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Conversion of Isopropanol over Treated CuO Supported on γ-Al_2O_3

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Abstract: The catalysts used in this study were prepared by co-precipitation and wet impregnation methods of copper oxide supported over alumina with extent of loading from 0.01 – 0.2 mole CuO and 0.15CuO /Al_2O_3 catalysts prepared by wet impregnation method were doping by oxides of group IA such as lithium, sodium, potassium and cesium using different concentrations of 0.5, 1, 2 and 3 % metal oxides. The selective prepared catalysts were characterized by several techniques such as : DTA, TGA, XRD, nitrogen adsorption at – 196°C and catalytic conversion of iso-propanol using the flow system. Thermogravimetric analysis (TGA) was carried out on the aluminum hydroxide, copper hydroxide and 0.20 of copper hydroxide supported over aluminum hydroxide by co-precipitated method (0.2CuO/Al_2O_3). X-ray diffraction patterns were determined for the original oxides of Al, and Cu and also for the samples (0.01,0.05 and 0.2) CuO/Al_2O_3 prepared by co-precipitation and impregnation preheated at 400°C in air. The catalytic activity of the supporting catalysts of the Al_2O_3, CuO, 0.01CuO/Al_2O_3 , 0.05CuO/Al_2O_3 and 0.2CuO/Al_2O_3 catalysts prepared by co-precipitation and impregnation preheated at 400°C in air were studied by conversion of iso-propanol to produce acetone and propene

Key words: Catalytic activity, metal oxides-support interaction, alcohol dehydration and doping oxides.

INTRODUCTION

Catalysts are among the most important technological materials, being used in the manufacture chemicals, used, fuel, foods, clothing, pharmaceuticals and materials such as organic polymers [1-3].

The catalytic activity of metal oxides appears to be one of the most significant factor in heterogeneous catalysis. Supported transition metal or oxides are commonly employed to catalyze several reactions including oxidation-reduction, dehydration, dehydrogenation, cracking, alkylation……ect[4-6]. It is known that the of oxide catalyst supported on alumina depends on many factors such as method of preparation [7,8], calcinations conditions, extent of loading, its dispersion on the surface of alumina[9] and the interaction between the different components of the catalyst. The latter is very important factor and some investigations are cited in the literature concerning this subject [10].

The catalytic activity of most transition metal oxides can greatly improved by doping with foreigen cations of different valence states, supportation on an active carrier such as γ-Al_2O_3 and subjecting or gamma radiation[11].

Aluminum oxide support much increases the degree of dispersion of the catalytically active component. Furthermore, it prevents the grain growth of the catalyst particles thus retarding its sintering process [12,13].

The interaction between metal oxide and γ-alumina was explained by various mechanisms as diffusion the active cation into surface-lattice vacancies till saturation [14] or occupation the tetra and octahedral sites of γ-alumina forming a surface spinel compound [15].

To improve the catalytic activity and selectivity of γ-alumina can be achieved by treating with different ions such as Na^+, Fe^{+2}, Zn^{+2}, Mg^{+2},Cu^{+2}, Ni^{+2} and also by subjecting ionizing radiation as well as by heating at various temperatures [16,17].

The textural properties of CuO/Al_2O_3 samples containing different amount of copper oxide were determined from N^2- adsorption at 77k [18]. They observed that the surface area decreases and the mean pore radius r^- increases upon increasing CuO content of the sample. The structure of CuO/Al_2O_3 catalyst depends on both metal loading and calcination temperature [19].

Garbowski et al [20] postulated that addition of CuO to Al_2O_3 substitute's surface OH groups in alumina and Cu^{+2}bridged two Al-O surface groups Because of the surface OH group's density, the number of isolated Cu^{+2} bonded is limited. As soon as the number of copper species exceeds the exchange capacity of the support, Cu^{+2}formed sintered particles of the bulk oxide. At high loading isolated Cu^{+2} disappeared and bulk oxide formed.

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Increasing the calcinations temperature of CuO/Al_2O_3 catalyst decreases its activity towards CO oxidation by O_2 due to the formation of metal aluminum compound [$CuAl_2O_4$] [21].

N.H.Amin et al. [22] found that the solid –solid interaction between CuO and alumina support occurs at 650^0C and this reaction is completed at 1000^0C. The rate of reaction between metal oxide and alumina decreases in the following order: Cu>Co >Ni> Fe, the activity of metal aluminates lower than that of the metal oxide itself [23].

Doping the support employed can readily modify the catalytic activity and selectivity of different metal oxides loaded on to convenient support. The doping process may change the concentration and/ or the nature of catalytically active species and hence lead to an effective change in there catalytic activities [24]. The doping process can proceed via different mechanisms depending on the preparation of solid catalysts and the nature of dopant ions [25].Diffusion of dopant ions in the lattice of solid catalysts may affect their physicochemical, electrical, magnetic, stoichiometric,surface and catalytic properties [26]. The surface and catalytic properties of some metal oxides supported on γ-Al_2O_3 have been greatly modified by treating with foreign cations such as Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{+2}, C^{+2}, Zn^{+2}, Ga^{+3}andCe^{+4} [27].

The effect of doping of CuO/ γ-Al_2O_3 solids with $Li_2O$and Na_2Ohinders the $CuAl_2O_4$ formation of Li orNa-aluminates which cover the surface of Al_2O_3 particlesand suppress the diffusion of copper species in the interior of Al_2O_3 particles [28]. It has reported by Youssef *et al* [29] that loading of CuO on alumina decreased the dehydration activity which disappeared completely at 16.2 wt.%ofCuO.

2.Experimental:

2.1.Catalyst preparation: The catalysts used in this study were prepared by both co-precipitation and impregnation methods.

2.1.1. Co-precipitation Method for Preparation of Cuo/al$_2$o$_3$ Catalysts: CuO/Al_2O_3 series were prepared from aluminum nitrate (Win Lap.) solution with different proportions of copper nitrate (National Co.) solution using ammonium hydroxide (Porlabo) at 70^0C and pH =8 .The precipitate was washed with distilled water till free from ammonium and nitrate ions then filtered and dried at 110^0C for 6 h.The molar ratio of CuO/Al_2O_3 were 1,2,3,5,10,15 and 20%. The chemical compositions of produced catalysts are given in Table (1).

2.1.2. Impregnation Method for Preparation of CuO/Al_2O_3 catalysts: CuO/Al_2O_3 series were prepared by a wet impregnation method .A known mass of prepared Al_2O_3 was impregnated with solutions containing different amounts of copper nitrate dissolved in the least amount of distilled water. The obtained samples were dried at 110^0C for 4 h and calcinied at 400^0C for 6 h to form the required system. The chemical compositions of produced catalysts are given in Table (2).

2.1.3. Preparation of Doped Catalysts: Elements of group 1A in the periodic table such as lithium , sodium , potassium and cesium were doped over the sample of $0.15CuO/Al_2O_3$,prepared by wet impregnation method. A known weight of $0.15CuO/Al_2O_3$was impregnated with solution containing different amounts of lithium , sodium, potassium and cesium nitrates (Aldrech) to produce catalysts 0.5 ,1.2 and mol % of Li^+ ,Na^+, K^+ and Cs^+ to produce catalysts dissolved in the least amount of distilled water . The obtained samples were dried at 110^0C for 4 h and calcinied at 400^0C for 6 h to form the required system. The chemical composition of produced catalysts are given in Table (3)

2.2. Physicochemical Techniques: The chemical composition and structure of the various solid catalyst samples were characterized using thermogravemetric analysis, X-ray diffraction and BET surface area measurements.

2.2.1. Thermal Analysis: Thermogravemetric analysis (TGA) were carried out using “Shimatzu” TGA-50 thermogravemetric analyzer (faculty of science, Cairo University) from room temperature to 850^0C, the rate of heating was kept at 10^0C min^{-1} and the rate of nitrogen flow was 30 ml min^{-1}.

2.2.2. X-ray Diffraction Analysis: The nature of the solid phase investigated by means of x-ray diffraction analysis using a Bruker Axs D8 Advance diffractometer model 2001 (Tepeen institute of Metals) at 40kv and 40 mA with monochromatic filter and Cu as target.

2.2.3. Surface Area Measurements: The surface area measurements of the samples were performed by BET method from nitrogen adsorption isotherms obtained at 77k using a Quantachrome NOVA model 2003 version 2.1. (Metals institute of Tepeen)

RESULTS AND DISCUSSIONS

3.1. Thermal analysis:

3.1.1. Thermogravemetric analysis (TGA): TGA was carried out on the prepared aluminum hydroxide, copper hydroxide and 0.2 copper hydroxide supported on aluminum hydroxide prepared by co-precipitation method 0.2 CuO/Al_2O_3.The result obtained are represented in Fig. (1)Which give the relation between the percent weight loss of the sample as a function of temperature.

3.1.2. Differential thermal analysis DTA: DTA was carried out on the prepared aluminum hydroxide, copper hydroxide and 0.2 copper hydroxide supported on aluminum hydroxide prepared by co-precipitation method 0.2 CuO/Al_2O_3. The result obtained are represented in Fig. (2).The DTA curve obtained for aluminum hydroxide fig. (2a) displays one endothermic peak at 370^0C ,which begins at about 350^0C and ends at about 400^0C and corresponding to the dehydration of aluminum hydroxide. This peak is in agreement with that reported by Mackenzie [30].

For Cu $(OH)_2$ (Fig.2b)shows two small endothermic peaks at 276^0C and 392^0C, the first indicates the evaluation of some small bound water, as indicated in TGA,and the second for conversion of $Cu(OH)_2$ to Cu2O.

The DTA thermogram obtained for 0.2 co-precipitated $Cu(OH)_2/Al(OH)_3$ sample shown in (Fig.2c), one sharp endothermic peak is observed at 382^0C which indicates that aluminum hydroxide surround the copper hydroxide to form a sort of shielding [31]. This is due to low percent of copper hydroxide in the sample.

3.2. X-ray diffraction analysis

3.2.1. XRD of CuO/Al_2O_3 system prepared by co-precipitation method: X-ray diffraction patterns of CuO/Al_2O_3 samples heated at 400^0C for 6 h are shown in Fig.(3). Evidently, by increasing the molar ratio of CuO over γ-Al_2O_3, the main peak of CuO sample disappears.

Fig.(3b) represents the diffraction patterns of the sample 0.01CuO/ γ-Al_2O_3 which show the poor lines of CuO at d-spacing of 2.32 and $2.52A^0$ with relative intensities of 81.9% and 100%, respectively, but most of the lines of this sample for γ-Al_2O_3. This is due to the shielding effect of CuO inside the crystal of tetrahedral structure of γ-Al_2O_3. The degree of crystallinity of CuO phase increase by increasing the extent of loading from 0.01 to 0.2 mol% CuO over γ-Al_2O_3.These results indicate the relatively limited role of alumina in decreasing the particle size of CuO crystals precalcined at 400^0C as shown in Fig. (3) and Table (4).

3.2.2. XRD of CuO/Al_2O_3 system prepared by impregnation method: X-ray diffraction patterns of 0.01, 0.05 and 0.2 CuO/Al_2Owere investigated. The obtained diffraction patterns are given in Fig.(4). In these samples as the previous co-precipitated samples,the main lines of copper oxides disappear and some of few peaks of copper oxide appear at 20% and at d-spacing of 2.32A and $2.52A^0$ with relative intensities of 81.9% and 100%, respectively. These weak lines increase in intensities with increasing the copper oxide content.

It can be summarized from the results of XRD that, the γ-Al_2O_3 preheated at 400^0C showed amorphous phase and the impregnation samples of (1-10%) of copper oxide with γ-Al_2O_3 did not show any crystalline patterns. This means that CuO is homogenously distributed on the surface of alumina without any formation of their crystalline phase. The increase of CuO on γ-Al_2O_3 up to 20% shows the CuO crystalline phase at d-spacing of 2.32 and $2.52A^0$ as shown in Table (5).

3.3. Surface characteristics:

3.3.1. the Adsorption Isotherms: The adsorption isotherms of nitrogen were measured at -196^0C for γ-Al_2O_3 and the supported catalysts of 0.01CuO/ γ-Al_2O_3, 0.05CuO/ γ-$Al_2O_3$and 0.2CuO/ γ-Al_2O_3 prepared by both co-precipitation and impregnation methods preheated at 400^0C in air.

Figs.(5,6) show the adsorption isotherms in which the amount adsorbed, represented as volume of gas adsorbed per gram adsorbed (cc/gm), is plotted as a function of the relative pressure (p/p^0) and the adsorption characteristics for the tested samples are summarized in Tables (5,6). The adsorption isotherms are all essentially of type II of Brunaures classification [32].

3.3.2. BET method: The texture parameters were estimated, these are the specific surface areas (m2/g).The specific surface areas were evaluated by the application of the BET equation in its normal range of applicability (0.0 5< p/p^0> 0.35). The respective plots of $\frac{p/p^0}{v(1\frac{p}{p^0})}$ versus p/p^0 are shown in Figs. (7,8). From the slope and intercept of the BET plots. The monolayer capacities (V_m) and BET-constants were calculated. Adopting the value of 1.62 nm for the crossectional area of the nitrogen molecule, the specific surface area (S_{BET}) was readily computed for the different samples. The total pore volume of a solid (V_p,ml/g.) is usually estimated from the amount held at the saturation vapor pressure of nitrogen (p/p^0) =1

Specific surface areas S_s are calculated and the values are given in Tables (6,7) together with the corresponding (S_{BET} and S_t) values for comparison .It's found a good agreement between the values of S_{BET}, S_s and S_t.

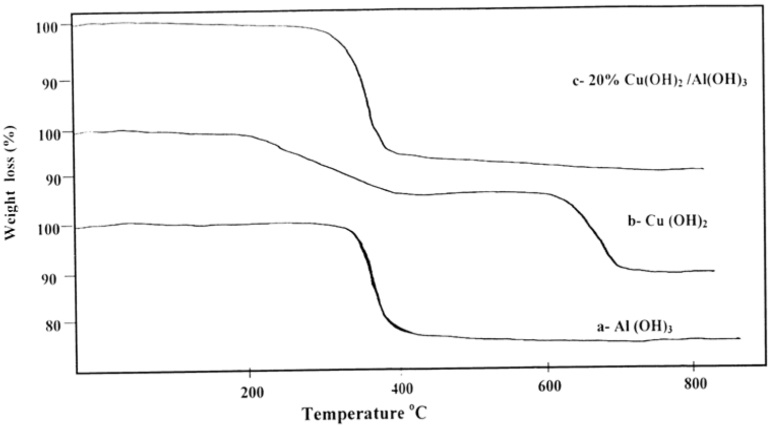


Fig. 1: Thermogravimetric analysis (TGA)of samples:
(a)-Aluminum hydroxide (b)- Copper hydroxide (c)- Mixed hydroxide

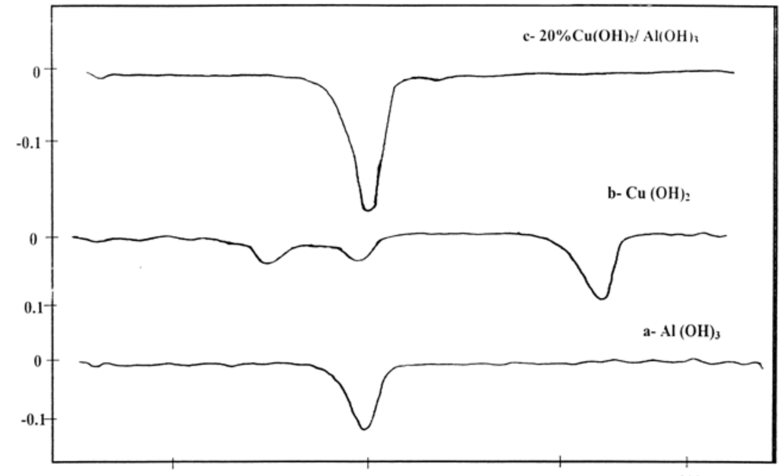


Fig. 2: Differential analysis (DTA)of samples:
(a)-Aluminum hydroxide (b)- Copper hydroxide (c)- Mixed hydroxide

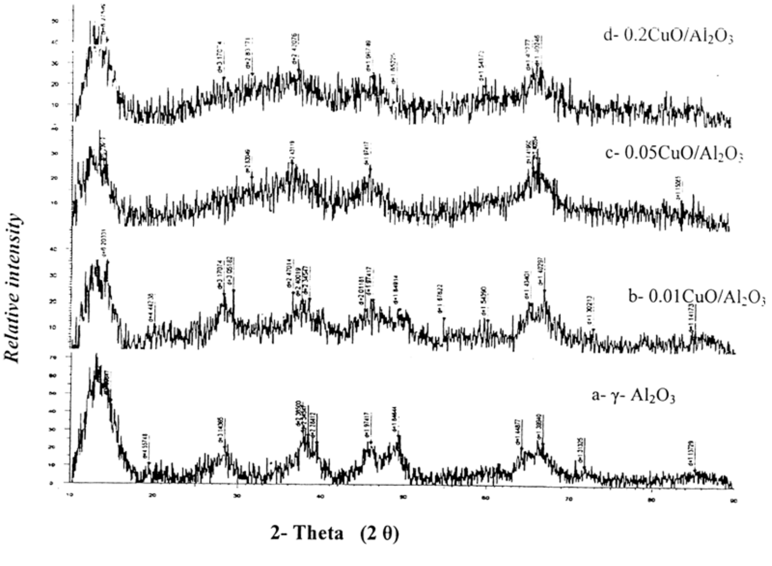


Fig. 3: X-ray diffraction patterns XRD of (a) Al2O3, (b) 0.01CuO/Al2O3,(c)0.05CuO/Al2O3 and (d) 0.2CuO/Al2O3 prepared by impregnation.

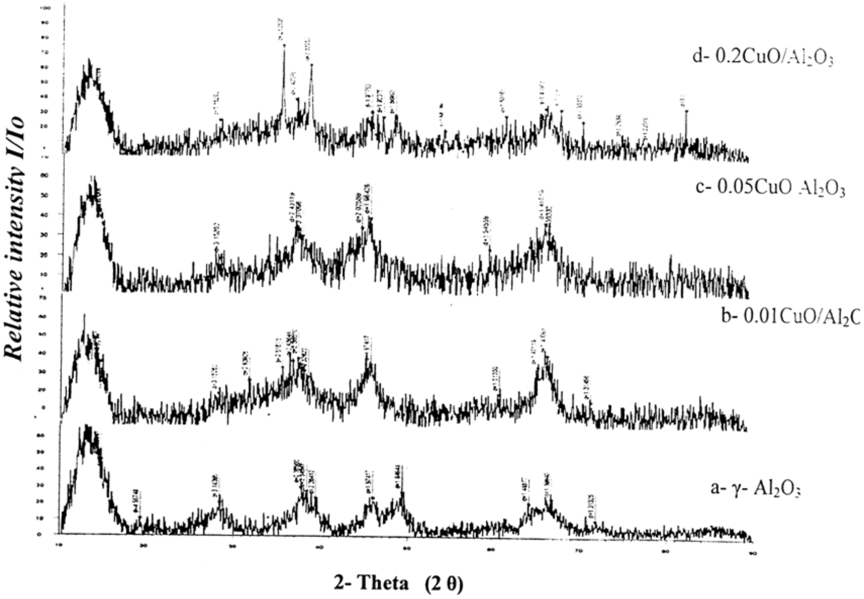


Fig. 4: X-ray diffraction patterns XRD of (a) Al2O3, (b) 0.01CuO/Al2O3,(c)0.05CuO/Al2O3 and (d) 0.2CuO/Al2O3 prepared by co-precipitation

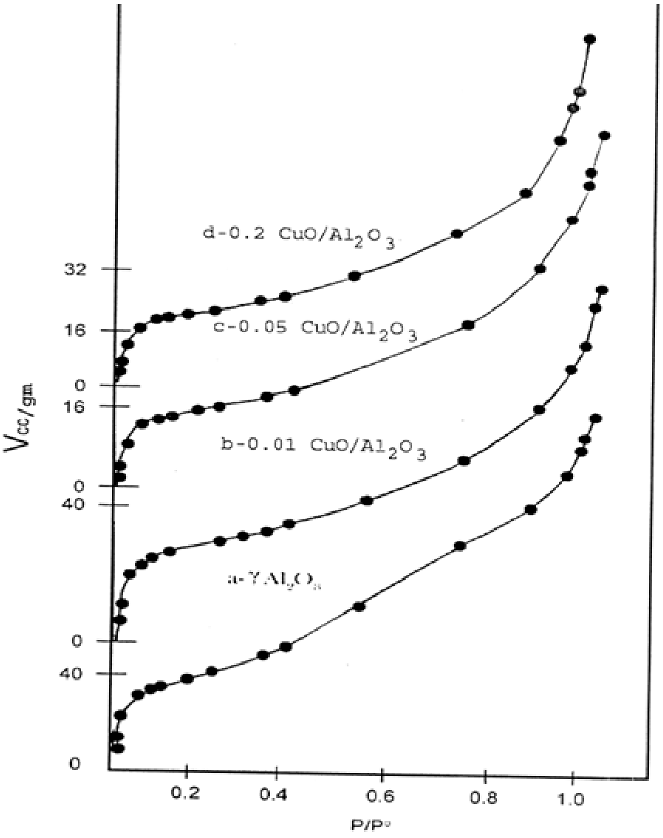


Fig. 5: Nitrogen adsorption isotherms for (a)γ-Al2O3, (b) 0.1CuO/ γ-Al2O3, (C)0.5 CuO/ γ-Al2O3 and (d) 0.2Cuo/ γ-Al2O3 prepared by impregnation and calcined at 4000C

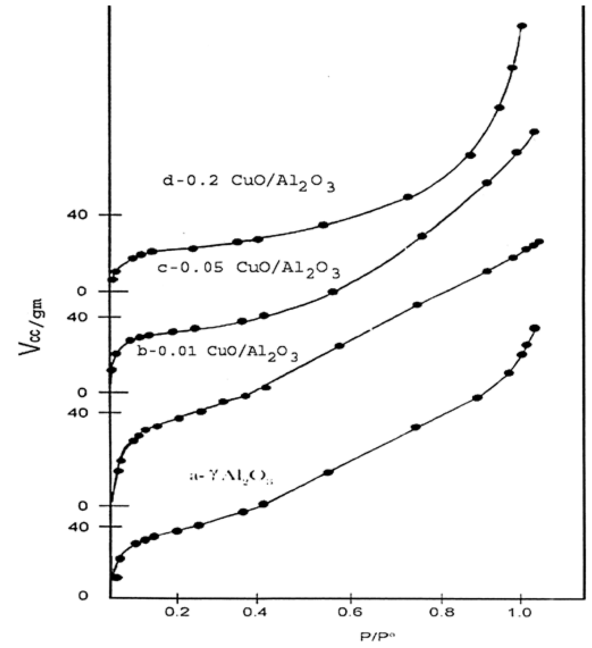


Fig. 6: Nitrogen adsorption isotherms for (a)γ-Al2O3, (b) 0.1CuO/ γ-Al2O3, (C)0.5 CuO/ γ-Al2O3 and (d) 0.2Cuo/ γ-Al2O3 prepared co-precipitaion and calcined at 4000C

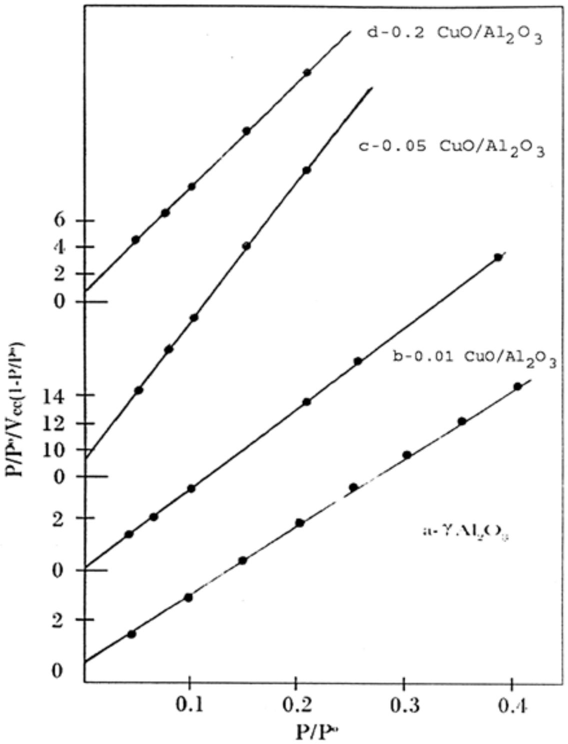


Fig. 7: Application of BET- equation for nitrogen adsorption of the samples (a) γ-Al2O3, (b)0.01CuO/ γ-Al2O3 ,(c) 0.05CuO/ γ-Al2O3 and (d) 0.2CuO/ γ-Al2O3 prepared by impregnation and calcined at 4000C

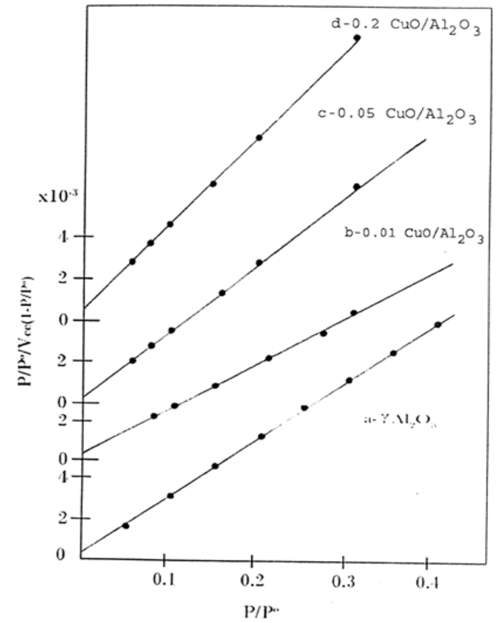


Fig. 8: Application of BET- equation for nitrogen adsorption of the samples (a) γ-Al2O3, (b)0.01CuO/ γ-Al2O3, (c) 0.05CuO/ γ-Al2O3 and (d) 0.2CuO/ γ-Al2O3 prepared by co-precipitation and calcined at 4000C

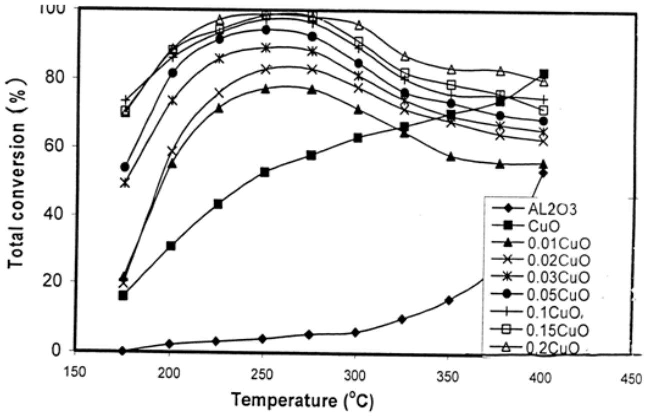


Fig. 9: Total Conversion of isopropanol as a function of reaction temperature over pure Al2O3, CuO and solides of CuO/ Al2O3 prepared by imperegenation

Table 1: Chemical compositionof CuO/Al_2O_3 system prepared by co-precipitation method.

Soilds	CuO content	
	Mol%	Wt.%
0.01CuO/Al_2 O_3	0.99	0.77
0.02CuO/Al_2 O_3	1.96	1.54
0.03CuO/Al_2 O_3	2.91	2.28
0.05CuO/Al_2 O_3	4.76	3.75
0.10CuO/Al_2 O_3	9.09	7.23
0.15CuO/Al_2 O_3	13.04	10.47
0.20CuO/Al_2 O_3	16.66	13.49

Table 2: Chemical composition of CuO/Al_2O_3 system prepared by impregnation method.

Soilds	CuO content	
	Mol%	Wt.%
Al2O3	0	0
0.01CuO/Al_2 O_3	0.99	0.77
0.02CuO/Al_2 O_3	1.96	1.54
0.03CuO/Al_2 O_3	2.91	2.28
0.05CuO/Al_2 O_3	4.76	3.75
0.10CuO/Al_2 O_3	9.09	7.23
0.15CuO/Al_2 O_3	13.04	10.47
0.20CuO/Al_2 O_3	16.66	13.49

Table 3: Chemical composition of various catalysts of Li_2O, Na_2, K_2O and Cs_2O doped CuO/Al_2O_3

Solids	Dopant content	
	Mol%	Wt.%
0.5%Li_2O/0.15CuO/Al_2O_3	0.43	0.13
1%Li_2O/0.15CuO/Al_2O_3	0.86	0.26
2%Li_2O/0.15CuO/Al_2O_3	1.71	52
3%Li_2O/0.15CuO/Al_2O_3	2.54	0.78
0.5%Na_2O/0.15CuO/Al_2O_3	0.43	0.27
1%Na_2O/0.15CuO/Al_2O_3	0.86	0.54
2%Na_2O/0.15CuO/Al_2O_3	1.71	1.08
3%Na_2O/0.15CuO/Al_2O_3	2.54	1.61
0.5%K_2O/0.15CuO/Al_2O_3	0.43	0.41
1%K_2O/0.15CuO/Al_2O_3	0.86	0.82
2%K_2O/0.15CuO/Al_2O_3	1.71	1.62
3%K_2O/0.15CuO/Al_2O_3	2.54	2.42
0.5%Cs_2O/0.15CuO/Al_2O_3	0.43	1.22
1%Cs_2O/0.15CuO/Al_2O_3	0.86	2.42
2%Cs_2O/0.15CuO/Al_2O_3	1.71	4.72
3%Cs_2O/0.15CuO/Al_2O_3	2.54	6.92

Table 4: The relation between 2θ and crystal size of co-precipitation samples of CuO/ γ-Al_2O_3.

2θ	Crystal size(nm)			
	CuO	0.01CuO/Al_2O_3	0.05CuO/Al_2O_3	0.2CuO/Al_2O_3
36.81	131.5	17.9	25.9	34.3
42.78	126.1	16.9	17.2	17.8
62.09	115.2	14.4	16.9	18.9
74.45	58.6	3	10.7	13.8
78.31	40.8	16.3	17.4	20.4

Table 5: The relation between 2θ and crystal size of impregnation samples of CuO/ γ-Al_2O_3.

2θ	Crystal size(nm)			
	CuO	$0.01CuO/Al_2O_3$	$0.05CuO/Al_2O_3$	$0.2CuO/Al_2O_3$
36.81	131.5	25.7	28.7	29.3
42.78	126.1	24.3	26	27.9
62.13	115.2	24.4	26.7	32.2
74.45	58.6	16.6	17.9	19.5
78.42	40.8	21.8	32.3	32.9

Table 6: The calculated values of S_{BET} ,S_t ,S_s,$V_m$and C-constant for samples of alumina and supported CuO/Al_2O_3prepared by co-precipitation method

Sample	V_m,(ml/g)	S_{BET}(m^2/g)	S_t(m^2/g)	S_s(m^2/g)	C-constant
Al_2O_3	33.33	145.1	155.5	152.5	6.00
$0.01CuO/Al_2O_3$	42.92	186.86	182.26	185.76	77.66
$0.05CuO/Al_2O_3$	29.67	129.67	118.58	119.66	134.20
$0.2CuO/Al_2O_3$	23.47	102.18	96.83	96.66	85.20

Table 7: The calculated values of S_{BET} ,S_t ,S_s,$V_m$and C-constant for samples of alumina and supported CuO/Al_2O_3prepared by impergenation method

Sample	Vm,(ml/g)	SBET(m2/g)	St(m2/g)	Ss(m2/g)	C-constant
Al_2O_3	33.33	145.1	155.5	152.5	6
$0.01CuO/Al_2O_3$	22.75	99.25	100.21	101.4	17
$0.05CuO/Al_2O_3$	19.22	83.69	81	80.01	87. 60
$0.2CuO/Al_2O_3$	11.38	49.52	47.2	47	146.5

The surface areas of the co-precipitated samples are higher than those of the impregnated ones; this is because of the good interaction between CuO and alumina in the samples prepared by the co-precipitation method and the creation of pores. It is found that the relation between the BS_{BET} and percent of CuO supported on alumina decreases with increasing the support content. This behavior indicates that the low percent of CuO content (1%) does not affect the porosity of alumina, but by increasing the content of CuO agglomeration or grain growth of the particle occurs giving rise to an increase in particle size and blocking the pores giving a continuous decrease in surface area.

`Aroa et al [34] found that the adhesion of the solid particles causing growth , migration of the lattice ions along the outermost surface layers of alumina and causing the surface irregularities and cracks between the neighboring crystallites to be filled up and shrinkage of the microspores causing decrease of surface area.

4.Catalytic activity: The catalytic activity towards the conversion of isopropanol for γ-Al_2O_3 and 0.01, 0.02, 00.03, 0.05.0.10, 0.15 and0.2 CuO/ γ-Al_2O_3 catalysts prepared by both co-precipitation and impregnation method were calcined at 400^0C for 3 hrs at the reaction temperature range 150-400^0C. Using 200mg catalyst diluted with granulated glass which is catalytically inert and (20ml/min) argon. The partial pressure of isopropanol was kept constant at about 100 Torr. The reaction mixture was analyzed using a gas chromatograph (Perkin Elmer Auto system XL with flame ionization detector) equipped with capillary column (fused silica) of 15 m length, 0.25 mm internal diameter packed with carbowax 20M. It was found that under these reaction conditions ,the products are acetone (dehydrogenation) and propene.

4.1. Catalytic Activity of CuO/Al_2O_3 System:

4.1.1. Catalytic Activity of $_{CuO/Al2O3}$ System Prepared by Impregnation Method:

4.1.1. 1.Effect of Extent of CuO Loading on the Catalytic Activity as a Function of Reaction Temperature: The catalytic conversion of isopropanol was carried out for Al_2O_3,CuO,$0.01CuO/Al_2O_3$,0.02 CuO/Al_2O_3, 0.03 CuO/Al_2O_3, 0.05 CuO/Al_2O_3, $0.1CuO/Al_2O_3$, 0.15 $CuO/Al_2O_3$and 0.2 CuO/Al_2O_3.

Fig.(9) shows the effect of extent of CuO loading on the total conversion of isopropanol as a function of reaction temperature for all the previous samples .The products were fond acetone and propene.

Inspection of Fig.(9) shows that pure CuO is devoiced with the highest catalytic activity, as the reaction temperature reaches 350^{0}C. It is shown also that for CuO and Al_2O_3 catalysts the catalytic activity increased by increasing the reaction temperature. For CuO/ Al_2O_3 catalysts, the catalytic activity increased with increasing the CuO content and the catalytic activity increases the reaction temperature increases up to 250 or 275^{0}C. However its slightly decreases by increasing the reaction temperature, this is may be attributed to the inward diffusion of Cu spices from the surface to the bulk[22].

4.1.1.2.effect of Extent of CuO Loading on the Products Selectivity as a Function of Reaction Temperature: Fig.(10) show the effect of extent of CuO loading on the products selectivity towards acetone (a) and propene (b).formation as a function of reaction temperature., this figure shows that: (i) at low temperature for both pure CuO and Al_2O_3 the dehydrogenation reaction is a predominant reaction up to 250^{0}C, and above this temperature the selectivity toward acetone begin to decrease with increasing temperature, while the selectivity towards propene formation progressively increases as a function of reaction temperature.(ii) In case CuO and Al_2O_3solids the selectivity towards propene formation generally improved by increasing the the reaction temperature and CuO content, while the selectivity towards acetone formation decreases with increasing the reaction temperature and CuO content.

The above results could be discussed as: (i)The location of Cu ion in octa and/ or tetrahedral position of the alumina make two-dimensional copper aluminates surface compound take place in case of CuO loading of 0.05 to 0.1mol% CuO.(ii) The progressive separation of copper species forming finally divided CuO crystallites in the range of loading 0.1-0.15 Mol% CuO. The complete separation occurs by increasing the extent of CuO loading from 0.15 to 0.2Mol%.

However, it is well known that the catalytic activity of CuO is greater than that of Cu. These leads to the concept that the progressive formation of finally divided CuO crystallites byincreasing the percentage of loading of CuO above 0.1 Mol% is normally accompanied by a progressive increase in the catalytic activity of the employed solids.

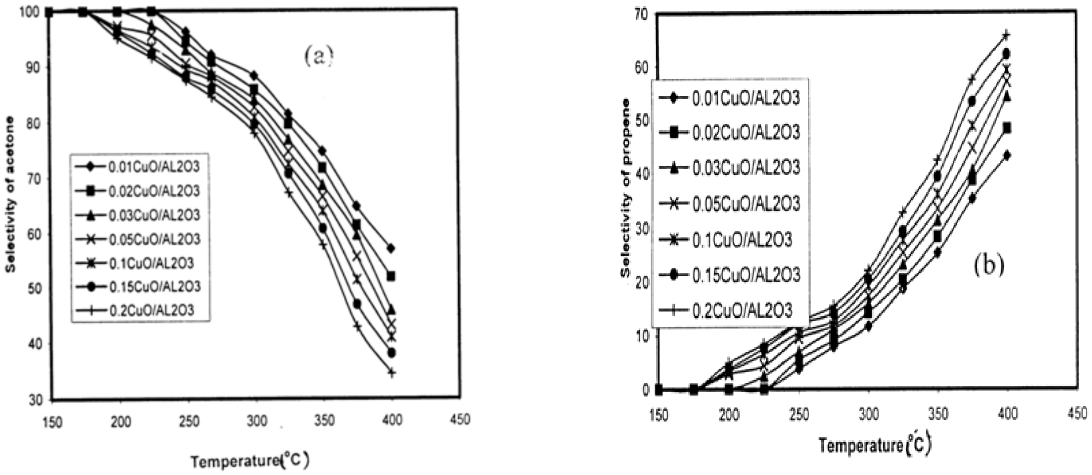


Fig. 10: Effect of CuO loading on the selectivity as a function of reaction temperature over Al2O3 prepared by impregnation

4. 2.Catalytic activity of CuO/Al_2O_3 prepared by co-precipitation method:

4.2.1. Effect of CuO Exetent on Catalytic Activity as a Function of Reaction Temperature: The catalytic conversion of isopropanol was carried out over 0.01, 0.02, 0.03, 0.05, 0.05, 0.1, 0.15 and 0.2 CuO/Al_2O_3 prepared by co-precipitaion method and also over pure oxides of Al_2O_3 and CuO in the temperature range 175-400^{0}C.

Fig. (11) Shows the effect of CuO content on the total conversion of isopropanol as a function of reaction temperature over CuO loaded on alumina and also pure oxides of Al_2O_3 and CuO. In case of CuO/Al_2O_3, the catalytic activity increased progressively as the extent of CuO increased and by increasing the reaction temperature up to 325-350^{0}C, after this temperature the catalytic activity begins to decrease with increasing the reaction temperature. These results may be explained as: in the co-precipitation Cu^{+2}species at the surface of Al_2O_3 and in the bulk, the addition of CuO to Al_2O_3 substitutes surface OH groups in alumina and Cu+2bridged two Al-O surface groups. Because of the surface OH groups density the number of isolated Cu+2 bonded is limited. As soon as the copper species exceeds the exchange capacity of Al_2O_3, Cu^{+2} formed sintered particles of the bulk oxides [35].

4.2.2. Effect of CuO Extent on the Products Selectivities as a Function of Reaction Temperature: Fig. (12) Shows the effect of CuO extent on the products selectivity towards acetone (a) and propene (b) formation as a function of reaction temperature .It is seen from this figure that (i) at lower reaction temperature acetone formation was the predominant product up to 250^{0}C. (ii) The selectivity towards propene formation generally improved with increasing the the CuO content and reaction temperature. (iii) The selectivity towards acetone formation decreased with increasing CuO extent.

It can be conducted that: The catalytic activity of CuO/Al_2O_3 catalysts prepared by impregnation is higher than that of co-precipitation method. The Solid-solid interaction was found to take place at lower temperature for the catalysts prepared by impregnation than that by co-precipitation method.

4.3. Effect of the Oxides Group 1A Elements Doping on the Catalytic Activity and Selectivities of the Employed CuO/Al_2O_3 system:

4.3.1. Effect of Doping on the Total Conversion of Isopropanol over 0.15 CuO/Al_2O_3 Sustem: The change in the catalytic conversion of isopropanol to produce acetone and propene due to doping of 0.15 CuO/Al_2O_3 with Li^+, Na^+, K^+ and Cs^+ as a function of the reaction temperature represents in Figs.13-16) which show that the total conversion of isopropanol increased with increasing the temperature from 175-275^{0}C and decreased with increasing the temperature from 275-400^{0}C.The results were found to be in agreement with the behavior of CuO/ Al_2O_3which showed two types of oxides Cu_2O and CuO in XRD.

Doping of Al_2O_3 support with different cations viz. Li^+, Na^+ ,K^+ and Cs^+ affect the catalytic activity of 0.15 CuO/ Al_2O_3 solids resulting in a progressive decrease in the activity of the undoped catalyst. These results may attributed to that Li, Na, K and Cs much affect the $CuO-Al_2O_3$ interaction yielding the formation of $CuAl_2O_4$.However, it must be remembered that Li_2O much retarded $CuAl_2O_4$ formation due to the formation of $LiAl_5O_8$ [28,36] hindering the diffusion of Cu ions into tetrahedral position of γ- Al_2O_3 lattice. On the other hand, Cs_2O much promoter the $CuO-Al_2O_3$ interaction leading to the formation of $CuAl_2O_4$.

4.3.2.effect of Doping on the Product Selectivities over 0.15 CuO/Al_2O_3: Effect of Li_2O,Na_2O,K_2O and Cs_2O doping on the 0.15 CuO/Al_2O_3 system was investigated. The results obtained are graphically represented in Figs.(17-20)

Inspection of these figures shows that: The selectivity towards acetone formation decreased by increasing the amount of Li_2O,Na_2O,K_2O and Cs_2O added Figs (17-20 a) and the selectivity towards propene formation increased by increasing the amount of Li_2O,Na_2O,K_2O and Cs_2O added Figs (17-20 b).

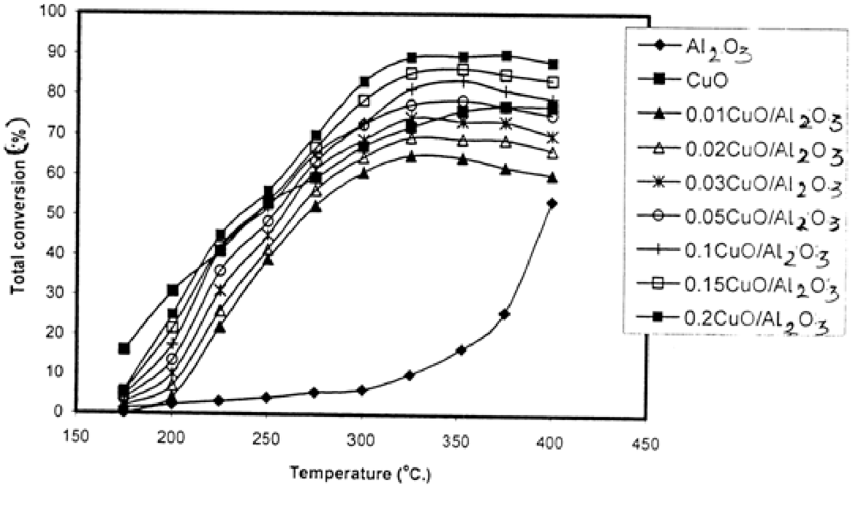


Fig. 11: Total Conversion of isopropanol as a function of reaction temperature over pure Al_2O_3,CuOand various exetent of CuO/ Al_2O_3 preapared by co-precipitation

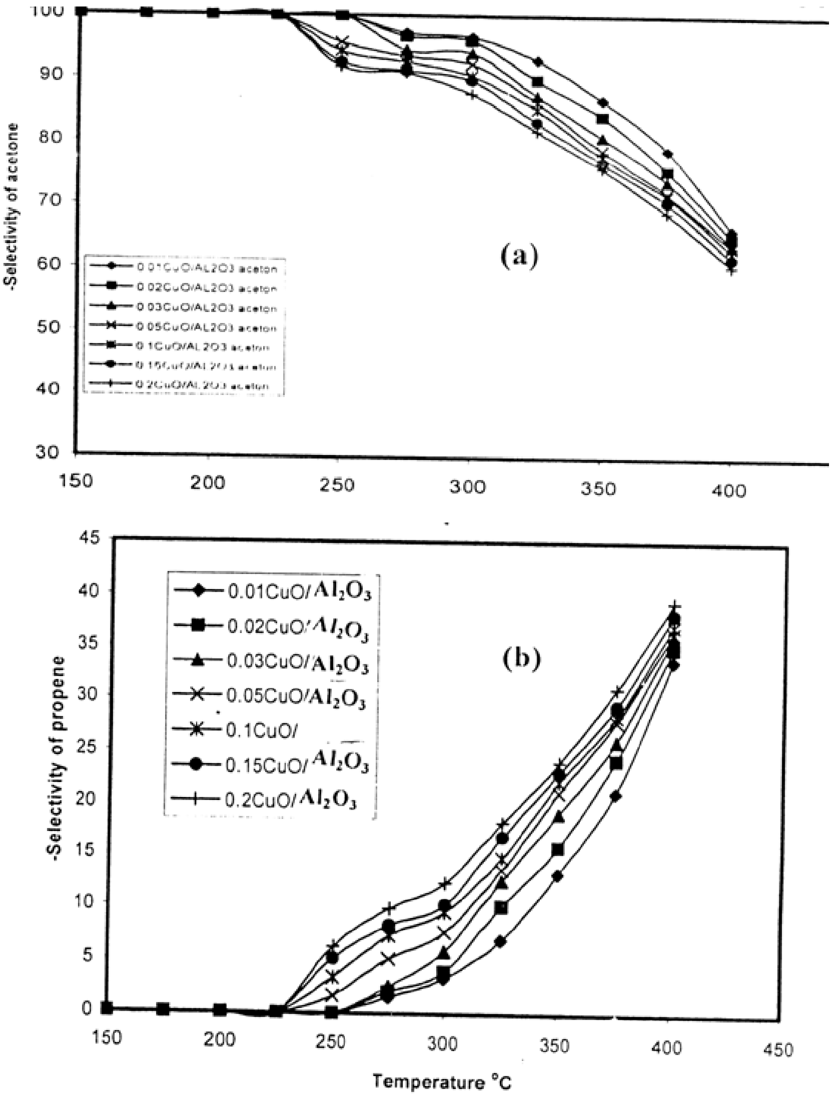


Fig. 12: Selectivity towards acetone (a) and propene (b) as a function of reaction temperature over CuO/Al_2O_3

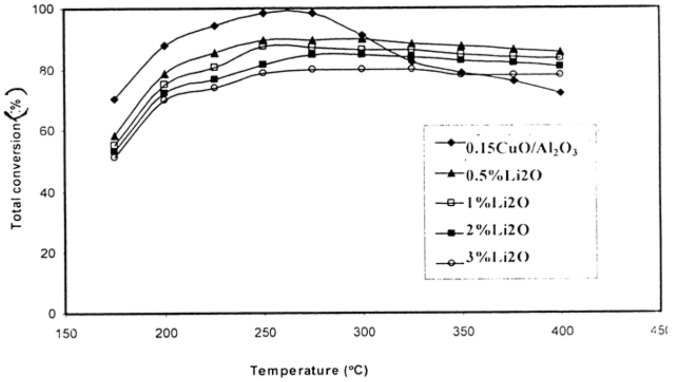


Fig. 13: Total Conversion of isopropanol as a function of reaction temperature over 0.15 CuO/AL_2O_3 and various extent of Li_2O 0.5,1,2 and 3 Mol.%

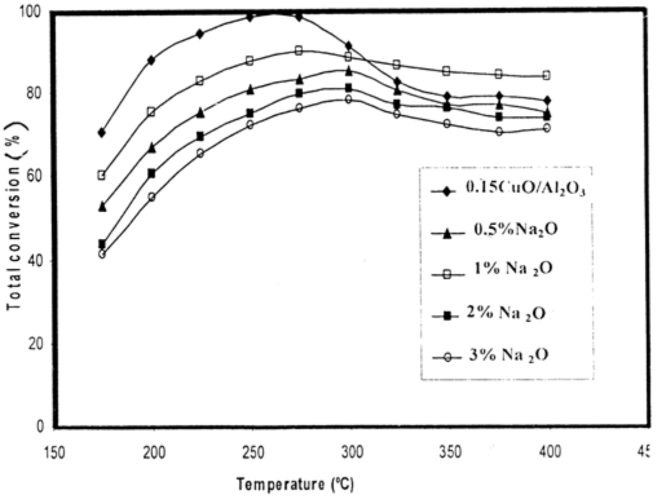


Fig. 13: Total Conversion of isopropanol as a function of reaction temperature over 0.15 K_2O/AL_2O_3 and various extent of Li_2O 0.5,1,2 and 3 Mol.%

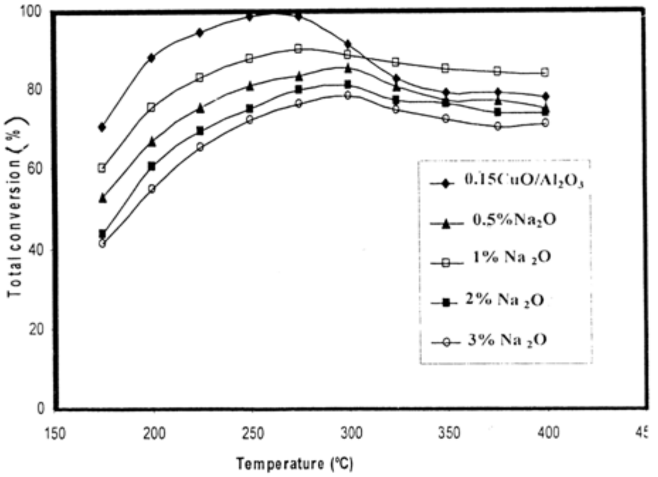


Fig. 14: Total Conversion of isopropanol as a function of reaction temperature over 0.15 Na_2O/AL_2O_3 and various extent of Li_2O 0.5,1,2 and 3 Mol.%

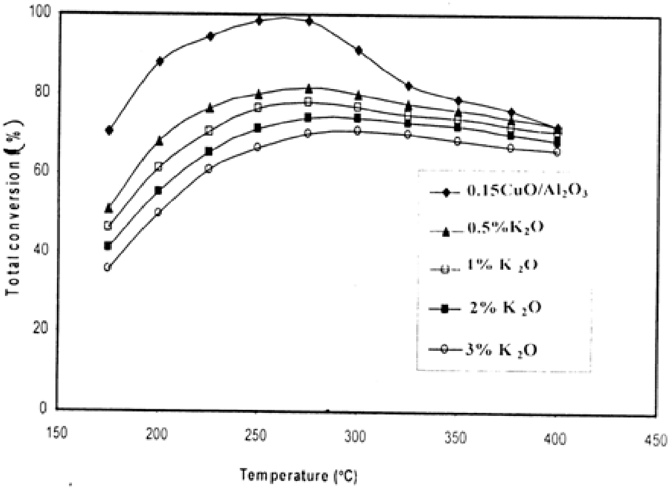


Fig. 15: Total Conversion of isopropanol as a function of reaction temperature over 0.15 K_2O/AL_2O_3 and various extent of Li_2O 0.5,1,2 and 3 Mol.%

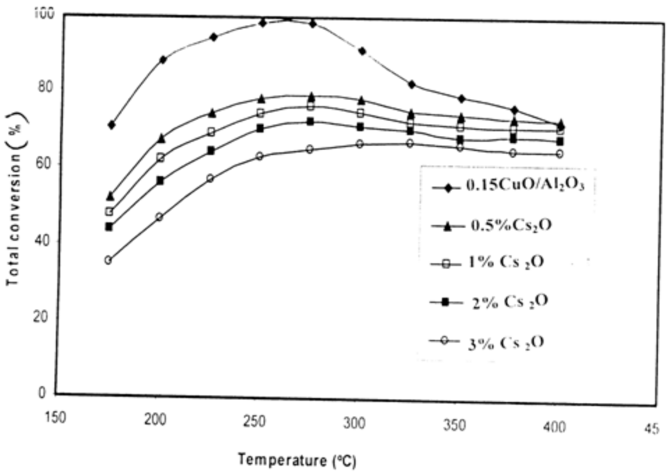


Fig. 16: Total Conversion of isopropanol as a function of reaction temperature over 0.15 Cs2O/AL2O3 and various extent of Li2O 0.5,1,2 and 3 Mol.%

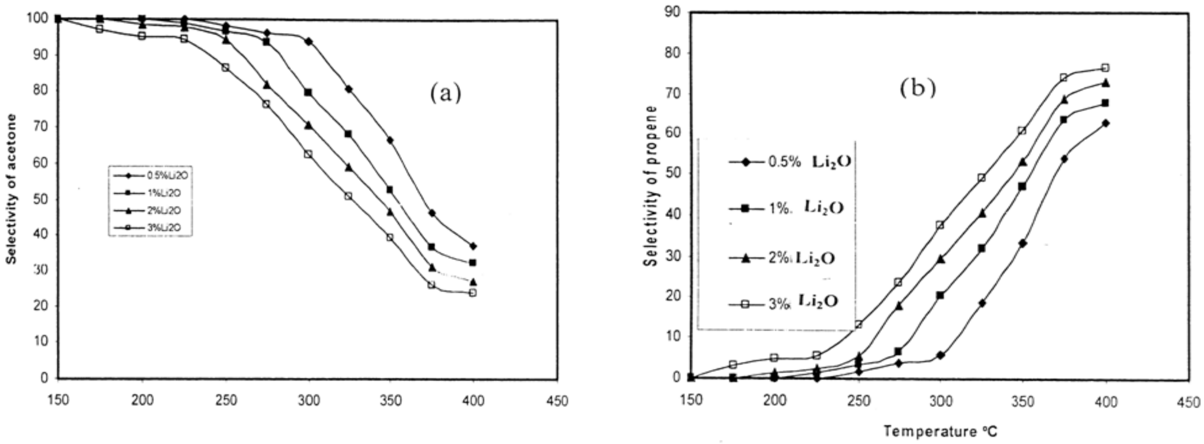


Fig. 17: Selectivity towards acetone (a) and propene (b) over over different concenteration of Li_2O(0.5,1,2 and3 Mol.%) over 0.15 CuO/Al_2O_3

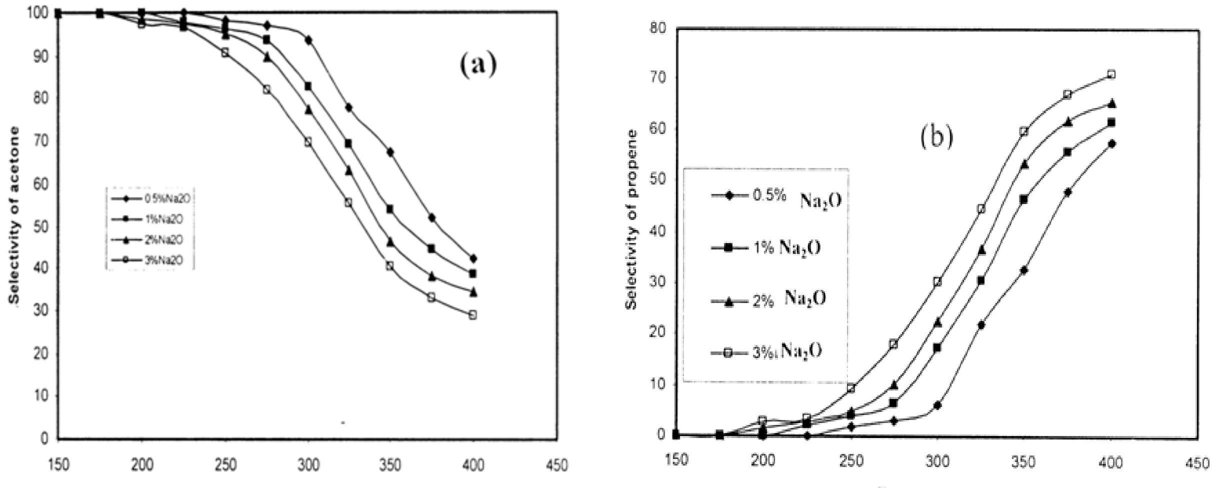


Fig. 18: Selectivity towards acetone (a) and propene (b) over over different concenteration of Na_2O(0.5,1,2 and3 Mol.%) over 0.15 CuO/Al_2O_3

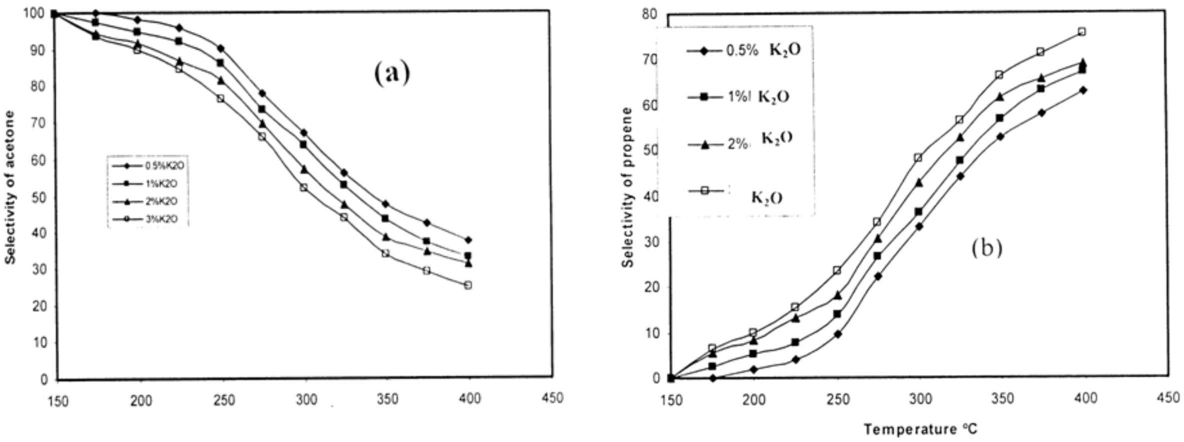


Fig. 19: Selectivity towards acetone (a) and propene (b) over over different concenteration of K_2O(0.5,1,2 and3 Mol.%) over 0.15 CuO/Al_2O_3

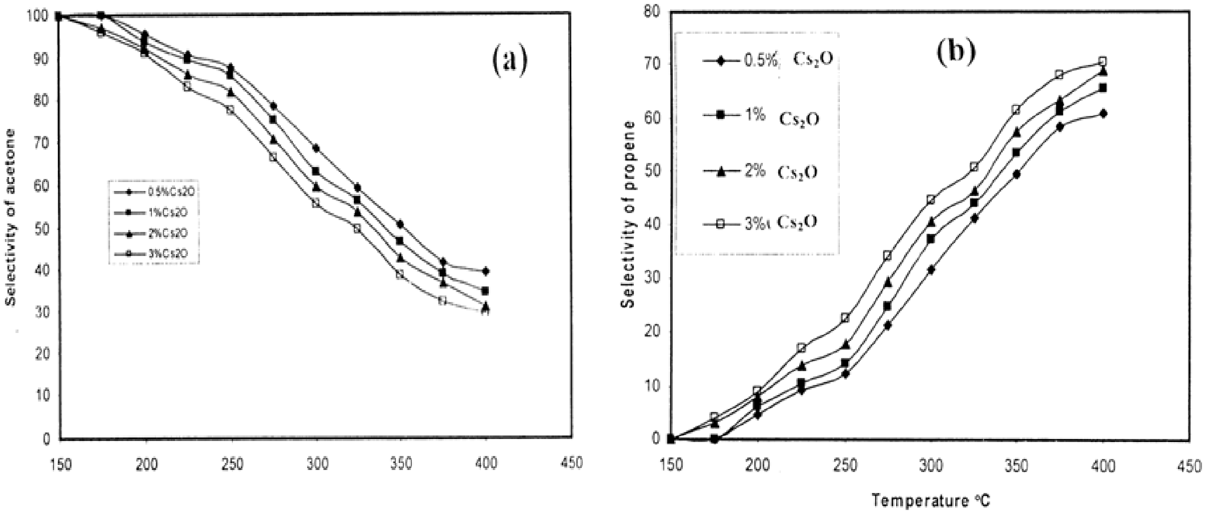
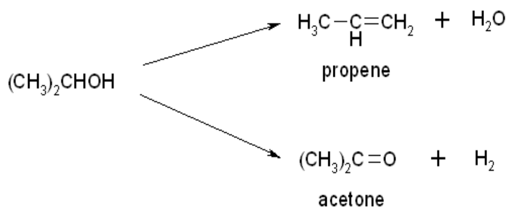


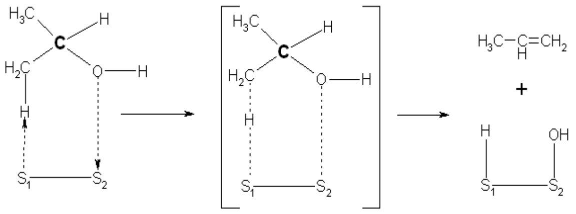
Fig. 20: Selectivity towards acetone (a) and propene (b) over over different concenteration of CS_2O(0.5,1,2 and3 Mol.%) over 0.15 CuO/Al_2O_3

These results point out to the role of alkali cations in much decreasing the particle size of CuO crystallites. In other words, the doped alkali cations hindered the grain growth process of CuO crystallites. This effect might led to an increasing the concentration of catalytically active constituent which is responsible of increasing the catalytic activity of dehydration reaction (propene formation). Moreever, doping with alkali cations may lead also to the formation of the layer of type $LiAl_5O_8$ [37] which is responsible for decreasing the catalytic activity of dehydrogenation reaction (acetone formation).

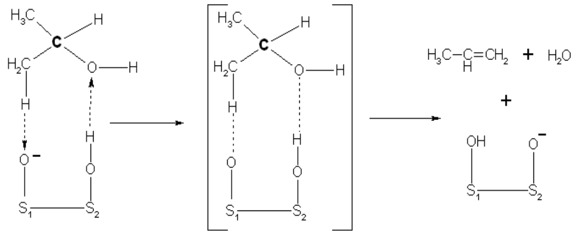
5. Mechanism of Iso-propanol Conversion: Several authors studied the mechanism of iso-propanol conversion over oxides to produce propene and acetone [38,39,40].



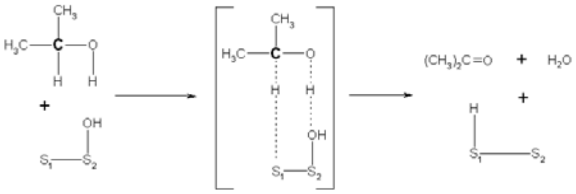
5.1. Mechanism of Propene Formation: The formation of propene depends on the acid centers (by E_2-mechanism) in which there are synchronous eliminate of B- hydrogen in iso-propanol and hydroxyl groups to the catalyst surface [41] as follows: Scheme (1)



While in other work [42] the mechanism was as follows: Scheme (2)



5.2.. Mechanism of Acetone Formation: Scheme (3) The production of acetone depends on a basic centers [43]. It is reported that oxides are considered to have the capacity of displaying Lewis acids and Lewis bases function simultaneously. These are localized in the surface sites , cations accessible for molecules from the gas phase as well as portions of hydroxyl groups being electron pair acceptor sites, Oxygen ions being electron pair donar sites



Summary and Conclusions: The catalysts used in this study were prepared by co-precipitation and wet impregnation methods of copper oxide supported over alumina with extent of loading from 0.01 – 0.2 mole CuO and 0.15CuO /Al_2O_3 catalysts prepared by wet impregnation method were doping by oxides of group IA such as lithium, sodium, potassium and cesium using different concentrations of 0.5, 1, 2 and 3 % metal oxides.

The selective prepared catalysts were characterized by several techniques such as: DTA, TGA, XRD, nitrogen adsorption at – 196^{o}C and catalytic conversion of iso-propanol using the flow system.

The main conclusions that can be drawn from the obtained results are :

[1]- Thermogravimetric analysis (TGA) was carried out on the aluminum hydroxide , copper hydroxide and 0.20 of copper hydroxide supported over aluminum hydroxide by co-precipitated method (0.2CuO/Al_2O_3).

(a) DTG for aluminum hydroxide $Al(OH)_3$ shows that most of the water is evolved in the temperature range 300^{o}C-410^{o}C in which the hydroxide is decomposed to form the oxide. At lower temperatures below 250^{o}C some little adsorbed water seems to be evolved, the remaining traces of water are then evolved at higher temperatures over 500^{o}C .

(b) DTG of copper hydroxide shows that some loosely bound water is evolved in the temperature range of 50-150^{o}C leading to the decomposition of copper hydroxide to copperic oxide and copperous oxide at 392^{o}C and 650^{o}C respectively

(c) DTG of the co-precipitated 0.2$Cu(OH)_2$/$Al(OH)_3$ at 100^{o}C and ends at 260^{o}C indicates that the evolution of some loosely bound water observed at 100-260^{o}C. Solid- solid interaction between the two oxides is observed at 390^{o}C.

(d) The DTA thermogram shows that for aluminum hydroxide the dehydration of aluminum hydroxide occurs at about 400^{o}C .

(e) For $Cu(OH)_2$ shows that $Cu(OH)_2$ transformed to Cu_2O at 392^{o}C and CuO at 695^{o}C .

(f) DT.A for 0.2 co-precipitated $Cu(OH)_2$/$Al(OH)_3$ shows that Al_2O_3 occurs only at 382^{o}C .

[2] -X-ray diffraction patterns were determined for the original oxides of Al, and Cu and also for the samples (0.01,0.05 and 0.2) CuO/Al_2O_3 prepared by co-precipitation and impregnation preheated at 400^{o}C in air.

(a) Al_2O_3 shows the presence of mainly γ – alumina (γ- Al_2O_3) phase and traces of boehmite (aluminum oxide hydrated $Al_2(OOH)_2$.

(b) X-ray diffraction of the preheated Cu hydroxide at 400^{o}C shows diffraction lines of both CuO and Cu_2O phases .

(c) X-ray diffraction patterns of supported CuO over γ-alumina prepared by co-precipitation and impregnation with its different concentrations (0.01, 0.05 and 0.2 mol %) can be summarized as follows : The γ- alumina preheated at 400^{o}C showed amorphous phase and either the impregnation or co-precipitation samples at (0.01-0.10%) of copper oxide with γ-alumina did not show any crystalline patterns (amorphous phase), as indicated in the X-ray diffractograme . This means that CuO is homogenously distributed on the surface of the alumina without any formation of crystalline CuO oxide phases. The increase of CuO on γ- alumina up to 0.10% shows a CuO crystalline phase at d-distance 2.32 and 2.52A^{o} for impregnation

[3]-Surface characteristics of the Al_2O_3 and $0.01CuO/Al_2O_3$, $0.05CuO/Al_2O_3$, $0.2CuO/Al_2O_3$ catalysts, prepared by co-precipitation and impregnation preheated at 400ºC in air were measured by the adsorption of nitrogen at – 196ºC . It is found that the adsorption isotherms are all essentially of type II of Brunauer's classification .In all samples the surface area decreases with increasing the loading content of CuO over Al_2O_3 prepared by co-precipitation and impregnation .The surface areas of the co-precipitated samples are higher than that of impregnated.

[4] -The catalytic activity of the supporting catalysts of the Al_2O_3, CuO, $0.01CuO/Al_2O_3$, $0.05CuO/Al_2O_3$ and $0.2CuO/Al_2O_3$ catalysts prepared by co-precipitation and impregnation preheated at 400ºC in air were studied by conversion of iso-propanol to produce acetone and propene .A number of pointes of considerable importance that :

(a) The increasing of CuO loading improves the total conversion of iso-propanol .

(b) The selectivity towards acetone formation decreased as a function of both reaction temperature and CuO loading .

(c) The selectivity towards propene formation increased as a function of both reaction temperature and CuO loading .

[5]- The catalytic conversion of iso-propanol was carried out over 0.01, 0.02, 0.03, 0.05, 0.10, 0.15 and 0.20 CuO/Al_2O_3 prepared by co-precipitation method and calcined at 400ºC for 3hrs. in the temperature range 175-400ºC. A number of pointes of considerable importance that:

(a) Increasing of loading extent CuO improves the total conversion of iso-propanol.

(b) The selectivity towards acetone formation decreases as a function of both reaction temperature and CuO extent .

(c) The selectivity towards propene formation improved as a function of both reaction temperature and CuO extent .

(d) The stability of the catalysts improved by increasing the CuO extent of loading .

(e) The catalytic activity of CuO/Al_2O_3 catalysts prepared by impregnation is higher than that prepared by co-precipitation method .

(g) The solid – solid interaction was found to take place at lower temperature for the catalysts prepared by impregnation than that prepared by co-precipitation .

[6] -Doping the metal oxide catalysts with foreign ions. In this study the effects of doping of $0.15CuO/Al_2O_3$ catalysts prepared by impregnation with Li_2O, Na_2O, K_2O and Cs_2O at different concentrations (0.5,1,2and 3 mol%) on its catalytic activity were studied. Besides all samples were calcined in air at 400ºC. It is found that doping Li_2O, Na_2O, K_2O and Cs_2O over $0.15CuO/Al_2O_3$ system shows that:

(a) The total converion of iso-propanol over doped and undoped catalysts increased with increasing the temperature from 175-275ºC and decreased with increasing temperature from 275-400ºC.

(b) The catalytic activity of $0.15CuO/Al_2O_3$ doped with different cations viz. Li^+, Na^+, K^+ and Cs^+ affected solids resulting in a progressive decrease in the activity of the undoped catalyst.

(c) The selectivity towards propene formation increases progressively by increasing the amount of Li_2O, Na_2O, K_2O and Cs_2O added.

(d) The selectivity towards acetone formation decreased by increasing the amount of Li_2O, Na_2O, K_2O and Cs_2O added.

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