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DEACTIVATION OF LOW TEMPERATURE SHIFT CATALYSTS

Part I Poisoning by Hydrogen Sulphide

By

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Abstract

Premature failure of Low Temperature Co-Conversion Catalyst in industrial converters is mostly due to poisoning by sulphur and chlorine. The present study was undertaken with four varieties of commercial catalysts to determine the quantitative relationship between the amount of poison and the extent of deactivation. The results show that poisoning is cumulative in nature and the loss of catalyst activity depends on the total amount of poison as well as its rate of introduction. The poisoning curves generally indicate homogeneous absorption of the poison. Some amount of pore mouth poisoning also takes place.

The activity of the fresh and the poisoned catalyst bears a linear relationship with copper surface area of catalyst. The higher the loss of copper area, the more severe is the deactivation. Again loss of copper area does not depend on the copper content or copper surface area of fresh catalyst. Alumina containing catalyst seems to have high sulphur tolerance.

Introduction

The incorporation of low temperature (hereinafter referred to as LT) shift catalyst for the conversion of CO ($CO+H_2O=CO_2+H_2$) has become a standard practice in the design of modern ammonia plants. The two factors that are responsible for LT catalyst failure are thermal sintering and poisoning. It has been shown earlier[1] that thermal sintering can be greatly eliminated by correct catalyst formulation.

For a properly formulated catalyst, working under correct operating conditions, poor performance may be attributed to the poisoning of the catalyst by traces of sulphur and chlorine present in the feed gas and the

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rate of introduction of these poisons determines the useful life of the catalyst. Although the design of most of plants includes a bed of ZnO upstream LT catalyst for sulphur removal, chlorine guards are much less popular. The role of these poisons though well known for a long time, publication dealing with mechanism of poisoning and its quantitative relationship with deactivation is surprisingly absent.

The present work deals with poisoning of LT catalysts by hydrogen sulphide in fixed bed laboratory reactors. For the utilization of the results of such studies for evaluating catalyst life in industrial converters, it is necessary that the laboratory experiments should duplicate plant conditions. This is rather difficult, since the poisons are effective even in very small concentrations and much difficulty is generally faced for their feeding and analysis. In fixed bed reactors, a gradient of poison is known to exist[2~3] with respect to the bed length which again cannot be duplicated in the laboratory. However, experimental conditions have been chosen to represent industrial conditions as far as practicable. The surface changes of the catalyst has been followed by physical measurements like Cu surface, ZnO surface and total surface to get an insight into the mechanism of poisoning.

Experimental

Four varieties of commercial LT catalysts were taken for this investigation. The chemical composition of these catalysts are given in Table 1.

TABLE 1. Chemical Composition of Catalysts

Item	Catalyst			
	A	B	C	D
% L.O.I.*	11.60	2.10	11.96	1.20
% CuO	25.30	33.00	10.25	32.00
% ZnO	28.50	62.50	24.60	66.00
% Al_2O_3	26.70	—	52.80	—
% TiO_2	4.10	—	—	—
% Fe_2O_3	3.10	1.50	—	—

* Loss on ignition at 500°C

The activity measurements and poisoning were carried out in an apparatus shown in Fig. 1.

Feed gas: Pure methanol-water mixture was cracked over nickel catalyst at 700°C and the resultant gas was mixed with steam, passed through a

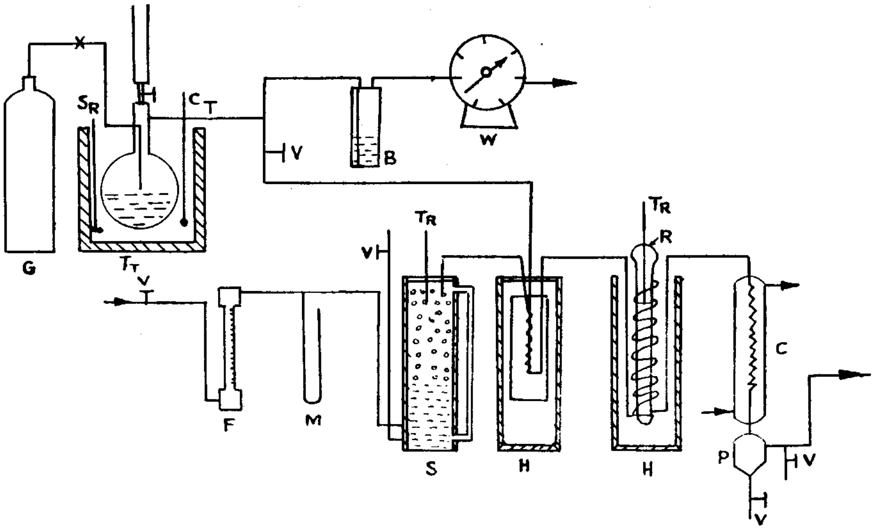

Fig. 1. Apparatus for poisoning and activty test.
G-Nitrogen gas cylinder, S_R-Stirrer, T_T-Thermostat, C_T-Contact thermometer, V-Valve, B-Bubbler, W-Wet gas meter, F-Rotameter, M-Manometer, S-Saturator, T_R-Thermometer, H-Furnace, R-Reactor, C-Condenser, P-Condensate trap.

bed of LT catalyst to reduce the CO content and to remove sulphur compounds if present. The gas after dilution with nitrogen had the following volumetric percentage composition: carbon monoxide = 10.5, carbon dioxide = 13.0, hydrogen = 57.0, nitrogen = 15.7 and methane = 3.8. This gas was compressed and stored in pressure vessel, passed over copper at 300°C, and scrubbed with water before feeding to the reactor. No H_2S could be detected in the feed gas.

H_2S dosing: H_2S was prepared by the reaction of sodium sulphide with oxalic acid. Saturated solution of oxalic acid was taken in a flask placed in a thermostat at 60°C and sodium sulphide (0.006 N) was added from the separating funnel drop by drop. The rate of addition was controlled by using a fine capillary. The generated H_2S was chased with nitrogen flowing at constant rate. The method was found to be very satisfactory for obtaining constant rate of H_2S evolution. The concentration could be changed whenever necessary by varying either the sulphide concentration or the rate of addition. The H_2S content of the carrier nitrogen was determined by precipitating as cadmium sulphide followed by iodimetric titration. A measured portion of N_2-H_2S mixture containing 30 ppm H_2S was then mixed with feed gas. In two sets of experiments, H_2S concentration in N_2 was maintained at 300 ppm. Equivalent H_2S concentration in wet feed gas were 6 and 60 ppm respectively.

Activity test and poisoning: The original catalyst pellets were crushed and sieved to obtain granules of $-16+20$ mesh (BSS) size. 5 cc catalyst were used and the height of the catalyst bed was 6.3 cm.

Catalyst activity was always determined under the following fixed conditions, space velocity = 10,000, steam/gas ratio = 1.0, pressure = 1 atm., catalyst bed temperature (top) 220°C. Reduction was carried out with 1% hydrogen in nitrogen/steam mixture and the catalysts were worked for 24 hours before determining the initial activity. Introduction of H_2S was then started by mixing carrier nitrogen containing H_2S, with the feed gas. After dosing of certain amount of H_2S, activity was determined with H_2S free gas. Poisoning and activity measurements were continued till the relative activity was about 25% (except sample A, where the fall in activity was very low). During H_2S dosing dry gas space velocity was maintained at 2,000 to ensure complete absorption of H_2S by the catalyst. This was confirmed by testing the exit gas for H_2S which was never detectable and by the analysis of discharged catalyst which showed that all the sulphur has been retained by the catalyst. Further the sulphide sulphur content of the catalyst was found to equal the total sulphur figure indicating that all the sulphur has been absorbed as sulphide. In order to confirm the results, the experiments were duplicated by simultaneously charging each catalyst sample in two reactors. The difference between the results were negligible and average value has been reported.

The results of the activity test has been expressed as specific reaction rate constant k, calculated by using the rate equation developed by MOE.[4)]

$$\frac{k}{SV}=\frac{K}{\sqrt{-q}}\left[\ln\left[\frac{2WX-U-\sqrt{-q}}{2WX-U+\sqrt{-q}}\right]-\ln\left[\frac{-U-\sqrt{-q}}{-U+\sqrt{-q}}\right]\right] \qquad (1)$$

where, SV = vol. of wet gas/hour/volume of catalyst
K = Thermodynamic equilibrium constant
$W=K-1$
$U=K(A+B)+(C+D)$
$\sqrt{-q}=\sqrt{U^2-4WV}$
$V=K(AB)-(CD)$

where A, B, C and D are initial concentrations of CO, H_2O, CO_2 and H_2 respectively (in molar units). X = CO converted in mole fraction.

Surface area and pore size distribution: After the activity measurements, the sample was cooled to room temperature and carefully transferred to a specially designed sample tube under nitrogen flow and thus oxidation was prevented. The sample tube was sealed at bottom and then attached to an all glass volumetric adsorption apparatus.

Cu-Surface Area: The surface area of copper in the catalyst was determined in a manner described earlier.[5] In this method the catalytic room temperature oxidation of carbon monoxide by oxygen has been utilized to estimate the amount of oxygen adsorbed on cuprous oxide. This reaction is characteristic of cuprous oxide and there will be no interference by the oxides present in LT catalyst as they catalyse the reaction only at higher temperatures.

ZnO Surface Area: The surface area of ZnO was determined by hydrogen chemisorption following the method of TAYLOR and LIANG.[6] The absorption of hydrogen at −196°C and 1 atm. pressure has been taken to be 80% of the monolayer volume. The capacity of other constituents for hydrogen chemisorption has been assumed to be negligible under the experimental conditions. The area of ZnO was calculated using the relationship

$$\text{ZnO area} = \frac{V_{H_2} \times 100}{80} \times \frac{N\sigma \times 10^{-23}}{22.4}\, m^2$$

σ = Cross sectional area of nitrogen molecule, Å^2
N = Avogadro number
V_{H_2} = Vol. of H_2 adsorbed at 760 mm pressure
(Extrapolated value).

Total surface area: The BET surface area was determined by nitrogen adsorption at −196°C.

Pore size distribution: The pore size distribution was measured by the mercury penetration method. The total pore volumes were determined by mercury and helium displacement method.

Results and Discussion

A. Deactivation

Fig. 2 shows the loss in activity of different LT catalysts as a function of the quantity of sulphur dosed. The rate of sulphur introduction was maintained at 6 ppm in wet gas. For all the samples, initially, the activity decreases approximately linearly with increasing amount of sulphur until substantial part of the catalyst has been deactivated. It is then followed by an inflection, when the fall in activity is much less steep. In these type of poisoning graphs,[7] the effect of poison upto the region of inflection can be represented by an equation,

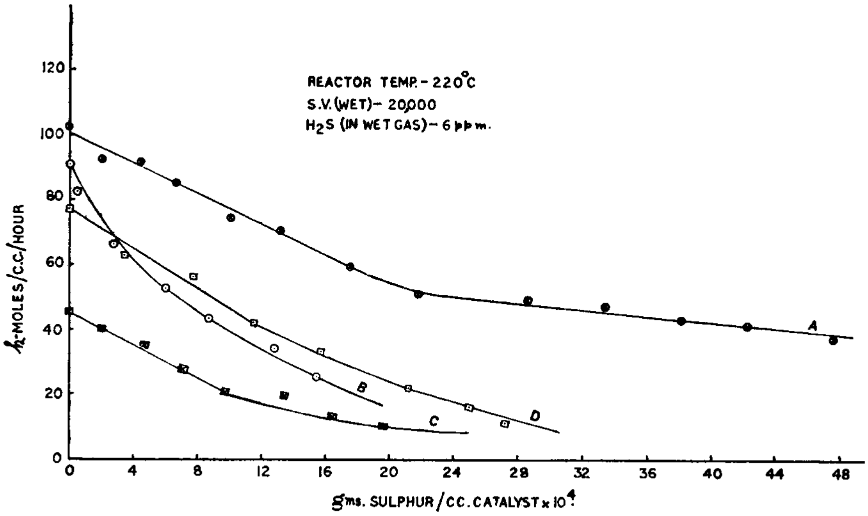

Fig. 2. Dependence of activity with amount of sulphur.

$$K_c = K_0(1-\alpha C) \qquad (2)$$

where, K_0 = Original activity of the catalyst

K_c = Activity in the presence of a poison concentration C

and α = The poisoning co-efficient which can be evaluated from the slope of the main linear portion of the poisoning curve.

The value of α gives a convenient method for the quantitative comparison of the relative susceptibility of different catalysts towards a particular poison. The values of α as calculated by above method is given in Table 2.

TABLE 2. Poisoning co-efficient

Sample No.	$10^{-3}\alpha$	
	6 ppm of sulphur in wet gas	60 ppm of sulphur in wet gas
Catalyst A	2.477	—
Catalyst B	9.139	3.05
Catalyst C	2.766	1.11
Catalyst D	3.294	—

It can be seen that the susceptibility of different catalysts towards sulphur are in the order $B \gg D > C > A$. Two interesting observations worth mentioning are Alumina based catalysts (Sample *A* and *C*) showed higher tolerance, whereas catalysts (*B* & *D*) having similar chemical composition displayed widely different sulphur tolerance. Fe_2O_3 content of the catalysts does not seem to influence the value of α, as the two catalysts containing Fe_2O_3 (Sample *A* and *B*) show the highest and lowest sulphur tolerance.

Sulphur poisoning data of two catalysts with higher sulphur concentration (*i.e.* 60 ppm in wet gas) in the feed has been plotted in Fig. 3. The values of α for both the samples, as can be seen from Table 2, are much lower than the corresponding values of α with lower sulphur content in the feed gas. This shows that the extent of deactivation is dependent not only on the amount of poison but also on the rate of its introduction. A possible explanation of different degrees of deactivation for the same quantity of sulphur dosed under varying sulphur concentration in the feed, may be that, with lower sulphur, active centres over a substantial part of the catalyst bed preferentially absorb sulphur, while with higher sulphur, major part of the sulphur may react to form bulk sulphides.

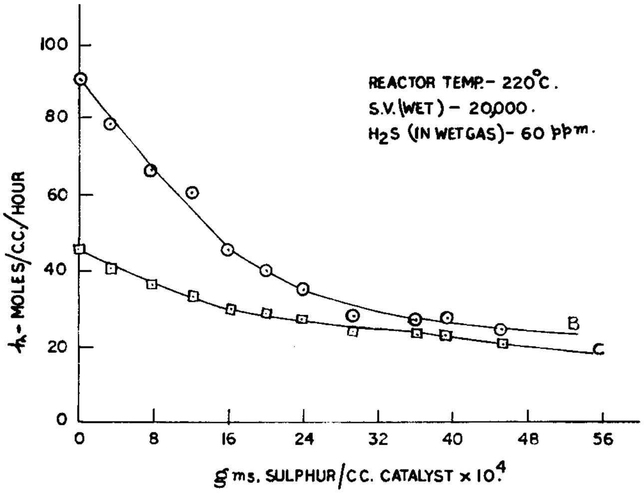

Fig. 3. Dependence of activity with amount of sulphur.

B. Reaction with H_2S

Under the reaction conditions of LT Catalyst, both copper and zinc oxide, which are invariably present in all formulations may react with H_2S. The thermodynamic equilibria for the reactions are given in Table 3.

From the much higher value of K_p for ZnS formation, it may be expected that ZnO will preferentially absorb sulphur and thus protect copper

TABLE 3. Thermodynamic equilibria of reactions

Reaction	Temp. °C	K_p	ΔH Kcal/mole	ΔF Kcal/mole
$Cu+H_2S=Cu_2S+H_2$	220	1.2×10^5	−14.2	−11.46
$ZnO+H_2S=ZnS+H_2O$	220	7.9×10^7	−18.3	−17.81

from sulphurization. This is one of the consideration for incorporation of ZnO in the catalyst. But the surface area data, as will be shown later, does confirm that Cu-surface is also effected presumably by sulphurization even when enough ZnO is available for reaction with H_2S. This is because the thermodynamic properties of pure components may be modified in the mixture.

C. Surface Area

The results of surface area of poisoned and nonpoisoned samples are given in Table 4.

TABLE 4. Surface area of poisoned and nonpoisoned samples

Sample No.	Surface area of nonpoisoned catalyst m^2/gm			Surface area of poisoned catalyst m^2/gm		
	BET	Cu	ZnO	BET	Cu	ZnO
Catalyst A	85.9	14.5	28.1	70.6	6.9	24.9
Catalyst B	36.0	15.2	14.1	33.6	2.8	10.5
Catalyst C	112.4	6.3	39.8	98.0	3.3	31.5
Catalyst D	18.8	8.2	8.4	16.5	3.3	6.2

It is evident from Table 4 that, for all the samples studied, Cu and ZnO surfaces and total surface area in the poisoned samples is less as compared to those in the corresponding nonpoisoned samples. The extent of reduction of Cu-surface in all the samples is much more than that of ZnO surface, which clearly indicates that ZnO always absorbs a part of the sulphur but the rate of sulphurization of copper is always higher than that of ZnO.

Now, if it is assumed that the sulphur is homogeneously absorbed on the catalyst surface to form ZnO and Cu_2S, the loss of the ZnO and copper surfaces should be equivalent to the amount of sulphur dosed. The loss of Cu and ZnO sites and the equivalent sulphur requirement can be calculated from surface area data. An example of the calculations on sample A is shown below:

1. Determination of ZnO sites

It is assumed that during surface area measurements the dissociative chemisorption of hydrogen on ZnO take place and from the knowledge of the volume of hydrogen chemisorbed, the ZnO sites can be calculated.
In the non-poisoned sample (A) volume of H_2 chemisorbed $= 5.2$ ml/gm cat.

$$\text{Number of ZnO sites (molecules)} = 2 \times \frac{6.023 \times 10^{23} \times 5.2}{22400} /\text{gm cat.}$$

$$= 2.77 \times 10^{20}/\text{gm cat.}$$

Similarly for the poisoned sample (A), vol. of H_2 chemisorbed $= 4.6$ ml/gm cat. and the number of ZnO sites (molecules) $= 2.45 \times 10^{20}$/gm cat.
Therefore number of ZnO sites (molecules) poisoned $= 0.32 \times 10^{20}$/gm cat.

2. Determination of Cu-sites

In the determination of surface area of copper in a low temperature shift catalyst, G. SENGUPTA *et al.*[5] have shown that it is possible to calculate the surface area of the cuprous oxide layer as 5.20×10^{18} sites/m^2 which is also equal to the Cu sites present/m^2 surface of catalyst.

Therefore the number of Cu sites (atoms) in the nonpoisoned sample $= 0.75 \times 10^{20}$/gm cat. and in the poisoned sample $= 0.35 \times 10^{20}$/gm cat.
Therefore, the number of Cu sites (atoms) poisoned $= 0.40 \times 10^{20}$/gm cat.
Amount of sulphur required to poison these ZnO and Cu-sites to form ZnS and Cu_2S will be equal to 2.741×10^{-3} gm/gm cat.

TABLE 5. Sulphur feed *vs* calculated amount of sulphur required to poison the catalyst

Sample No.	Sulphur feed gm/gm cat. $\times 10^{-3}$	No. of atoms (molecules) poisoned/ gm cat. $\times 10^{20}$		Sulphur required to poison total atoms (molecules) gm/gm cat. $\times 10^{-3}$
		Cu	ZnO	
Catalyst A	4.106	0.390	0.321	2.741
Catalyst B	1.749	0.640	0.350	3.560
Catalyst C	1.950	0.157	0.811	4.725
Catalyst D	1.807	0.257	0.217	1.841

The results of all the samples thus calculated has been shown in Table 5. An analysis of the data reveals some interesting facts. Calculated sulphur requirement for sample *A* is less than the amount of sulphur dosed. This shows a part of the sulphur has been absorbed by components other than Cu and ZnO. Accordingly deactivation of the catalyst with sulphur is expected to be less, which is confirmed by results of activity test as shown in Fig. 2. While analysing the results of sample B and C, it will be seen that the picture is reverse of sample A, as the calculated sulphur requirement is much higher than the amount of sulphur dosed. It follows that the sulphur is not absorbed homogeneously but must have blocked some pore mouths and thus reduced the Cu and ZnO surfaces drastically. From the foregoing arguments, the poisoning effect in the case of these two samples should be much more severe than in the case of sample A. But the results of poisoning coefficient for the two samples are widely different. While sample B confirms more severe deactivation because of the highest value of α, sample C has much lower poisoning co-efficient. An analysis of the surface area data reveals that in sample B poisoning has resulted in loss of maximum number of Cu-sites, while in semple C, rate of loss of copper sites is much lower. As Cu is the active component in the catalyst, higher loss of this surface will naturally lead to more severe deactivation. In the case of sample D, the amount of dosed sulphur is practically same as the calculated value showing homogeneous adsorption of poison.

D. Pore size distribution

The pore size distribution of the different poisoned and non-poisoned samples are shown in Figs. 4 and 5. It is seen that the distribution curves for both the poisoned and the corresponding non-poisoned sample

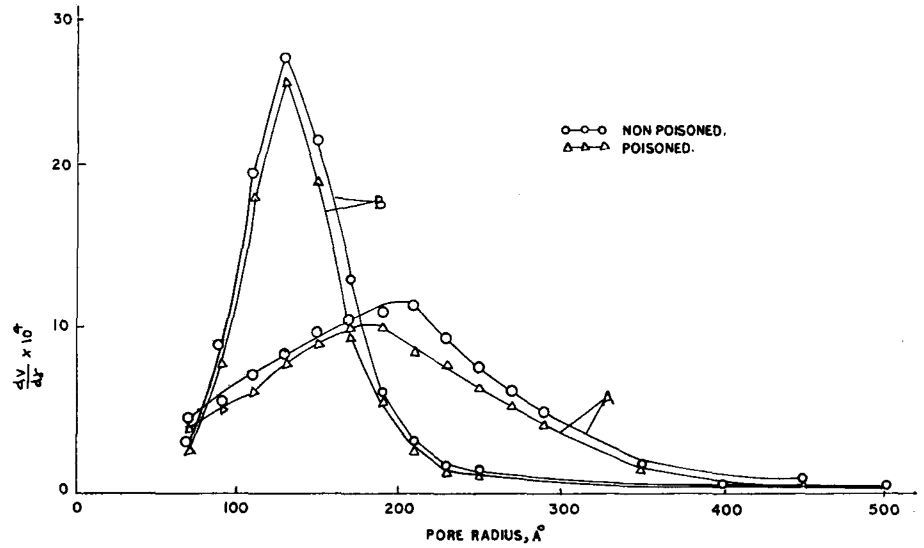

Fig. 4. Pore size distribution for samples A and B.

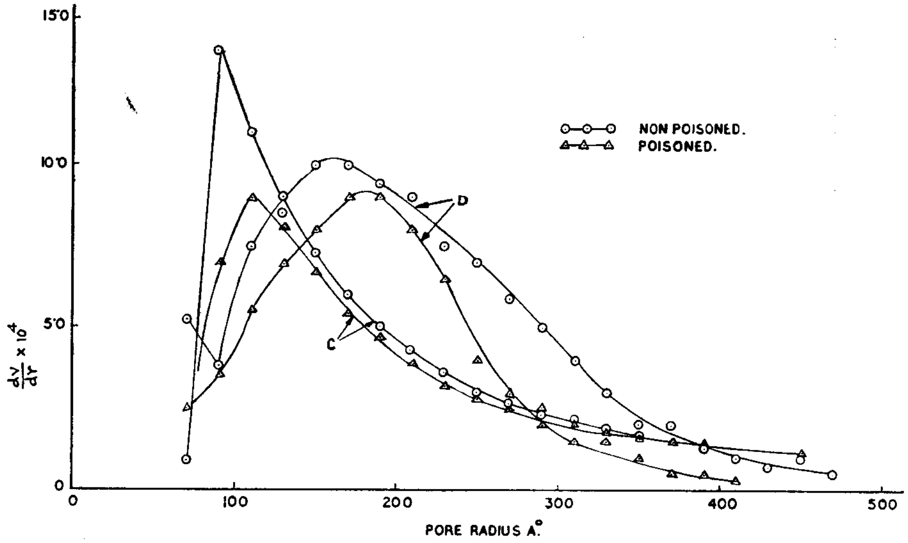

Fig. 5. Pore size distribution for samples C and D.

follow a similar pattern. But the volumes of the pores of any particular radius decreases on poisoning. This indicates that, in the region of pores that could be studied (upto 60 Å), there is no preferential poisoning of any particular type of pore. For each sample there is a decrease of surface area which is reflected in the pore size distribution curves. Earlier it has been indicated that for samples *B* and *C* some pore mouth blocking could have taken place. This appears for sample *B* where the concentration of pores in the vicinity of 100 Å radius has drastically decreased. For sample *C* there is however no such change. May be that the pores below 60 Å are affected, but pores of this range could not be studied in the present case.

E. Copper Surface and Activity

Fig. 6 shows the relationship between copper surface area and activity of the non-poisoned as well as the poisoned catalysts. An approximately linear relationship indicates that activity of the catalyst, poisoned or non-poisoned, depends on their Cu surface. Analysis of data in Table 1 and 4 shows that distribution of copper on the surfece may vary widely for samples (*e.g. B* & *D*) having similar copper content. The initial activity of the catalysts does not depend on copper content of the catalyst but on the development of Cu–surface. During poisoning, deactivation occurs due to loss of Cu–surface and the value of poisoning co-efficient increases with the percent loss of Cu–surface. The rate of loss of copper surface is

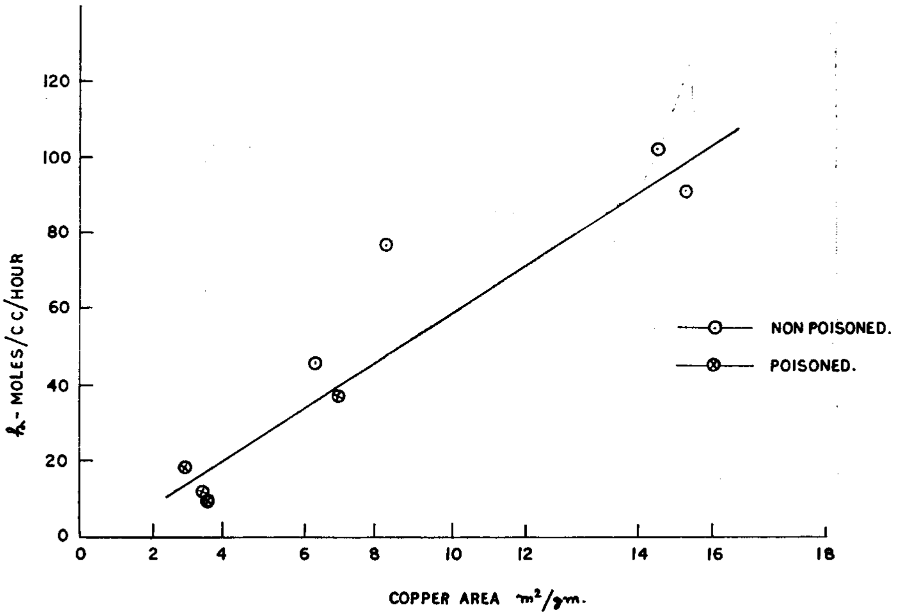

Fig. 6. Relationship between copper area and catalyst activity.

however not dependent on the initial copper area of the catalyst and may be related to the method of preparation of the catalyst.

Conclusion

The poisoning of LT catalyst is cumulative in nature and the poisoning curves indicate homogeneous absorption of poison. Some amount of pore mouth poisoning resulting in the decrease in the concentration of pores of all sizes in the poisoned sample also takes place.

During poisoning both copper and zinc oxide are sulphurized. The ratio of the extent of loss of copper and zinc oxide surfaces varies with different samples. The activity of the catalyst, both poisoned and non-poisoned bears a near linear relationship with copper surface area of the catalyst. Accordingly the higher the loss of copper area, the more severe is the poisoning. The extent of loss of copper surface vis-a-vis activity may be widely different for catalysts having similar chemical composition. This may be dependent on the method of preparation of catalyst. Alumina containing catalysts, seems more resistant towards sulphur poisoning.

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