

Research article

## Catalytic and surface characteristics of CoO/Al<sub>2</sub>O<sub>3</sub> by the catalytic oxidation of carbon monoxide

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### Abstract

Different weight percent of cobalt oxide supporting alumina were prepared, then calcinations of selected catalysts of different wt % CoO at temperature ranged from 500- 900C<sup>0</sup>. the structural properties of the catalysts calcinations were determined in through the different thermal analysis (D.T.A), and from the X. ray diffraction ( XRD ) of the prepared catalysts. The textural properties ( surface area, porosity ) of all catalysts were obtained by the B.E.T analysis of nitrogen adsorption isotherms measured at -196C<sup>0</sup>. the chemisorptions of hydrogen at 200C<sup>0</sup> was carried out on all the selected catalysts, where the results were analyzed to determine the metal surface area, the dispersion percent and the crystallite size. The catalytic oxidation of carbon monoxide with oxygen was performed at 200C<sup>0</sup> using flow rate system.

Calcinations catalysts containing less or equal 14wt% CoO did not show or exhibit any evidence for the existence of cobalt containing phase.

Catalysts which containing 25% wt of CoO and calcined at 500- 800°C exhibit the lines characteristic of CoO, the intensity of these lines increases with the increase of the calcinations temperature, But If the calcinations performed to 25% wt CoO at 900C<sup>0</sup>, the lines characteristic to CO/Al<sub>2</sub>O<sub>3</sub>. The surface area decreases and the mean pore radius increases with the increase of metal loading and due to the rise of the calcinations temperature. The metal surface area of dispersion percent decreased so the crystallite size increased with the increase of metal loading and calcinations temperature.

The number of molecules of carbon monoxide converted to carbon dioxide per atom of exposed (cobalt metal per second) of catalytic oxidation of carbon monoxide is related to the metal surface area. dispersion percent and is independent on the specific surface area.

**Key words:** Preparation technique, D.T.A, XRD, GC, textural properties and specific catalytic activity.

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## Introduction

It has been well established that the performance of a heterogenous catalyst does not only depend on the intrinsic activity of its components, but also on its texture and stability.<sup>(1)</sup>

The texture and the stability of supported metallic catalyst are mainly dependent on the chemical composition,<sup>(2)</sup> method of preparation,<sup>(3)</sup> calcinations temperature<sup>(4)</sup> doping with certain foreign cations<sup>(5)</sup> and subjecting to ionizing radiations.<sup>(6)</sup>

Cobalt supported on alumina, silica or zirconium has been found to exhibit high activity towards hydrogenation of benzene,<sup>(7)</sup> carbon monoxide and carbon dioxide, the conversion of cyclopentadiene to cyclopentene and low temperature reduction of (NO)<sub>x</sub><sup>(8)</sup>.

For supported metallic catalyst, the surface area of the metal is the most important factor in determining the catalytic performance, particularly when the metal atoms at the surface act as active sites for the reaction.

The metal surface area is measured from the uptake of a gas, which is chemisorbed on the metal surface but is only adsorbed to a relatively small value on the nonmetallic components.

More investigations are therefore required for a better understanding of multi-component catalysts.

Transition metals exchanged or loaded alumina have been studied experimentally as catalysts for several redox reactions particularly those of environmental concern such as oxidation of carbon monoxide and reduction of (NO)<sub>x</sub><sup>(9)</sup>.

The present work is concerned to study the effect of the extent of loading<sup>(10)</sup> and calcinations temperature on the textural properties of CoO/ Al<sub>2</sub>O<sub>3</sub> catalyst.

The effect of these parameters on the chemisorptions of hydrogen and on the catalytic activity of oxidation of carbon monoxide with oxygen was investigated.

## Experimental

Alumina and cobalt hydroxide were prepared from their corresponding nitrate solutions using 2M NaOH. Precipitation was made at constant pH of 9 and at 50C<sup>0</sup>, with continuous stirring.

The precipitates thus obtained were washed with bi-distilled water till free from nitrate ions and followed by warmed at 70C<sup>0</sup> to transform into slurries.

Appropriate amounts of the slurries were mixed using an electric mixer during 5 hour, then dried at 120C<sup>0</sup> and kept in Stoppard bottles before calcinations.

Samples 1,2,3,4 and 5 containing 2,4,8,14 and 25g of CoO per 100g of all samples were obtained, the above samples were calcined at 500,600,700,800 and 900C<sup>0</sup> in open air for six hours the sample-2 will stand for the catalyst containing 4 wt% CO, calcined at 600C<sup>0</sup>.

Differential thermal analysis (D.T.A) of preparative samples from 1-5 was performed.

The thermal changes justified the choice of the temperatures of calcinations X-ray diffraction (XRD) patterns of calcined catalysts were determined.

The adsorption of nitrogen at -196C<sup>0</sup> was measured for all catalysts, from the adsorption and the outgasing at 200C<sup>0</sup> for six hours under a reducing pressure of 10<sup>-6</sup> torr.

Nitrogen adsorption was followed up to a relative vapor pressure of about 0.95 to determine the total pore volume of the selected catalyst. Desorption was also followed until the hysteresis. loops are closed.

Hydrogen adsorption measurements were performed at 127C<sup>0</sup> in a conventional constant volume high vacuum apparatus on catalyst reduced at 400C<sup>0</sup> for six hours at hydrogen flow rate of 0.2 mol/h, followed by outgassing for six hours at the same temperature.

The catalyst temperature was reduced at 127C<sup>0</sup> and left for three hours before hydrogen adsorption at this temperature.

The linear nature of the adsorption isotherm is extrapolated to zero pressure to discard physical adsorption.

The catalytic activities of different prepared catalysts for carbon monoxide oxidation with oxygen were also measured at atmospheric pressure and at 200C<sup>0</sup> by using a flow reactor. In the catalytic system, the gaseous reactants carbon monoxide and oxygen were maintained at 80 and 40 torr, respectively with nitrogen gas being employed to control the total pressure to one atmosphere. All gases were supplied from appropriate cylinders, which were connected to the reaction tube using stainless steel tubing. The temperature was monitored via a thermocouple in contact with the catalyst bed. A Varian 3300 gas chromatograph (GC) with TCD detector was used to analyze the products. A 3m column packed with hayesep DB 100/120 used a temperature ranged from 40 to 100C<sup>0</sup> separate N<sub>2</sub>, O<sub>2</sub>, CO and CO<sub>2</sub>

## Results and Discussion

### 1 Structural Properties

Fig-1 shows that D.T.A curves of preparations 1,2,3,4, and 5, exhibit well-developed endothermic change around 117C<sup>0</sup> and a less developed endothermic at 107C<sup>0</sup>. The 117C<sup>0</sup> endotherms may stand for the loss of the free water adhering to the solid and the endotherms at 107C<sup>0</sup> are related to the loss of specifically sorbed water. The endothermic peaks located at 367-377C<sup>0</sup> are due to the transformation of Al(OH)<sub>3</sub> to Al<sub>2</sub>O<sub>3</sub>.

The preparative catalyst 4 and 5 exhibit poorly developed endotherms at 600C<sup>0</sup>, but there are an exception of catalyst- 5 showed an exothermic effect around 900C<sup>0</sup> which may be attributed to the reaction between Al<sub>2</sub>O<sub>3</sub> and CoO forming new spinel structure.

The XRD patterns of all the thermal catalysts containing less or equal to 14w% CoO, showed completely amorphous structures.

There are an exception of the catalyst-4 at 900C<sup>0</sup> is poorly developed peaks characterizing CoO phase are shown in Fig-2. The absence of any crystalline phase in the above mentioned catalysts may be attributed to the high surface area of the alumina support, which allowed well dispersion of CoO.

For catalyst-5 at 500, 600, 700 and 800C<sup>0</sup>, the obtained lines characterizing CoO exist and their intensity increases with the rise of the calcinations temperature. The XRD of catalyst-5 at 900C<sup>0</sup> indicated the appearance of new spinel structure CoAl<sub>2</sub>O<sub>3</sub>. The same results have been previously reported<sup>(11)</sup>. Where XRD of CoO/Al<sub>2</sub>O<sub>3</sub> catalysts with less or equal 14w% CoO did not show any cobalt phase calcinations.

The dependence of the crystalline structure on the chemical composition and thermal treatment temperature indicates that the crystallization is rendered to the heat and mass transfer<sup>(12)</sup>.

There are no evidence has been obtained from XRD to explain the endotherms exhibited by preparations of catalysts 4 and 5 at 600C<sup>0</sup>.

### 2 Textural Properties

The adsorption of nitrogen at -196C<sup>0</sup> on all the calcined products proved to be rapid indicating the absence of ultra- fine pores in which adsorption is controlled by activated diffusion, the equilibrium was attained in 20 min, where 30 min intervals was allowed between successive adsorption measurements to prove the equilibrium conditions. The adsorption of nitrogen on all the investigated catalysts exhibited isotherms between catalyst-2 and catalyst-4.

The depress of the initial portions of the nitrogen adsorption isotherms becomes less pronounced with the rise of the calcinations temperature.

The desorption branch meets the adsorption branch at some intermediate relative pressure giving closed hysteresis loop. The area of the hysteresis loop increases with the rise of the calcinations temperature of the catalyst, representative adsorption – desorption isotherms of nitrogen are shown in Fig-3. The specific surface area  $S_{BET}$  ( $m^2/g$ ) were calculated by applying the conventional BET equation to the adsorption isotherms.

The total pore volume  $v_t$  ( $ml/g$ ) was obtained from the volume of nitrogen adsorbed at relative pressure equal to 0.95, i.e. attaining to saturation pressure.

The mean pore radius  $r_p$  (nm) for each catalyst were also calculated from the relationship  $r_p = 2v_t / S_{BET}$  Fig-4.shows the textural properties<sup>(13)</sup>  $S_{BET}$  and  $r_p$  as a function of cobalt percentage.

It is evident from Fig-4.that  $S_{BET}$  continuously decreased and  $r_p$  increased with the increasing of cobalt content. Alumina becomes the major component in all the catalysts investigated which may act as a support for cobalt or cobalt oxide.

The dispersion and crystalline size of the latter depend on its content in the system. the textural properties<sup>(14)</sup>  $S_{BET}$  and  $r_p$  are also dependent on the calcinations temperature, the specific surface area decreases and the mean pore radius increases with the increases and the mean pore radius increases with the increases of the calcinations temperature.

In the bases of thermal treatment of a solid, two processes may be appears activation at relatively low temperature and sintering at high temperatures<sup>(15)</sup>.

During sintering of solids, the following phenomena are observed, particle – particle adhesion, grain growth, pore widening, shrinkage and some times collapse of the structure<sup>(16)</sup>.

At some what higher temperatures, solid reactions giving crystalline phases may take place and are associated with considerable changes in the textural properties<sup>(17)</sup>.

Fig-5.shows that the  $\log S_{BET}$  versus  $1000/T$ , where (T) is the calcinations temperature in Kelvin.

The examination of Fig-5.showing that, in the temperature range from ( $500$  to  $800C^0$ ), the relation ship is quite linear, regardless of the chemical composition. Since, the slops of these straight lines varies with the chemical composition of cobalt content being 0.2, 0.3, 0.5, 0.9 and 1.4 for catalysts 1,2,3,4 and 5 respectively.

The above values, refers to the importance of the chemical composition in determining the textural characteristics of di and poly component systems. At  $800C^0$ , a pure deviation from linearity which increased with cobalt oxide content is noticed. Above  $800C^0$ , other processes may be appeared to operate the following different mechanism than exhibited between  $500$  and  $800C^0$ .

It has been previously mentioned that the (XRD) of catalyst-4 at  $800C^0$  indicated the existence of CoO phase and for catalyst-5of  $900C^0$  showed the existence of spinal structure  $CoAl_2O_3$ . The appearance of new crystalline phase at  $900C^0$  may be referred to the acceptable changes in the textural properties of the catalysts calcined at this temperature.

### 3 Chemisorption of Hydrogen

The hydrogen uptake of each catalyst is given in table-1,these values allowed the determination of some interesting adsorption parameters. The use of chemisorptions for metal surface area determination requires the knowledge of chemisorptions action ( $X_m$ ), at monolayer coverage and the number of metal atoms per unit area of the surface ( $n_s$ ). For the determination of ( $X_m$ ), the adsorption was followed by the increase of hydrogen pressure up to 200 torr. to a very high pressure compared to the location of the monolayer, and the linear part of the isotherm when extrapolated to zero pressure to discount physisorbed hydrogen, ( $n_s$ ) was taken as  $1.47 \times 10^{19}$  atom/ $m^2$ <sup>(18)</sup>. The adsorption parameters considered in the investigation are S, D and R. where :

S : is the metal surface area of the catalyst.

D : is the crystallite size of cobalt.

R : is the percentage dispersion of cobalt on alumina surface.

The following relationships correlate these different parameters S, D and R ,Since:

$$S \text{ (m}^2\text{/g)} = X_m / ns$$

% R= No of available Co atom at the surface / Total No of Co atom of bulk

$$D = 6 \times 10^3 / \rho.s.$$

Where

$\rho$  : is the density of cobalt = 8.86 g/ cm<sup>3</sup>.

The values of S,D and R are tabulated respectively in table-1

It is clear that metal surface area and the dispersion percentage decreases, while the crystallite size increases with the increase of metal content and with the increase of the calcinations temperature.

These pronounced changes may probably affect the catalytic performance of Co/Al<sub>2</sub>O<sub>3</sub> catalysts.

#### 4 Catalytic Oxidation of Carbon Monoxide

The catalytic oxidation of carbon monoxide with oxygen was performed at 200C<sup>0</sup>. The number of molecules of carbon monoxide which converted to carbon dioxide per atom of exposed cobalt metal per second also calculated for different alumina supported cobalt catalysts are given in table-1, some trials were made to relate the catalytic oxidation activity to some parameters characterizing metal- supported catalysts.

Fig-6 shows that (TON) decreases with the increase of metal loading. For each set of catalysts prepared at the same temperature, a separated curve represents the relation between (TON) and metal loading. It is also seems that (TON) is dependent also on other catalytic parameters.

Fig-7 shows that (TON) as a function of metal surface area, one straight line with a slight deal of scattering is obtained for all the catalysts, regardless of their calcinations temperature or metal loading. This refers to the important real of the active surface area in determining the catalytic oxidation activity. It is well established that in the system under investigation and also in similar system under investigation and also in similar systems, the metal atoms at the surface represent actually the active sites for carbon mono oxide oxidation with oxygen<sup>(19)</sup>. The extrapolation of the straight line intersects the metal surface axis at a certain value corresponding to zero oxidation activity. The second successful trial was made between (TON) and the percentage dispersion of the metal atoms.

Fig-8 shows the relation. Once again a single straight line can satisfactorily represent the relationship. It is seemed that the dispersion of the active sites is a controlling factor in determining the activity of the catalyst. The dispersion axis at a certain value which corresponding to zero oxidation activity.

After investigation there is no measurable catalytic oxidation activity was exhibited by catalyst-5 at 900C<sup>0</sup>. For this particular catalyst, the R- value is lower than the point of zero oxidation activity depicted from Fig-8,the crystallite size of catalyst-5 at 900C<sup>0</sup> is considerably high and may refers to the formation of the spinal structure which illustrated by (X R D).

It remains now to point out that the specific surface area  $S_{\text{BET}}$  of the catalyst as determined from nitrogen adsorption at  $-196\text{C}^{\circ}$ ,<sup>(20)</sup> is not an important factor in determining the catalytic oxidation activity. No quantitative or even qualitative reactions relation could be predicted between  $S_{\text{BET}}$  and TON, as shown in Fig-9.

The major fraction of the specific surface area of metal supported catalyst is contributed by the support and support and in the specific surface area of the support decreases upon supporting other metal or metal oxide on the surface of this support. It can be assumed that the specific surface area only make allowance for good dispersion of the active sites of cobalt metal atoms in the present investigation.

## 5 Conclusions

Finally, from the above results and discussion, it can be concluded that the oxidation of carbon monoxide and possibly of other reactants, with oxygen is the structural sensitive reaction in which the total surface area is not a controlling factor<sup>(21)</sup>. The metal atoms at the surface represent the active sites for oxidation. The area of the surface metal atoms is considered as the active surface area responsible for the catalytic oxidation activity.

The efficient dispersion of the metal atoms contributes significantly to the activity of supported metal catalysts.

**Table 1: Catalytic parameters of Co/Al<sub>2</sub>O<sub>3</sub> catalysts**

Catalyst (No)	Calcinations Temperature (C <sup>0</sup> )	(X <sub>m</sub> )x10 <sup>5</sup> (mol/g)	S (m <sup>2</sup> /g)	D (nm)	% R	TONx10 <sup>-3</sup>
1	500	14	496	1.47	97	66
	600	13.9	493	1.48	96	64
	700	13.8	487	1.50	94	60
	800	12.6	437	1.65	87	54
	900	10.4	347	2.06	65	40
2	500	23.4	440	1.66	90	60
	600	23.2	436	1.67	89	55
	700	21.8	428	1.70	84	52
	800	19.6	370	1.68	75	47
	900	15.2	201	2.20	63	31
3	500	40	390	1.90	86	50
	600	39.1	381	1.94	84	49
	700	37.6	360	2.02	81	46
	800	32.5	310	3.26	71	42
	900	23	312	4.31	60	23
4	500	44	290	2.60	56	30
	600	42	280	2.70	54	28
	700	40	260	2.51	43	20
	800	35	222	3.57	36	16
	900	25.9	160	4.63	24	5

5	500	59	260	2.63	46	19
	600	52.4	210	3.69	42	15
	700	42	161	4.75	33	12
	800	31.2	136	2.75	25	9
	900	22.4	100	7.89	17	-

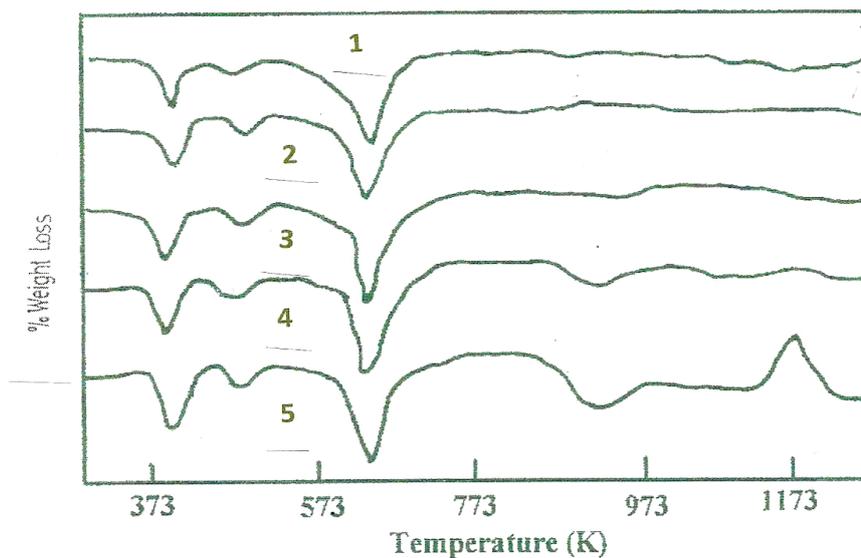


Figure 1: DTA Curves of 1, 2, 3, 4 and 5

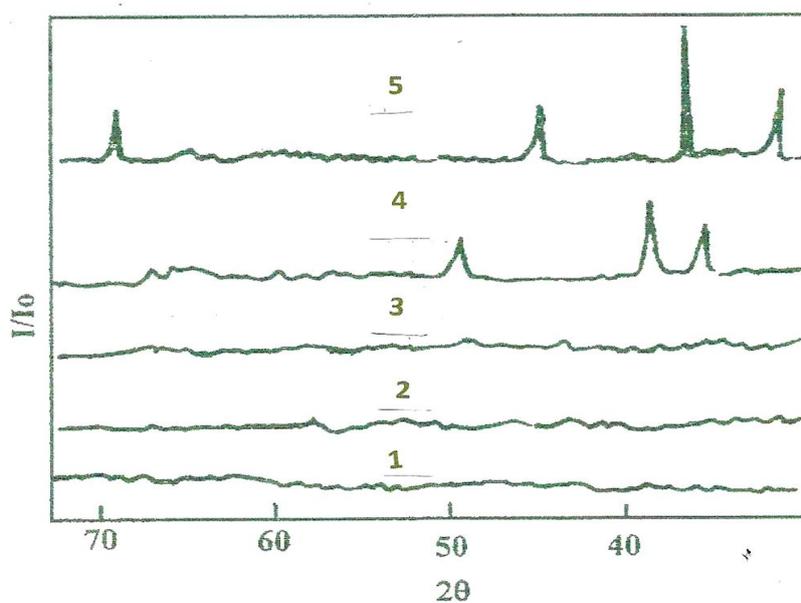


Figure 2: XRD of 900°C- Calcinations products

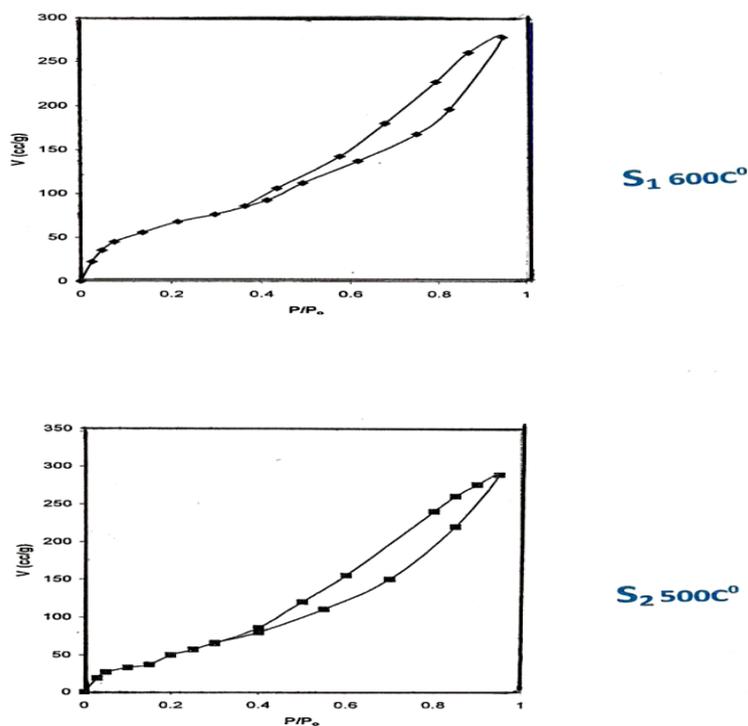


Figure 3: Representative adsorption-desorption isotherms of nitrogen at  $-196^\circ\text{C}$ .

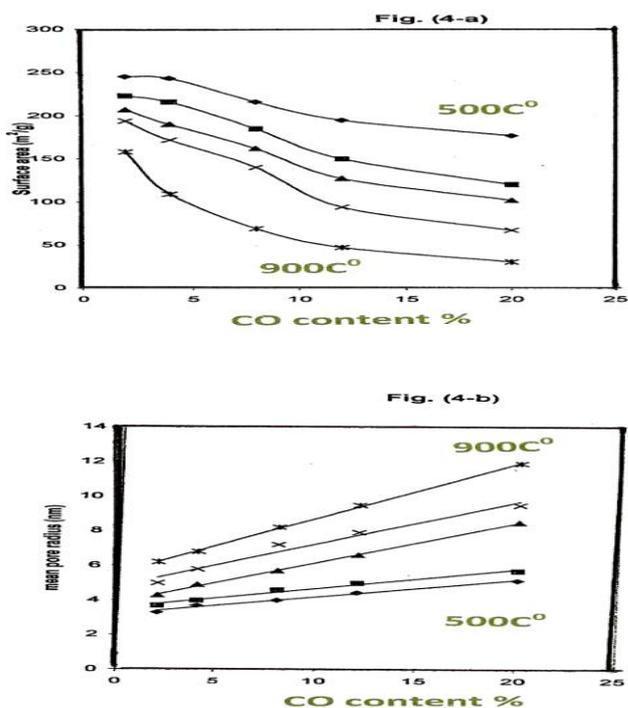


Figure 4:  $S_{\text{BET}}$  and  $r_p$  as function of Co constant (Wt%)

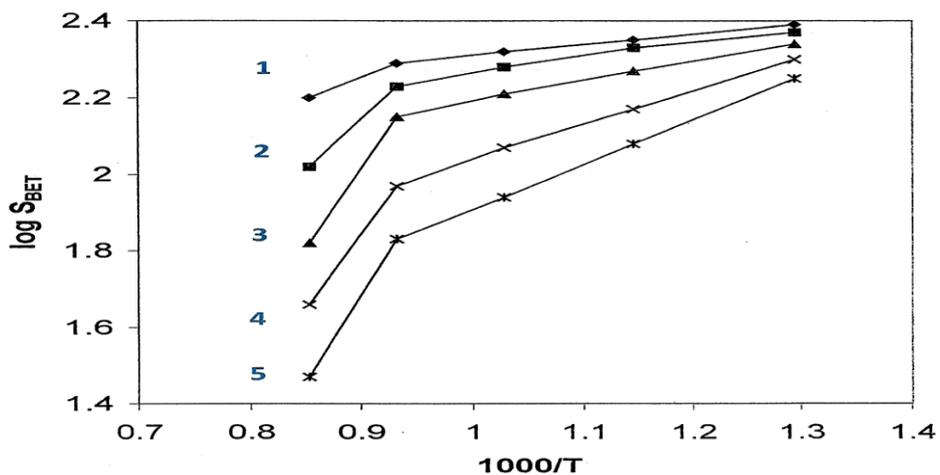


Figure 5: Log S<sub>BET</sub> versus 1000/T

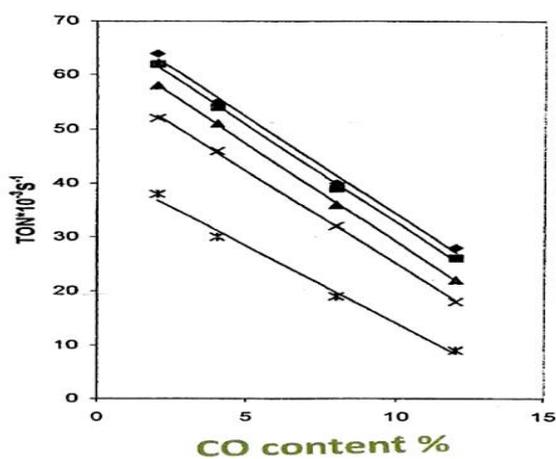


Figure 6: TON versus metal loading

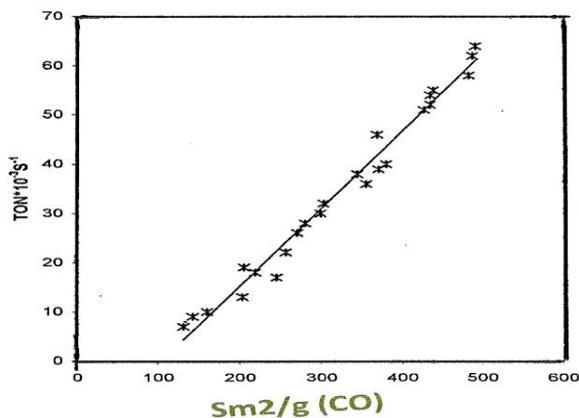
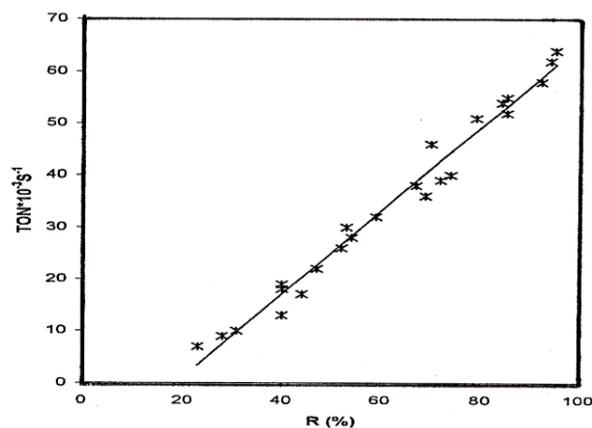
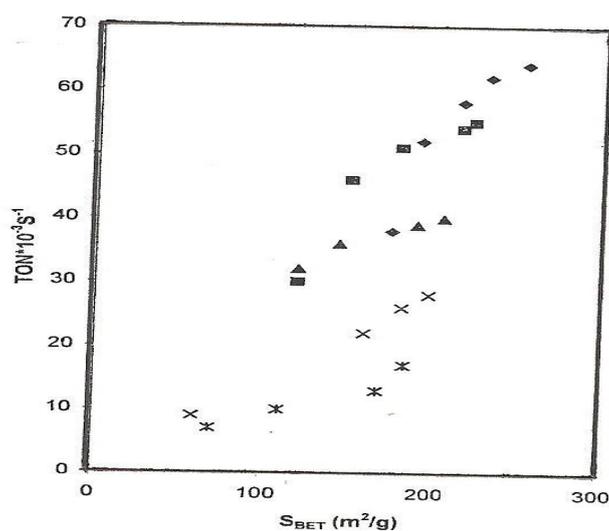


Figure 7: TON as a function of metal surface area



**Figure 8:** TON versus % dispersion of metal atoms



**Figure 9:** TON versus S<sub>BET</sub>

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