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DEACTIVATION OF LOW TEMPERATURE SHIFT CATALYST

Part II Poisoning by Chlorine

By

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Abstract

Chlorine poisoning of Low Temperature CO-conversion catalyst (Cu-ZnO, Cu-ZnO-Al_2O_3 systems) has been investigated using four varieties of commercial catalysts. Studies have been made to determine the rate of deactivation of different brands of catalysts with the accumulation of chlorine. It is observed that the poisoning coefficient for different catalysts is not same and the copper surface area of all the catalysts decreases on poisoning. Further, the activity of the deactivated catalyst can be regenerated by washing with water irrespective of the brand of the catalysts studied. Electron microscopic studies show that zinc chloride formed on the catalyst surface during poisoning can be removed by washing with water. Surface coverage by zinc chloride appears to be the main cause of catalyst deactivation rather than permanent structural damage.

Introduction

In commercial plants, the deactivation of Low Temperature Shift (LTS) catalyst is mainly due to poisoning by traces of sulphur and chlorine present in the feed gas. These poisons are initially retained on the top of catalyst bed and the poisoned zone moves down with time of operation. The effective catalyst volume thus decreases progressively and the overall conversion efficiency at any particular time depends on the amount of unpoisoned catalyst.

Poisoning by sulphur has been recognised from the beginning of commercial application of LTS catalyst but chlorine poisoning remained unmarked for some time for two reasons. Firstly in most plants, the amount of sulphur present in the discharged catalyst is many times higher than that of chlorine and secondly chlorine present in the feed gas (about 0.001 ppm) is below the level detectable by conventional methods. However, chlorine is now considered a major problem for catalyst life and cases of severe chlorine

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poisoning has been observed in some plants. In commercial plants, main sources of chlorine are quench water used for temperature control, boiler solids carried with steam and refractories used for vessel insulation.

Study of the poisoning rate is relevant in the matter of assessment of catalyst life as well as development of poison resistant catalyst. The author's findings on the sulphur poisoning of LTS catalyst has been reported earlier[1] and the present investigation deals with that of chlorine. An attempt has been made to elucidate the mechanism of poisoning by electron microscopic studies and measurement of copper surface area.

Experimental

Four varieties of commercial LTS catalysts as reported in earlier work[1] were taken for this study. The chemical composition of these catalysts are given in table 1 for ready reference.

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.

Poisoning of catalyst: Two methods were followed for poisoning the catalyst.

(a) *Poisoning by dosing HCl gas*: The catalyst was charged in the reactor and reduced with nitrogen/steam mixture containing 1% hydrogen. Poison concentration was then built up on the catalyst by dosing HCl gas obtained by passing nitrogen (freed from oxygen by passing over porous copper catalyst at 300°C) through a solution of concentrated hydrochloric acid. A measured amount of this N_2–HCl mixture containing around 15 ppm chlorine was mixed with the feed gas in a preheater while another portion of gas was absorbed in sodium hydroxide solution and the chlorine content was estimated by mercurimetric method.[2] The chlorine concentration in wet feed gas was about 3 ppm.

(b) *Poisoning by soaking in HCl solution*: Catalyst samples were poisoned by soaking catalyst tablets in dilute solution of hydrochloric acid. Samples of different chloride content could be prepared by varying the strength of hydrochloric acid solution. After one hour soaking the tablets were removed and then heated at 300°C for two hours. For the determination of the chloride in the catalyst, samples were digested three times with water and the chloride in the water extract was estimated.

Activity measurements: The apparatus for activity test, method of feed gas preparation and its composition, the procedure for catalyst reduction and activity measurement are same as described earlier.[1] 5 cc of catalyst granules of $-16+20$ (BS) mesh size was charged in the reactor. In the first method of poisoning, feed gas mixed with HCl vapour was passed over the reduced catalyst. After dosing about 0.8 cc of HCl gas the catalyst activity was determined with HCl free feed gas. The activity thus determined was found to decrease on running the catalyst with poison free gas. Catalyst was therefore run with clean feed gas till stable activity was obtained. Further poisoning followed by determination of stable activity at different levels of poison were carried out till the catalyst activity declined to about 50% of the original activity. In case of second method of poisoning where chlorine was built up by soaking in HCl solution, the activity measurements were continued till stable activity was obtained. Activity has been expressed as specific rate constant k, as well as % CO converted.

Catalyst regeneration: The regeneration of chlorine poisoned catalyst was performed *in situ*. The catalyst bed was cooled to room temperature in nitrogen flow. Demineralised water was then introduced through the bottom of the reactor and the flow was continued for ten hours at a rate of 50 cc/minute. The reactor was then drained and the drying of the catalyst was done by slowly raising the bed temperature to 120°C in a current of nitrogen. Bed temperature was then raised and activity test of the catalyst was done after reducing the catalyst in the usual manner.

Electron microscopic studies: For electron microscopic studies of the surface of the non-poisoned, poisoned and regenerated catalyst, samples were prepared in the following manner. The catalysts were crushed in agate mortar and thereafter dispersed in alcohol using an ultrasonic disintegrator. A drop of the suspension of the dispersed catalyst was fixed in a carbon covered copper grid. The prepared samples were examined at 80 kV in Siemens Electron Microscope and subsequently microphotographs were taken.

Copper surface area measurements: After the activity measurements, the sample was cooled to room temperature and transferred to a specially designed

glass sample tube under nitrogen flow (oxygen free). The copper surface area was determined by chemisorption of oxygen via nitrous oxide decomposition according to the method of Osinga *et al.*[3]

Results and Discussion

A. *Poisoning by HCl gas and by soaking in HCl solution*

While measuring the activities of catalyst samples poisoned by dosing HCl gas, it was found that (1) HCl causes an immediate loss in activity, (2) catalyst deactivation continues even after the source of chlorine has been withdrawn and (3) the stabilization of the activity of the catalyst required more than two weeks (running time). The ultimate effect of the poison is therefore considerably greater than the initial effect. Similar ageing effect is also noticed in the case of catalysts poisoned by soaking, but the period of stabilization of activity is much shorter (about 30 hours). Uniform chlorine distribution in the second method of poisoning appears to be the reason for shorter stabilization period.

Fig. 1 shows the period required for the stabilization of the activity of the catalysts B and D by two methods of poisoning. Since extent of regeneration by washing was same in both the methods of poisoning and there was no evidence of selective attack at the Cu-ZnO interface in the second method of poisoning, we avoided the lengthy gas stream poisoning method and adopted the second method in most of our experiments.

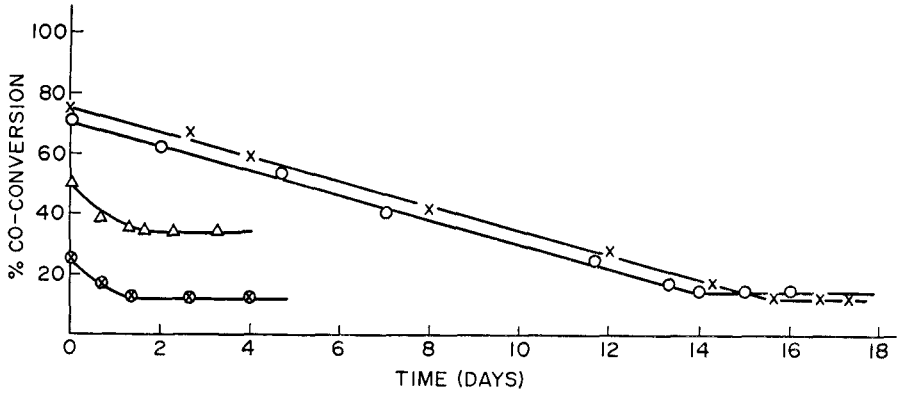

Fig. 1. Decline in activity of chlorine poisoned catalyst with time.
—×— Catalyst B, poisoned by HCl gas.
—△— Catalyst B, poisoned by soaking in HCl soln.
—○— Catalyst D, poisoned by HCl gas.
—⊗— Catalyst D, Poisoned by soaking in HCl soln.

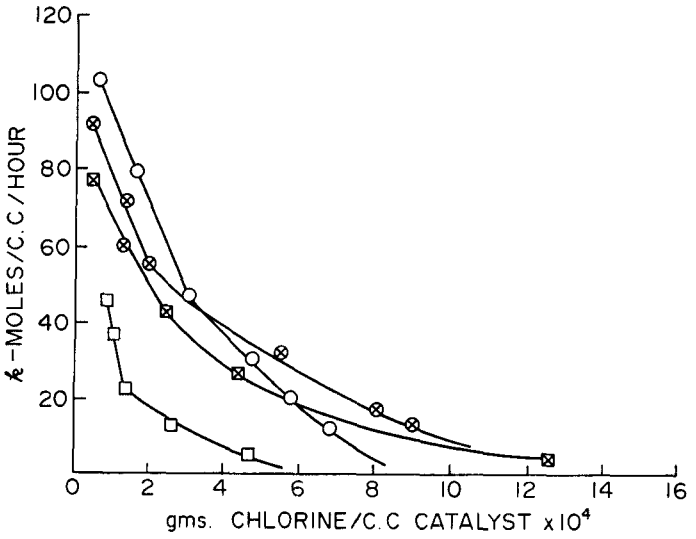

Fig. 2. Dependence of activity on amount of chlorine.
—○— Catalyst A —⊗— Catalyst B
—□— Catalyst C —⊠— Catalyst D

However, the ageing effect observed in the case of chlorine poisoning is contrary to the observation with H_2S poisoning where no such effect is noticed. The activity of catalysts reported in Fig. 2 are the stabilized activity of catalysts poisoned by soaking.

B. *Poisoning and deactivation*:

The effect of chlorine on the activity of four different catalysts is shown in Fig. 2. The results indicate that appreciable deactivation takes place even with 0.02% chlorine accumulation on the catalyst. Poisoning coefficients (α) were calculated following the method of Maxted[4] and are given in Table 2. Poisoning coefficients in case of sulphur poisoning taken from our earlier work[2] are also included in the table for the convenience of comparison.

TABLE 2. Poisoning coefficient

Sample	Chlorine poisoning α	Sulphur poisoning α
A	2.089×10^4	2.477×10^3
B	2.659×10^4	9.139×10^3
C	6.704×10^4	2.766×10^3
D	1.723×10^4	3.294×10^3

It can be seen that the values of poisoning coefficient for chlorine are much higher than those of sulphur. This is also confirmed from Fig. 3 which shows the deactivation of one catalyst sample with similar quantities of sulphur and chlorine.

It is evident from Table 2 that the relative susceptibility of different catalysts towards chlorine are in the order

$$C>B>A>D,$$

whereas for sulphur poisoning the order is

$$B>D>C>A$$

This shows that the relative susceptibility of these catalysts towards these two poisons are not same.

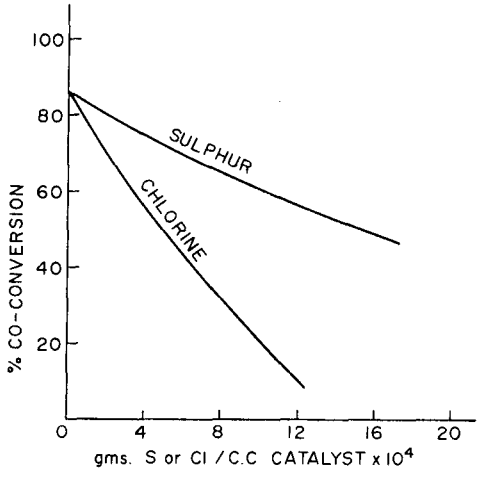

Fig. 3. Dependence of activity on amount of poison (catalyst-B).

C. *Catalyst regeneration*:

The activity of the poisoned catalyst regenerated by washing with water is shown in Table 3. It is seen that some amount of chlorine is still retained in the regenerated catalyst which may be due to insufficient washing. However, the activity of both the samples could be regenerated to about 84% of the original by washing with water.

TABLE 3. Catalyst regeneration.

Sample	Chlorine content (ppm. w/w)		Catalyst activity (% CO-conversion)			Relative activity after regeneration.
	Poisoned	Regenerated	Unpoisoned	Poisoned	Regenerated	
A	469	180	84.0	33.0	70.0	83.0
D	414	150	80.0	22.5	68.9	85.0

D. *Electron microscopic studies*:

These studies were undertaken with the aim of obtaining an insight into the changes that take place on catalyst surface during the process of poisoning and regeneration.

The electron micrographs of the three samples A, B and D are depicted

in Figs. 4 to 7. Each set comprising of 3 figures corresponds to different stages of treatment. For properly assessing the difference in texture of three catalysts certain general facts regarding the contrast in electron microscopic pictures have to be stressed in the beginning. Since the contrast in bright field image depends largely on the thickness of the crystallites, the zinc oxide phase appears in all the micrographs as dark massive plates or semi-transparent flakes. Copper particles on the other hand appear as small dark and round specks.

Fig. 4 depicts the electron micrographs of all the three catalysts in unpoisoned condition. In Fig. 4 (a), corresponding to the catalyst A, black massive particles of zinc oxide partly covering the porous alumina flakes are noticeable. The general location and distribution of these particles suggest that these tend to pin the relatively smaller and round specks of copper down to the positions around the edge of alumina flakes. In Fig 4 (b), corresponding to the catalyst B, small dark specks of copper are found to lay on top of zinc oxide crystallites which are also sometimes porous. In Fig. 4 (c), corresponding to the catalyst D, same type of dark specks of copper are distributed in a mass of zinc oxide which is mostly in the form of thick heavy plates, although at several places they appear in the form of semi transparent flakes. The zinc oxide particles at times have elongated appearance.

The sets of pictures in Fig. 5 show the electron micrographs of three catalysts after soaking in HCl solution. In Fig. 5 (a), the agglomeration of zinc oxide phase is visible although a sizeable number of alumina flakes characterised by their porous and flaky appearance are seen. A large number of copper particles are therefore burried under the zinc oxide agglomerates. In Fig. 5 (b), we find that the zinc oxide crystallites and therefore the overlying copper particles are pulled together. Thus we see isolated dark patches where copper particles have aggregated. In Fig. 5 (c), we find that the copper particles have the general tendency to fall apart while the zinc oxide particles start to glue together. At the top right hand corner we find an agglomerate whose edge definitions have nearly disappeared. The size of the copper particles remain uneffected at this stage. A difference between the catalysts B and D is worth recording. While the clustering of copper particles is clearly observable in B, evidence of such clustering of copper particles is absent in catalyst D. The dispersion of copper in catalyst A also remain less effected at this stage.

In Fig. 6, the changes in the texture of the catalysts after run in the reactor are depicted. In catalyst A, Fig. 6 (a), we find that the porosity of alumina flakes is completely destroyed. The increase in particle growth of

copper is less marked in this catalyst at this stage. Zinc chloride was confirmed on catalyst surface by electron micro diffraction, however it does

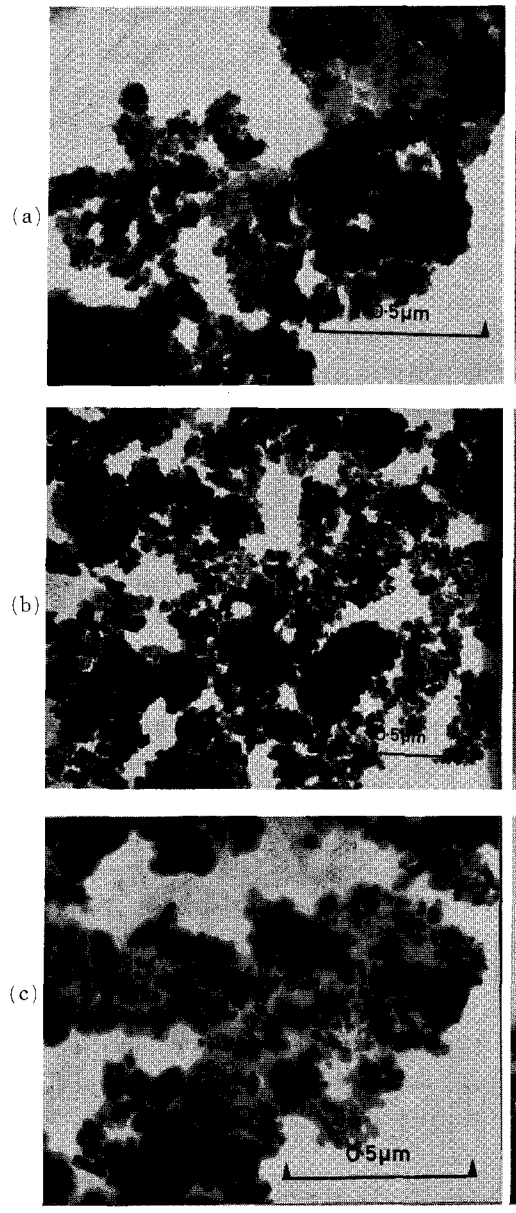

Fig. 4. Electron microphotographs of non-poisoned catalysts.

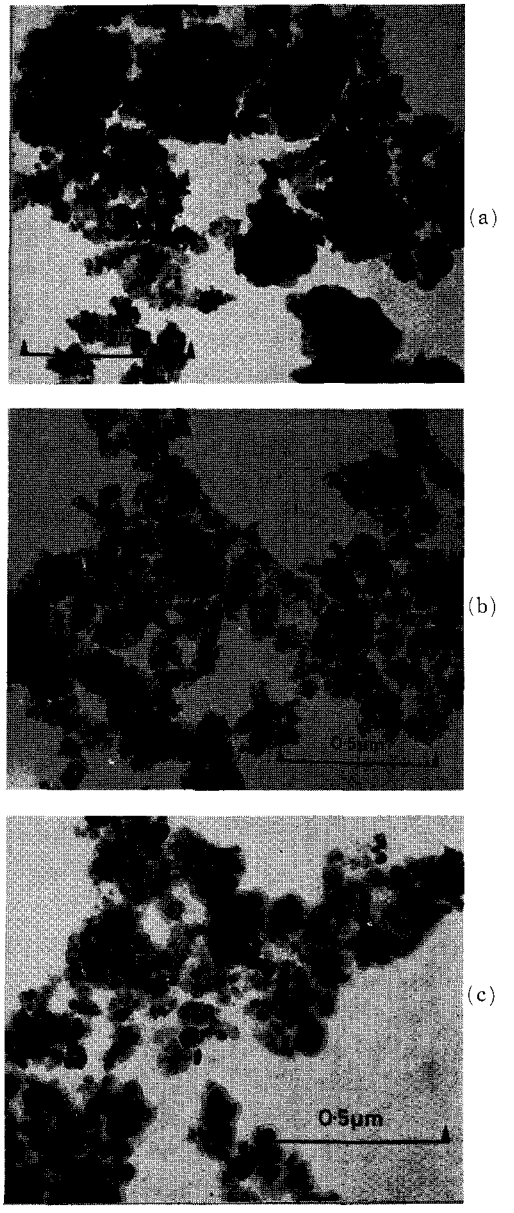

Fig. 5. Electron microphotographs of poisoned catalysts.

not appear to cover the copper particles. In Fig. 6 (b), again formation of zinc chloride was confirmed in the dark and grey regions of the photograph. A difference in the distribution of zinc oxide and copper particles is also

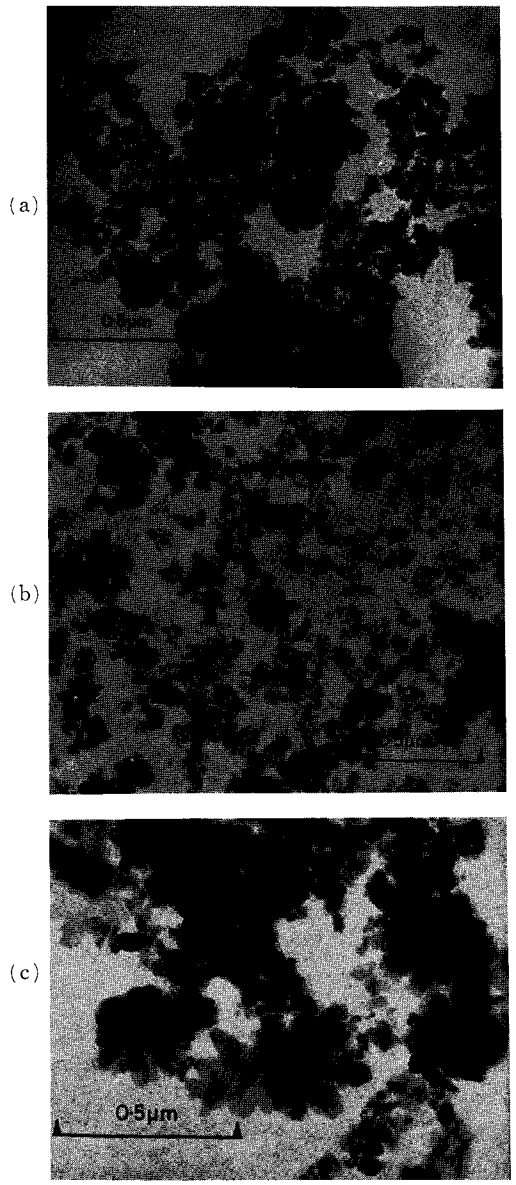

Fig. 6. Electron microphotographs of poisoned aged catalysts.

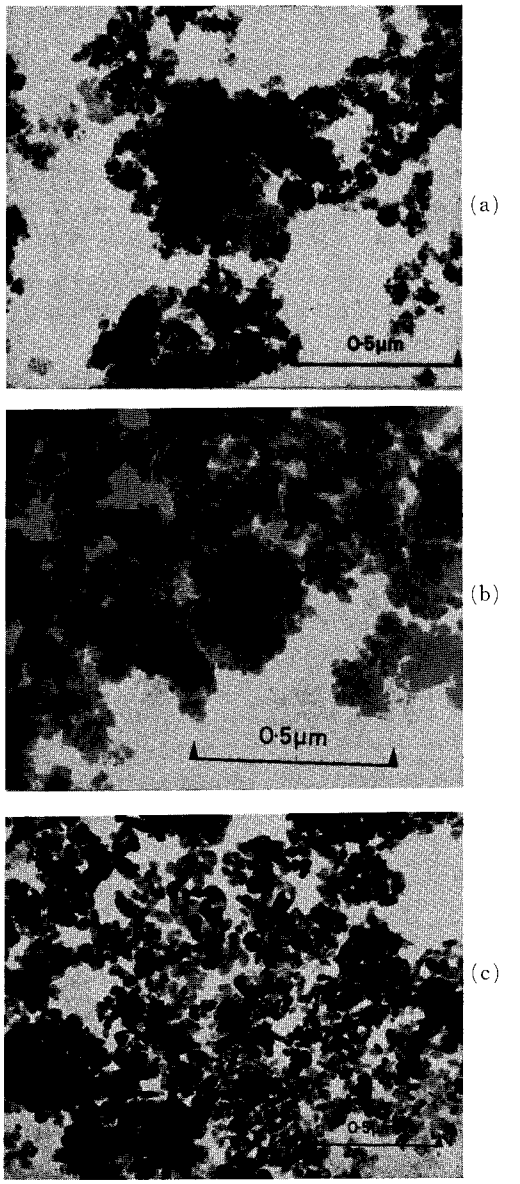

Fig. 7. Electron microphotographs of washed catalysts.

noticed between Fig. 4 (b) and 6 (b). The variation in the particle size of copper in Fig. 6 (b) is much less than in Fig. 4 (b) and further the overall statistically averaged size of copper seems to have increased at this stage. In Fig. 6 (c), the flowery aggregates observed in sample D were identified to be zinc chloride by electron micro-diffraction. Most of the copper crystallites seem enveloped within the zinc chloride matrix while a few with extremely small dimensions find their seat around the corner where zinc chloride is not covering them. Flowery texture of zinc chloride was not noticed in samples A and B presumably because of the initial difference in the particle size and morphology of the zinc oxide phase in the fresh catalyst.

Fig. 7 shows the resulting texture after washing of the poisoned catalysts. In Fig. 7 (a), we observed that the textural appearance has not changed significantly and traces of zinc chloride was found to be still present. The porosity of alumina flakes is observable once again while other features remain uneffected when compared to the texture in Fig. 6 (a). In Fig. 7 (b), the copper particles are found to be loosened from the mass but the dispersion of zinc oxide phase is not restored completely. Traces of zinc chloride is still present presumably due to insufficient washing. In Fig. 7 (c), we observe that the flowery aggregates appearing in Fig. 6 (c) have disappeared completely and when compared with Fig. 4 (c) the copper particles have increased in size with occasional bridges between them.

Copper particle size of the fresh and the washed samples are presented in Table 4.

TABLE 4. Comparative evaluation of the particle size of copper.

Sample	Size of Copper particles Å			
	Fresh Catalyst		Washed Catalyst	
	Range	Average	Range	Average
A	90–125	100	—	120
B	50–170	100	50–220	150
D	100–250	150	200–500	250

It can be seen that maximum increase in copper size has taken place in case of sample D. If the growth of copper crystallite was responsible for catalyst deactivation, catalyst D would be expected to deactivate at the highest rate which is contrary to our observation (Table 2). May be increase in particle size within the range does not influence the catalytic activity significantly.

To summarise, the following general observation can be made from the electron micrographs and electron micro-diffraction data.

(1) In the fresh catalyst the copper particles are better distributed in catalyst D than in either of catalysts B and A.

(2) After soaking the catalysts in HCl solution the extent of agglomeration of copper particles is in order D>A>B.

(3) In soaked and aged catalysts, flowery growth of zinc chloride is noticed only in catalyst D. The enveloping action of zinc chloride was more in catalyst D and catalyst B while it was localised in catalyst A.

(4) After washing, considerable amount of free copper surface in the form of uncovered particles is regenerated in catalyst D while in catalyst B the copper particles to a large extent seem embedded in the zinc chloride/zinc oxide phase. In catalyst A, however, porosity of alumina flakes is recovered to a considerable extent. The size of the copper particles increases as compared to the fresh samples.

E. *Copper surface area*:

It is known[5] that the activity of LTS catalyst is a function of copper surface area and the loss in activity could be due to the reduction in copper surface area. Fig. 8 shows that the copper surface area of all poisoned

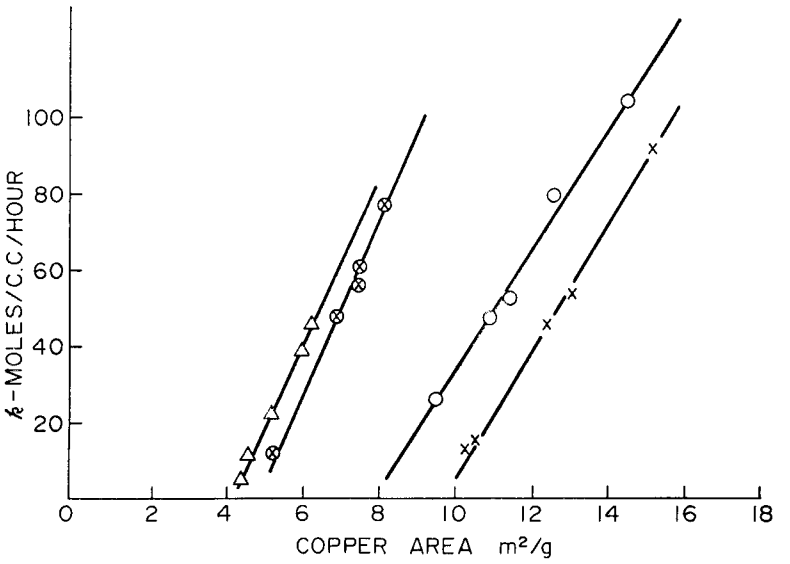

Fig. 8. Relationship between copper area and activity.
—○— Catalyst A —×— Catalyst B
—△— Catalyst C —⊗— Catalyst D

samples are lower than that of the fresh samples and for any particular catalyst the copper surface area bears a linear relationship with activity. But while comparing the results of copper surface area and activity of chlorine poisoned samples with those of H_2S poisoned sample[1], it is seen that in case of chlorine poisoning the loss of activity is much more for a smaller reduction in surface area. This suggest that the mechanism of poisoning in the two cases are different.

F. *Mechanism of poisoning*:

Copper and zinc oxide are the two principle constituents of all varieties of LTS catalyst. The equilibrium constants[6] for the reaction of chlorine with copper and zinc oxide are given in table 5.

TABLE 5. Thermodynamic equilibria of reactions.

Reaction	Temperature (°C)	K_P	ΔH (Kcal/mole)
$Cu+HCl=CuCl+\frac{1}{2}H_2$	220	6.5×10	-10.4
$Cu+2HCl=CuCl_2+H_2$	220	1.0×10^{-2}	-5.1
$ZnO+2HCl=ZnCl_2+H_2O$	220	1.8×10^{7}	-29.9

From the value of equilibrium constants it is expected that zinc oxide will preferentially react with chlorine to form zinc chloride. Young *et al.*[7] state that chlorine reacts with LTS catalyst to form zinc chloride which melts at LTS operating temperature. This results in the growth of the zinc oxide crystals which in turn causes growth in the copper crystals and the catalyst loses activity. According to Campbell[5] chlorine poisoning results in the increase of copper particle size leading to reduction in active metal area. If this is the mechanism of chlorine poisoning one should expect a higher degree of reduction in copper surface area and permanent damage to the catalyst structure. But the fact that major part of activity lost due to chlorine poisoning can be regenerated by water washing of the catalyst suggests that the extent of permanent damage to the catalyst structure is not much. Electron microscopic studies on the surface of poisoned and regenerated catalysts also support this view. The studies show that during poisoning, the size of the copper particles increases slightly and zinc chloride is formed. On washing the poisoned catalyst with water, zinc chloride can be removed from the catalyst surface and the dispersion of the copper phase improves significantly and the catalyst regains major part of its activity.

It is therefore reasonable to suggest that during LTS operation, zinc

chloride formed on the catalyst surface melts and covers the catalyst surface. This surface coverage is mainly responsible for catalyst deactivation.

Conclusion

When LTS catalyst is exposed to chlorine, zinc oxide present in the catalyst reacts preferentially with chlorine. Zinc chloride formed initially in the upper part of the catalyst bed melts under the reaction condition and spreads over larger areas of the catalyst bed. This probably explains the progressive loss of catalytic activity for a considerable period even after the source of chlorine is withdrawn. A comparision of catalyst deactivation by sulphur and chlorine shows that chlorine is a much more severe poison than sulphur. The loss of copper surface of chlorine poisoned samples is much less than that of sulphur poisoned samples. The fact that the activity of chlorine poisoned samples can be regenerated by water washing and comparatively lower loss of copper surface suggests that deactivation by chlorine is mainly due to surface coverage by zinc chloride rather than structural collapse.

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