</sub>O<sub>3</sub>. Since there is no direct relation between surface area and catalytic activity.

The kinetics of the catalyzed esterification of ethanol and butanol with acetic, and valeric acid were studied in presence of mixed metal oxides (Ni/CoO, Ni/ Cr<sub>2</sub>O<sub>3</sub>and Ni/ Fe<sub>2</sub>O<sub>3</sub> ) as catalyst. The effect of enrapture on the conversion of the above reactions is investigated at different temperature (50,55 and 60°C). The rate of conversion of the studied carboxylic acid follows an overall second order reaction.

The velocity constants K<sub>1</sub> (L.mol<sup>-1</sup>sec<sup>-1</sup>) were calculated from the linear plot relationship drawn through the experimental data at indicated temperatures and these are listed in tables 4-6.

A perusal of the data in tables 4-6. clearly show that the values of K<sub>1</sub>, as determined experimentally, at three different temperatures are in good agreement with the values obtained theoretically by applying equation (1).

$$\text{Log}^k_{\text{theor}} = m.\text{eq./gm}-E_a/2.303 RT \dots\dots\dots (1)$$

The effect of temperature on the conversion of these carboxylic acids was evaluated at temperature form 50°C to 60°C. The conversion increases with increase in temperature. In case of esterification of the ethanol and butanol alcohols with acids.

The K<sub>1</sub> values at different mixed metal

oxides for esterification reaction under study are in the order;

$$\text{Ni/CoO} > \text{Ni/Cr}_2\text{O}_3 > \text{Ni/ Fe}_2\text{O}_3$$

The K<sub>1</sub> values at different mixed metal oxides are of higher magnitudes as compared with the values obtained for the esterification on metal oxides indicating a higher rate of conversion in case of Ni/CoO.

In the esterification reaction of the ethanol and butanol alcohols with acids under the action of metal oxides and mixed metal oxides are in the order.

$$\text{Mixed metal oxides} > \text{Metal oxides}$$

The values of K<sub>1</sub> from (0.48 to 11.19) x 10<sup>-4</sup> (L.mol<sup>-1</sup>.sec<sup>-1</sup>) for metal oxides and mixed metal oxides, seem to be dependent upon on the molecular weight of the acid and alcohol employed.

The values of activation energy (E<sub>a</sub>) evaluated from the slopes of the linear-plots are collected in tables (4-6). It is obvious that E<sub>a</sub> increases with increasing the molecular weight of either alcohol or acid employed. From the values of E<sub>a</sub>, it is probable that the esterification reaction of two alcohols was controlled by the chemical reaction inside the particle size of the metal oxides and mixed metal oxides. This means that the sorption of the reacting species between the metal oxides and mixed metal oxides and solution phases is rapidly established and is maintained throughout the process.

Slow interparticle diffusion may reduce the overall rate, especially if the reaction molecules are if large molecular weight, and consequently have a low mobility in the metal oxides and mixed metal oxides.

It is found from tables 4-6 that, the energies of activation for the esterification of alcohols under study are in the order:

Ethanol < Butanol

This sequence of  $E_a$  can also be understood on the basis of the steric effect exhibited by higher molecular weight alcohols which need high activation energy for these reactions to proceed.

In the present study both alcohols and acids were found to suffer a marked loss of their internal degrees of freedom during their conversion into activated species. A slight variation in the  $\Delta S^*$  values was observed for all the investigated reactions, thus indicating a close similarity between the tendency of loss in the internal degree of freedom of either alcohols or acids. A slight dependence for this parameter on the molecular weights of such reactants is observed.

For all the esterification reactions, the values of  $\Delta G^*$  calculated, increase by increasing the temperature of the reaction. An increase in  $\Delta G^*$  is indicative of the salvation of the reactants. A slight increase in salvation was thus observed by increasing the reaction temperature.

The values of  $\Delta H^*$  calculated from the relation show that for all the investigated reactions,  $\Delta H^*$  has positive sign, indicating that all these reactions endothermic in character. The values of  $\Delta H^*$  increase along the acids used, i.e. by increasing their molecular weights, showing that the endothermity of these reactions increases by increasing the complexity of the reacting species. This explains that as the reacting species are of highly molecular weight they are in need of high energy to complete their reaction.

The prepared mixed metal oxides exhibit crystalline structure which was reached by XRD study.

The IR spectra of mixed metal oxides Ni / CoO, Ni / Cr<sub>2</sub>O<sub>3</sub> and Ni / Fe<sub>2</sub>O<sub>3</sub> confirm the presence of M-O due to the tetrahedral and octahedral complexes of Ni - M stretching bond which may be considered as index of the catalytic activity for the esterification reactions.

The study of the esterification reactions some alcohols having different structure with some acids at different temperature, in presence of mixed metal oxide catalysts. The rate constants were experimentally determined and theoretically calculated.

The activation energy  $E_a$ , enthalpy change  $\Delta H^*$ , free energy change  $\Delta G^*$ , and entropy change  $\Delta S^*$  were calculated.

The complexity of the reacting species this explains that as the reacting species are of highly molecular weight they are in need of high energy to complete their reaction.

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