Thermochimica Acta, 63 (1983) 1–8
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

AN INVESTIGATION OF THE CATALYST ZnO–CuO–Cr_2O_3 DURING ITS USE IN THE INDUSTRIAL REACTOR BY THERMAL ANALYSIS

G. RASULIC, S. JOVANOVIC and Lj. MILANOVIC
Control and Research Department, Chemical Industry "Pancevo", Pancevo (Yugoslavia)

(Received 25 May 1982; revised 29 September 1982)

ABSTRACT

The catalyst for low temperature carbon monoxide conversion used in the ammonia production process consists of copper, zinc and chrome oxides, of which the metal copper is the active component.

By applying differential thermal analysis and calorimetric techniques, an investigation of changes in the active components has been carried out in terms of the dependence on its time of use in the industrial reactor, as well as its position in the reactor during use.

On the basis of the investigations carried out, the specific area of cupric oxide as a measure of the active area of the samples investigated has been determined.

INTRODUCTION

The active component of the catalyst for low temperature carbon monoxide conversion is present as finely dispersed crystals of elemental copper distributed on stable oxide surfaces such as zinc oxide or zinc–chrome spinel [1].

If excessive causes of poisoning are excepted, then catalysts used in low temperature carbon monoxide conversion decrease in their activity or, more precisely, they "age" more with increasing time of use. It is supposed that this phenomenon is due to elemental copper crystals growing as the result of many factors of which the increase of temperature and poisons play the decisive roles. The poisons for this catalyst are sulphur and chlorine compounds.

The subject of this paper is the investigation of the catalyst for low temperature carbon monoxide conversion by thermal analysis, interpreted in terms of the active surface changes as a function of the time of use in the process of ammonia production, as well as the position of the catalyst in the industrial reactor. The investigations have been carried out using a commercial catalyst that contains about 36% zinc oxide, 18% copper oxide and 46%

0040-6031/83/$03.00

chrome oxide, calculated as Cr_2O_3. As a binding material in this catalyst, graphite has been used.

EXPERIMENTAL

The investigation has included a new, unused sample of the investigated catalyst and samples taken from the top and bottom of the catalytic bed of two parallel industrial reactors after 9, 16 and 28 months of use in the production process.

A review of the investigated samples, their positions, time in use and sample numbers, is given in Table 1.

The complex thermal analysis was carried out on the derivatograph in the temperature range 30–1000°C in a static atmosphere of air and on the differential scanning calorimeter DSC-1B in the temperature range 30–500°C in a dynamic atmosphere of hydrogen.

EXPERIMENTAL RESULTS AND DISCUSSION

Differential thermal analysis and thermogravimetric analysis in a static atmosphere of air up to 400°C for the new sample show no changes connected with the active catalyst component. This was expected because X-ray structural analysis of the new, unused sample, shows that the basic components of this catalyst are zinc, copper and chrome oxides, of which

TABLE 1

Review of the samples investigated

Sample no.	Sample position	Time in use (months)	Reactor
1	New, unused catalyst		
2	Top of the reactor	9	II
3	Top of the reactor	16	I
4	Top of the reactor	16	II
5	Top of the reactor	28	I
6	Lower part of the catalytic bed	28	I
7	Bottom of the catalytic bed	28	I
8	Top of the reactor	28	II
9	Lower part of the catalytic bed	28	II
10	Bottom of the catalytic bed	28	II

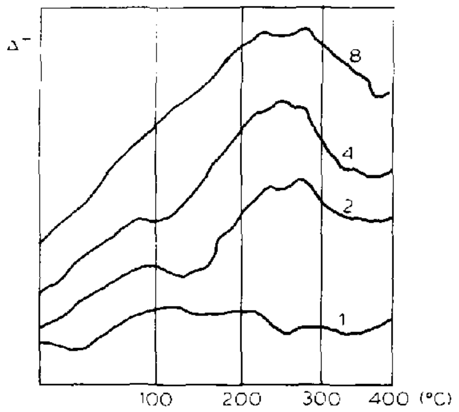
zinc and chrome oxides form a zinc–chrome spinel phase, and that the free oxides of zinc, copper and the oxides of hexavalent chromium occur in much lower concentrations [2]. Zinc and copper oxides, as well as the zinc–chrome spinel, in the investigated temperature range are not subject to changes that can be registered by thermal analysis. The thermal changes of hexavalent chromium cannot be registered due to its low concentration in the investigated sample.

In the temperature range 400–900°C, a complex exothermic peak is followed by a weight loss of 5.8–6.9 wt.%. This peak can be due to the combustion of the graphite present in the sample to form carbon monoxide and of the reduction of cupric and cuprous oxides to elemental copper by the carbon monoxide, with maxima at 520 and 610°C, followed by zinc oxide acting as a catalyst for the conversion of free Cr_2O_3 to CrO_3. Chromium trioxide obtained by oxidation reacts with zinc oxide, forming a zinc–chrome spinel, $ZnCr_2O_4$. The oxidation of Cr_2O_3 on zinc oxide develops in two stages, the first in the range 650–850°C, and the second from 900 to 1200°C [3].

The content of elemental copper in the investigated samples increases with increase in time of use of the catalyst in the industrial reactor. Differential thermal analysis in a static atmosphere of air has indicated an exothermic peak in the range 180–320°C, with the maximum at 230–290°C, caused by elemental copper oxidation. Above 400°C, no changes in the thermal behaviour of the used catalyst compared with the unused one have been observed and so only parts of the DTA curve for the temperature range from 30 to 400°C have been shown in the figures.

Figure 1 shows the results of differential thermal analysis of samples 1, 2, 4 and 8, i.e. the samples used on the top of the second industrial reactor for 9, 16 and 28 months compared with the unused catalyst. Investigations in a static atmosphere of air in ceramic crucibles do not allow complete oxidation of the copper in the whole mass of the sample, but the oxidation peak of elemental copper on the DTA curve shows a tendency to increase with increase in time of use of the catalyst in the industrial reactor. Due to other processes which occur at the same time in this temperature range, as well as to the fact that copper oxidation is impossible in the whole mass of the investigated sample, this peak could not be used for the quantitative analysis of the elemental copper present. The increase in weight due to elemental copper oxidation could not be registered on the basis of thermogravimetric analysis except for the samples that were at the end of their life, i.e. after 28 months use in the industrial reactor.

The exothermic peak caused by copper oxide reduction has been recorded by investigation of the same samples in a current of hydrogen on the differential scanning calorimeter DSC-1B in the temperature interval from



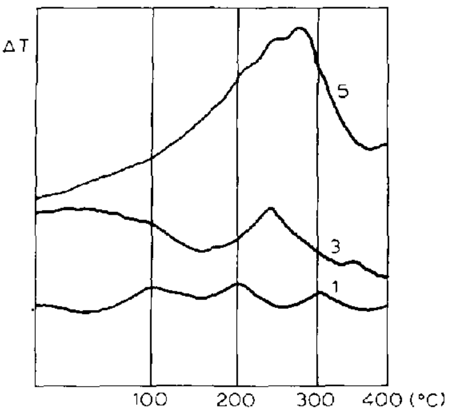


Fig. 1. DTA curves of samples 2, 4 and 8 used for 9, 16 and 28 months, respectively, in an industrial reactor compared with new, unused catalyst (sample 1).

Fig. 2. DTA curves of samples 3 and 5 used for 16 and 28 months, respectively, in the first industrial reactor compared with new, unused catalyst (sample 1).

140 to 200°C. The size of the peak decreases with increasing time of use of the catalyst in the industrial reactor.

Considering that the elemental copper contents of the samples increase with time of use of the catalyst, while at the same time the decrease of their activity is evident, this copper in the form of enlarged crystals is no longer the active catalyst component. The active catalyst component has been oxidised on taking the catalyst out of the reactor, and we have tried to determine it by measuring the thermal effect of elemental copper oxidation or by measuring the copper oxide reduction in the investigated samples.

The investigations by differential scanning calorimeter in a current of hydrogen were carried out with small sample weights of up to 10 mg, arranged as a fine layer, by which copper oxide reduction was practically possible in the whole mass of the sample.

Copper oxide reduction energy in the new, unused catalyst sample, calculated from the results of measurements, amounts to 128.90 J g^{-1} of the catalyst. Having in view that the catalyst contains 18% of cupric oxide, the reduction energy amounts to 716.33 J g^{-1} of cupric oxide present in the catalyst, while the reduction energy of pure cupric oxide, which has been used as reference, amounts to 579.19 J g^{-1} of CuO. As expected, the cupric oxide reduction energy on the catalyst is greater than the reduction energy of pure cupric oxide because the copper oxide in the catalyst has been distributed along the zinc–chrome spinel carrier which has areas very rich in cupric oxide.

The specific area of pure cupric oxide has been determined by the method of continuous flow. Supposing that the cupric oxide reduction energy is proportional to its specific area, we have calculated the specific area of cupric oxide in the catalyst on the basis of its known reduction energy using the reduction energy of pure cupric oxide and its specific area as reference. This determined specific area for the cupric oxide in the catalyst for low temperature carbon monoxide conversion, judging by the activity of the investigated samples, can be accepted as the active area of the catalyst.

Reduction energies calculated from the reduction peak areas, together with the specific area of cupric oxide as the active sample area, from the top of the catalytic bed of the second industrial reactor are shown in Table 2, according to the catalytic activity determined in the laboratory reactor.

According to Table 2, the reduction energy of copper oxide decreases with the time of use of the catalyst from 128.90 J g^{-1} in the new sample to 64.83 J g^{-1} in the sample after 28 months of use.

The same catalyst sample activity investigations in the laboratory reactor have shown that, in the range from 1 to 8, the activity decreases by about 60% [4], while the cupric oxide specific area, that is the active catalyst area, decreases by about 50%. Activity changes in the laboratory reactor and the active catalyst area determined from cupric oxide reduction energy are similar both in numerical value and the change from sample to sample. As the activity of the catalyst is proportional to its active area and the copper oxide reduction energy follows the catalyst activity change, we have used the reduction energy, i.e. the cupric oxide specific area, as the criterion of catalyst active area for low temperature carbon monoxide conversion.

Figure 2 shows the differential thermal analysis curves of the catalyst samples used for 16 and 28 months on the top of the first industrial reactor

TABLE 2

Energy change of the cupric oxide reduction and the catalyst active area with increase in time of use at the top of the second industrial reactor

Sample no.	Time in use (months)	Cupric oxide reduction energy		Cupric oxide specific area (catalyst active area) (m^2 g^{-1} cat.)	Catalytic activity as CO conversion (%)
		J g^{-1} cat.	J g^{-1} CuO		
1		128.90	716.33	1.78	96.5
2	9				86.3
4	16	88.47	491.85	1.22	79.5
8	28	64.83	341.19	0.90	59.3

compared with the new, unused catalyst. The increase in peak area for elemental copper oxidation with catalyst lifetime is even more distinct in this reactor, and indicates that the cupric oxide specific area decreases (Table 3).

The catalyst samples taken after the same period of use in the industrial reactor have been observed in the same way, but from different levels of the catalytic bed. The changes of the samples taken after 28 months of use have been separately observed in the first industrial reactor (Fig. 3 and Table 4) and in the second reactor (Fig. 4 and Table 5), although the catalytic bed in both reactors was in practically the same condition.

The DTA curves given in Fig. 3 show the distinct difference in the behaviour of samples 5 and 6, although the samples have almost the same active area, as can be seen in Table 4. The difference in behaviour of these samples can be explained by overheating of the catalytic layer, whereby the copper crystals "age", i.e. they enlarge and the active area decreases. Sample 5 was on the top of the reactor and was, therefore, much more exposed to the possibility of poisoning than samples 6 and 7. Thus, we can explain the difference in behaviour of these two samples by a bigger influence of poisoning on the "ageing" of sample 5, while in sample 6, overheating was decisive. This means that, for different samples of this type of catalyst with the same activity and the same active area, it is possible to explain the causes of the "ageing" process on the basis of the shape of the DTA curves.

Figure 4 and Table 5 show the results of the sample observations taken after 28 months of catalyst use from different levels of the catalytic bed in the industrial reactor. Sample 8 was from the top, sample 9 from the lower layer, and sample 10 from the bottom of the catalytic bed.

These results also show the decrease in catalyst activity with the sample from the bottom of the catalytic bed in somewhat better condition than the samples from the top and from the lower layer. Samples 8 and 9 differ from each other very much both in active area and in DTA curve shape. Sample 9,

TABLE 3

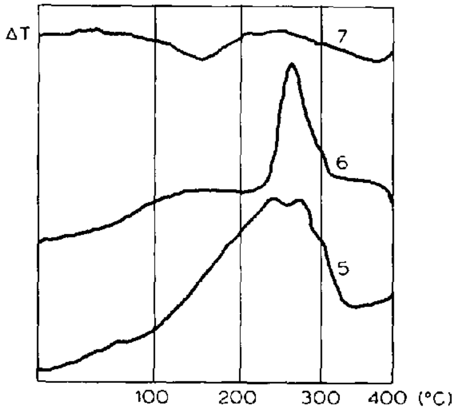
Energy change of the cupric oxide reduction and the catalyst active area with increase in time of use at the top of the first industrial reactor

Sample no.	Time in use (months)	Cupric oxide reduction energy		Cupric oxide specific area (catalyst active area) (m^2 g^{-1} cat.)
		J g^{-1} cat.	J g^{-1} CuO	
1		128.90	716.33	1.78
3	16	78.61	436.90	1.09
5	28	53.11	281.78	0.73

TABLE 4

Energy change of the cupric oxide reduction and the catalyst active area after 28 months of use as a function of the position in the first industrial reactor

Sample no.	Position of the sample in the reactor	Cupric oxide reduction energy		Cupric oxide specific area (catalyst active area) (m^2 g^{-1} cat.)
		J g^{-1} cat.	J g^{-1} CuO	
5	Top	53.11	281.78	0.73
6	Lower layer	50.20	278.90	0.69
7	Bottom	71.14	394.75	0.98



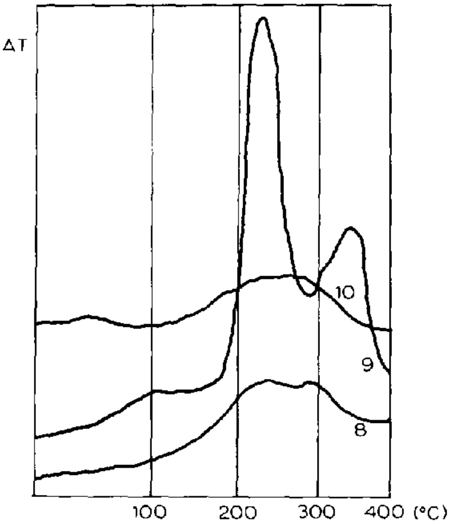


Fig. 3. DTA curves of samples taken from different levels after 28 months use in the first industrial reactor.

Fig. 4. DTA curves of samples taken from different levels after 28 months use in the second industrial reactor.

TABLE 5

Energy change of the cupric oxide reduction and the catalyst active area after 28 months of use as a function of the position in the second industrial reactor

Sample no.	Position of the sample in the reactor	Cupric oxide reduction energy		Cupric oxide specific area (catalyst active area) (m^2 g^{-1} cat.)
		J g^{-1} cat.	J g^{-1} CuO	
8	Top	64.83	341.19	0.90
9	Lower layer	17.10	93.86	0.24
10	Bottom	72.54	403.25	1.00

from the lower layer of the catalytic bed, has suffered from the overheating process much more than sample 6 from the first reactor. The ageing process of the sample from the top of the catalytic bed is evidently the result of other causes, of which the most important is poisoning, that caused the considerable decrease of its active area.

CONCLUSION

The catalyst based on copper, zinc and chromium oxides for low temperature carbon monoxide conversion has been investigated for changes in the active component as a function of time of use and position in the industrial reactor. The investigations have been carried out by differential thermal analysis and microcalorimetric measurements, and the results obtained have shown that

(a) in the new, unused catalyst, the active component is in the form of copper oxide and that in the used catalyst, it is in the form of the oxide as well as elemental copper;

(b) the elemental copper content increases with the time of use of the catalyst, but the catalyst activity decreases, indicating that the enlarged particles of elemental copper are no longer catalytically active;

(c) the catalytically active component of the catalyst samples investigated is copper oxide because it has been oxidised and is very active when taken from the reactor;

(d) decrease in the specific area of the cupric oxide, calculated on the basis of its reduction energy, and the time of use in the industrial reactor is followed by a decrease in catalyst activity and can therefore be considered as the criterion of the active area;

(e) under comparable conditions, catalyst activity decreases from the top of the industrial reactor, where it is mainly due to poisoning, to the bottom, where overheating is more important.

REFERENCES

1 P.M. Young and C.B. Clark, Chem. Eng. Prog., 69 (5) (1973) 69.
2 Ž. Jovanović, G. Rasulić, A. Badrljica and M. Stefanović, 6th Yugoslav Conf. Pure Appl. Chem., Sarajevo, 1979.
3 T. Ishii, R. Furrichi and Y. Hara, J. Therm. Anal., 11 (1977) 71.
4 Ž. Jovanović, B. Dijakova and M. Stefanović, ETAN, 6th Yugoslav Conf. Mater., Priština, 1980.