ACTA CHEMICA SCANDINAVICA 3 (1949) 639—643

Reactivation of Adsorptive Alumina Spent in Organic Chromatography

PAAVO KAJANNE

Department of Chemistry, Finland Institute of Technology, Helsinki, Finland

During the last ten years chromatography has attained a remarkable position as a tool in organic work. This development is particularly influenced by the investigation of Brockman and Schodder[1] from 1941 concerning the preparation of adsorptive alumina of different activity degrees and the method for defining this degree accurately, which makes it possible to choose a suitable adsorbent according to the adsorbability of the substances to be separated.

Although alumina standardized according to Brockman at present is produced on a large scale by different producers, its relatively high price considerably limits its use in investigations on wider scale. Several investigations have been carried out to restore the activity of spent alumina. The results differ largely from each other, often not being very promising. Strain[2] in his collective book concerning chromatography mentions only that adsorptive clays in the industry are reactivated by burning in special kilns which prevent the sintering of the clay itself. On the other hand Hesse[3] in a similar book advises to avoid the regeneration for the sake of the many difficulties arising. However, the reactivation can be done, according to him, by eluting with a suitable powerfull solvent, and burning thereafter, to which operation a treatment with steam and activated carbon can be adjoined.

Christensen[4] reactivates alumina used in the chromatographic analysis of Tinctura nucis vomicae by heating it for 2 hrs. over an open flame, and Gerstenberg[5] mentions the original activity to be completely restored after the material has been washed with organic solvents, alkali carbonate solutions at an elevated temperature and hydrochloric acid successively, finally having been heated with activated carbon. Sergeant[6] uses a mere heating, maintaining the temperature below 700° C. Alumina which has been used in the purification of transformer oil can, according to Harwood and Davies[7], be reused after being heated up to 650—700° C in a bed through which a flow of air is blown. Latham[8] mentions that waste alumina from transformers did not attain its original effectiveness in a treatment consisting of washing with paraffins, and burning or drying in air at 500—600° C. The method of Murata and Kakudo[9], which is discontinous and seems to be somewhat elaborate, comprises treatments with potassium bichromate in a sulphuric acid solution, aquous alkali and heat. The product is said to be of a good quality. Summarizing numerous investigations Eckart[10] states that the restoration can be effected in general to 80 per cent at most, and usually to 50—60 per cent only.

From the investigations mentioned above the conclusion can be drawn that the methods available for obtaining good results are either slow or elaborate. To remove strongly adsorbed substances an equally energetic treatment is needed, but the danger of damaging the micro structure of the material simultaneously arises especially if a high temperature acts long upon it. Weitbrecht and Fricke[11] have measured by means of ultramicroscopy and X-rays the dimensions of the pores in active γ-alumina and have obtained values between 25 and 150 Ångström units, the mean value being about 50 Å. For the molecular area they obtained the value of 45,000 square meters per mole, when a heating for 2 h at 500° C was used in the preparation of the sample. If the temperature was raised to 800° C, otherwise maintaining the conditions unchanged, the molecular area was reduced by about a third. A lengthening of the heating time was also found to have an effect in the same direction.

Usually in the preparation of active alumina the starting material is artificial aluminium hydroxide which on dehydration changes to γ-AlOOH. Hüttig and Grubitsch[12] refer to an unpublished paper of W. Schröder in which it is stated, that γ-AlOOH at 120° C, losing its constitution water, is converted into γ-alumina. In this condition the material, however, is found to be amorphous and very unstable, and a slow recrystallisation is observed. The rate of the recrystallisation increases but little when the temperature is raised up to 790° C from which point the speed-temperature curve rapidly rises. Thus the decrease in the molecular area mentioned above and obviously a decrease in the adsorption-activity can be explained.

Another reason for the deteriorating effect of long heating at high temperatures is the allotropic change of γ-alumina into the α-form or corundum. Weitbrecht and Fricke (*l. c.*) have found this to happen rather sharply at 1150° C by studying the X-ray diffraction patterns. On the other hand, Hückel[13] reparts a temperature as low as 750° C at which the α-modifikation begins to form at a measurable speed. The difference in the results might be regarded to be due to differing amount of impurities from one preparation to another particularly when it is known that alkali is left in adsorptive aluminas intentionally. Thus it is evident that conditions under which the irreversibile change to the ineffective corundum is possible, are to be avoided as well as the conditions aiding the recrystallisation of the active γ-form. Hence, a short time of action and low temperatures are favourable.

EXPERIMENTAL

Material and pre-treatment

The alumina used in the regeneration experiments was a 'Savory & Moore' product 'standardized according to Brockman'. It had been exhausted in different chromatographic separations of exclusively organic substances of varying and so far unravelled constitution. Substances left in the adsorbent could not be eluted with an methanol-benzene mixture.

The excess solvent was removed by burning off the alumina in an open kettle and thereafter heating the material with a bunsen burner in batches of about one kilogram until the small fountains caused by the solvents and moisture boiling off disappeared. During this manipulation there was a change in the colour to an evenly light tan. In ultraviolet light the material had a bright white fluorescence whereas the original one had a sandy coulour.

The material thus treated was ready for further reactivation experiments.

Treatment with ozone

As it could be supposed that the browning during the pre-heating was due to cracking reactions causing unsaturated linkages, an idea was at hand to break up and remove the substances by means of ozonization. 50 grams of the material were poured on a G 3 glass sinter filtering funnel forming a 15 mm thick layer. Through the sinter a flow of oxygen containing 5—6 vol. % ozone was lead upwards at a speed of 12 litres an hour. A reaction immediately began, changing the colour in the lowest layer into pure white and the reaction vessel warmed considerably. The escaping gas did not liberate iodine from a potassium iodide solution, thus showing the ozone absorption to be complete. The all-over reaction time rose to 50 min partially because the reaction layer, owing to a varying flowing resistance, advanced unequally. The treated material did not give a positive ozone reaction with potassium iodide-starch solution after heating up to 300° C for one minute.

The product was pure white but still gave a white fluoressence in ultraviolet light and did not belong to any activity class, tested according to Brockman [1]. It is obvious that a number of saturated linkages still have remained in the heating operation which linkages do not react with ozone, and on the other hand some decomposition products of the ozonides may not be easily removed by heat. The work in this direction was checked because of its elaborateness.

Application of direct heating

The brown material was heated with continous mixing in an open iron bowl over a strong gas flame in batches of about 500 g. In half an hour the alumina was changed to a grayish white matter. A sample taken did not belong to any standard class. Only after a heating of several hours and simultaneous mixing, products were obtained which belonged to different classes. The method proved to be uncertain, elaborate and slow.

Burning in oxygen

With regard to the viewpoints mentioned in the theoretical part an apparatus was constructed in which the organic substances could be burned off without using too high a temperature. The operation was performed, using the countercurrent principle, in a quartz tube surrounded by an electrical resistance and placed at an angle of 35° in respect to the horizon. The running time of the alumina through the tube was about 10 seconds. The length of the tube was 100 cm and the bore 16 mm. The heating mantle was placed on the upper portion and had a length of 75 cm. The lower end was connected with a rubber stopper to a 1 liter distillation flask, the oxygen inlet being through its side tube. The material was lead to the quartz tube from a dropping funnel, and the rate of flow of the alumina was controlled with the stopcock. Previously the material had been screened to remove extraneous particles. The burnt alumina was collected in the distilling flask. Temperature measurements were performed using a Pt—PtRh thermocouple inserted into the quartz tube.

The heating resistance was wound of Kanthal D 0.7 mm resistance wire in a spiral, the total resistance being 40 ohms. The whole construction was inserted into a Pyrex tube of an inner diameter of 40 mm and wound on the outside with asbestos tape. Using a 220 V current a temperature of 850° C could be achieved.

A number of regeneration experiments were run, changing the flow rates of alumina and oxygen at several temperatures. It was found that below 700° C the working rate had to be uneconomically slow, and on the other hand at about 800° C a slight sintering seemed to occur causing an uneven flow of the material. In the table test values from the

Table 1.

No.	Colour in ultraviolet light	Colour in day-light	cm^3 O_2/g alumina	g Alumina/min	Temperature ° C	Activity class acc. to Brockman	Elutable per cent
Original	S	W	—	—	—	I	0.001
1	L	G—W	307	1.3	750	I	0.005
2	S—L	G—W	144	1.4	720	I	0.001
3	S—L	G—W	105	3.8	760	I	0.002
4	S	G—W	63	5.4	770	I	0.002
5	S	G—W	55	7.6	750	I	0.004
6	S	G—W	51	3.7	760	I	0.004
7	S—W	G—W	67	3.2	710	I	0.002
8	W	B	20	12.5	750	II	0.002
9	W	B	16	12.2	770	II	0.001

Significances of the letters: S = sandy, L = lilac, W = white, G = grayish, B = brownish (tan).

interval 700—800° are collected. Values in the column »elutable per cent» are obtained as follows: about 12 grams of the regenerated alumina were washed on a sintered glass filter forming a column 19 × 50 mm. At first 30 cm^3 of ether, containing 3 % alcohol were used, and thereafter 20 cm^3 petroleum ether 40—60° C with the same amount of alcohol. The collected filtrates were evaporated to dryness, and the residue weighed.

The results show, that using 50 cm^3 or more oxygen for each gram of alumina, regeneration products belonging to the first standard class are obtained. A large excess of oxygen or too slow a rate of flow of the alumina, both cause an abnormally dark fluorescence colour which can render it difficult to perform chromatographic analyses in ultraviolet light. Changes in temperature between 700 and 800° C seem not to have any remarkable effect. The amount of eluable remains in every case insignificantly low. The grayish tinge of the reactivated adsorbent might be due to elementary carbon left in the pores and hardly causes any troubles.

By this method about 15 kilograms have been treated at our laboratory, a part of it three times, and the product has proved to be equal to the original. When handling oxygen sensitive substances it is preferable to remove the oxygen left by leading nitrogen through the material.

SUMMARY

1. The reactivation of alumina, used in the chromatographic separation of organic substances, has been investigated by treating it with ozone by burning in an open kettle, and by burning in oxygen.

2. The burning in countercurrent oxygen gave products of the first activity class »according to Brockman». The two other methods proved unsatisfactory.

REFERENCES

1. Brockman, H., and Shodder, H. *Ber.* **B 74** (1941) 73.
2. Strain, H. H. *Chromatographic adsorption analysis.* New York (1945) p. 159.
3. Hesse, G. *Adsorptionsmethoden im chemischen Laboratorium.* Berlin (1943) pp. 52—53.
4. Christensen, V. A. *Dansk Tids. Farm.* **18** (1944) 105.
5. Gerstenberg, Germ. pat. no. 605736, *Chem. Ztg.* **60** (1936) 153.
6. Sergeant, S. V. Proc. Tech. Sect., *Paper Makers' Assoc. G. t. Brit. & Ireland* **25** (1944) 260, *C. A.* **40** (1946) 447.
7. Harwood, J., and Davies, V. C. *Elec. Times* **107** (1945) 476, *C. A.* **40** (1946) 3207.
8. Latham, A. *Elec. Times* **105** (1944) 772, *C. A.* **39** (1945) 2865.
9. Murata, K., and Kakudo, A. *Rept. Osaka Municipal Research Inst. Domestic Sci. 17 no. 1* (1946) 199, *C. A.* **41** (1947) 4897.
10. Eckart, O. *Chem. Ztg.* **60** (1936) 153.
11. Weitbrecht, G., and Fricke, R. *Z. anorg. Chem.* **253** (1945) 9.
12. Hüttig, G. F., and Grubitsch, H. *FIAT Review of German Science, Inorganic Chemistry, part: Reaktionen im festen Zustand und die Grundlagen der Pulvermetallurgie* (manuscript).
13. Hückel, W. *Anorganische Structurchemie.* Stuttgart (1948) p. 659.

Received May 9, 1949.