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Catalysis Today 55 (2000) 51–60

CATALYSIS TODAY

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Rinse water purification using solid regenerable catalytic adsorbents

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Abstract

The catalytic wet and dry oxidation of organic substances adsorbed on mixed oxides in relation to the development of solid regenerable catalytic adsorbents for the recycling of rinse water from electronic industries is discussed. The modification of oxide-type adsorbents by copper improves their regenerability, both by increasing the rate of complete oxidation of the adsorbed organic substances (Na-gluconate and triethanolamine) and by reducing other negative aspects such as the formation of NO_x during the oxidation of triethanolamine, due to its role in catalyzing the oxidation in mild conditions of the absorbed species and the selective conversion to N_2 of the adsorbed amino groups. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Wet and dry oxidation; Copper; Rinse water; Triethanolamine; Sodium-gluconate

1. Introduction

New water quality regulations have led to a growing interest in improved technologies for wastewater purification and have stimulated especially in Europe, the development of efficient technologies for rinse water purification, since its recycling is economically attractive [1–3]. In fact, the cost of industrial water has increased nearly exponentially over the last two decades and for companies using large volumes of high purity water, the recycling of water has economic advantages which combine with additional benefits in terms of improved water management and use of natural resources [3]. This problem especially concerns the electronics industries (for example, in printed board manufacture [4–6]), due to their large volumes of rinse water effluents containing a great variety of organic/inorganic components in small amounts. The rinse water obtained during the cleaning and processing steps contains a large number of organic chemicals such as surfactants, brighteners, corrosion inibitors, complexing agents, residue from the lacquering processes, etc., which should be removed in order to recycle the water. A considerable proportion of these chemicals are not biodegradable.

Due to the low concentration of organics in water, direct wet oxidation is not economical [7–9], nor do other possible technologies appear to be suitable or efficient for the purpose, but a combination of technologies including an adsorption stage is the preferable choice [2,3]. Adsorption technologies are usually based on active carbons [9], but the cost and complex procedures necessary for their regeneration make the development of alternative technologies based on the use of regenerable solids necessary. Mixed oxides, perhaps containing transition metals such as copper to promote the catalytic oxidation of adsorbed substances, seem the most reasonable choice in terms of (i) the cost of the materials, (ii) the fact that their textural properties can be tuned, (iii) the easy of their large scale preparation even in the form of pellets with good

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PII: S0920-5861(99)00225-4

mechanical strength properties, and (iv) the fact that they can be modified by introducing catalytic components to improve their regenerability. Very limited information is available on this subject in literature.

The aim of this work is to explore the use of mixed oxides as regenerable solid catalytic adsorbents for the development of a technology for the removal by adsorption at room temperature of the organics present in the rinse water of the electronics industry and the regeneration of the adsorbent in mild conditions. The adsorbent contains a catalytic component able to promote the wet or dry oxidation of the adsorbed substances during regeneration. This work will focus in particular on the behavior of mixed oxides containing or not containing copper as a catalytic element in promoting the oxidation in milder conditions of the adsorbed substances either by dry or wet air oxidation. Organic substances representative of two main classes of compounds present in rinse water in the electronics industry were chosen as model compounds for the study. Since, however, the scope for using this technology is limited by the adsorption efficiency of the first adsorption step, some information on the behavior of the samples at this stage is also given.

2. Experimental

2.1. Materials

γ-Al_2O_3 (RP535 from Rhone–Poulenc) and SiO_2 (SI4-SP from Akzo) were commercial samples with surface areas of 110 and 400 m^2/g, respectively. Zirconia-alumina (10 wt.% of alumina) (hereinafter called ZA) was prepared by the sol-gel method, starting from the corresponding isopropoxide compounds, using acetic acid as the catalyst for gelation and using acetylacetonate as the moderator of the hydrolysis rate in order to obtain a very homogeneous mixed oxide. After ageing and drying, the sample was calcined at 550°C. The final surface area was 140 m^2/g. The preparation of a mixed zirconia–alumina oxide, with respect to the preparation of zirconia alone, makes it possible to prepare higher surface area samples with higher thermal stability, although the surface characteristics resemble those of pure zirconia [10].

The Ca/Al_2O_3 sample (10 wt.% as CaO) was prepared from RP535 alumina by the incipient wet impregnation method using an aqueous solution of Ca_2NO_3. After drying, the sample was calcined at 500°C overnight.

$Cu/ZrO_2–Al_2O_3$ (9 wt.% CuO) (hereinafter called CuZA) was prepared by adding Cu_2HCO_3 during the synthesis of the zirconia-alumina sample by sol–gel as indicated above. The relative amounts of zirconia and alumina in this sample were the same as those in the ZA sample, and the calcination procedure was also the same. The surface area after calcination was 145 m^2/g.

Prior to the tests, all oxide samples were pelletized in the form of small grains with dimensions ranging from 30 to 60 mesh and then washed with boiling double distilled water up to complete removal of the dissoluble organics.

The granular active carbon (GAC) used for comparison was a commercial bituminous coal sample from NORIT (PK 1–3, 12 × 40 mesh, surface area 800 m^2/g) activated at high temperature. Prior to the adsorption tests the active carbon was extensively washed with boiling water until a washing solution not containing organics dissolved from the active carbon was obtained. The GAC was used directly in the granular form.

2.2. Procedures

Adsorption tests were carried out at natural pH and room temperature using a stirred batch reactor containing 100 ml of solution with total organic carbon (TOC, mg/l) of about 100. The solution was prepared from RP grade chemicals (sodium-gluconate or triethanolamine) solubilized in double distilled water. 1 g of adsorbent was added to the aqueous solution and then the change in the concentration of the organic followed as a function of time.

The adsorption capacity of the sample was defined in terms of the amount of organic adsorbed after 5 h. The regenerability of the sample was defined in terms of the percentage of adsorption capacity recovered after the regeneration treatment with respect to the adsorption capacity of the fresh adsorbent.

Dry regeneration tests were carried out by loading the adsorbent in a flow reactor and rapidly increasing the reaction temperature to 250 or 450°C, and then maintaining isothermal temperature for 2 h, in a flow of synthetic air (6 l/h). Then the reactor was cooled down to room temperature and the solid tested to check the fraction regenerated by monitoring its adsorption behavior as described above. The solid, once recovered by filtration from the solution, was dried at room temperature overnight prior to being loaded in the reactor.

Temperature programmed oxidation (TPO) tests were carried out in a quartz flow reactor connected to an on-line mass quadrupole detector (VG SX200). After adsorption tests and room temperature drying, 0.1 g of the sample was loaded in the reactor. 20% O_2 and 80% He flow (6 l/h) was used as a carrier gas with a rate of temperature increase of 2°C/min. The partial helium pressure was used to normalize fluctuations in the total pressure in the vacuum chamber of the quadrupole. The possible overlap in mass intensities of different components was corrected.

Wet air oxidation tests were carried out in stainless steel autoclave apparatus containing 100 ml of water and 1g of the sample after the adsorption tests. The sample was contained in a basket suspended over the solution. After adding 20 bar of O_2 at room temperature, the temperature of the autoclave was raised to the temperature of the tests (150–230°C range). Only after stabilization of the temperature, was the basket containing the solid sample immersed in the aqueous solution. After 3 h the temperature was lowered to room temperature and the solid extracted from the basket to check its regeneration. The aqueous solution was also analyzed to determine the organic chemicals dissolved in it by TOC measurement and ionic chromatography analysis. The amount of copper leached into the aqueous solution was determined by atomic adsorption (AA) spectroscopy.

3. Results and discussion

In order to study the reactivity of the adsorbed compounds derived from the removal of organics from the rinse water of the electronics industry, (i) Na-gluconate (GLU) (brightener and chelating agent) and (ii) triethanolamine (TEA) (model of inhibitors of corrosion) were chosen as model compounds.

3.1. Adsorption of the model compounds

The behavior of some selected oxides or mixed oxides in the adsorption of the two model chemicals is reported in Figs. 1 and 2 (GLU and TEA, respectively). For comparison, the behavior of a typical granular active carbon (GAC) in the same reaction conditions is also reported. In the case of GLU both the rate of reaction and the adsorption capacity increase in going from silica to alumina and zirconia-alumina. The latter mixed oxide has been used instead of pure zirconia, because the presence of alumina (10 wt.%) added during the sol–gel synthesis makes it possible to increase the surface area (from about 80 m^2/g to 140 m^2/g) and stabilize the oxide with respect to thermal sintering and phase transformation above 450–500°C [10]. However, the chemical surface characteristics remain analogous to those of zirconia, indicating thus that alumina acts mainly as a structural matrix.

All three oxides show worse performances both in terms of rate and capacity of adsorption of GLU with respect to the active carbon (Fig. 1). However, when the oxides are doped with calcium, the performances were very comparable to those of the active carbon, as shown in Fig. 1 for the case of the Ca/Al_2O_3 sample. However, this doping significantly depresses adsorption behavior when an organic with different chemical properties is tested, as shown in Fig. 2 for TEA. In this case it may be observed, however, that silica behaves similarly to the active carbon. Data in Figs. 1 and 2 also show that modification of the oxides with a transition metal such as copper, which catalyzes the oxidative regeneration (see below), does not significantly change adsorption behavior. It was also established that copper does not leach during the adsorption experiments.

3.2. Regeneration in dry conditions and the catalytic effect of copper

Summarized in Figs. 3 and 4 is the behavior of the selected adsorbents after regeneration made by treatment at selected temperatures in an air flow. Data are reported as a percentage of the initial adsorption capacity recovered after the regeneration procedure in dry conditions and refer to the results obtained after three complete cycles of adsorption-regeneration,

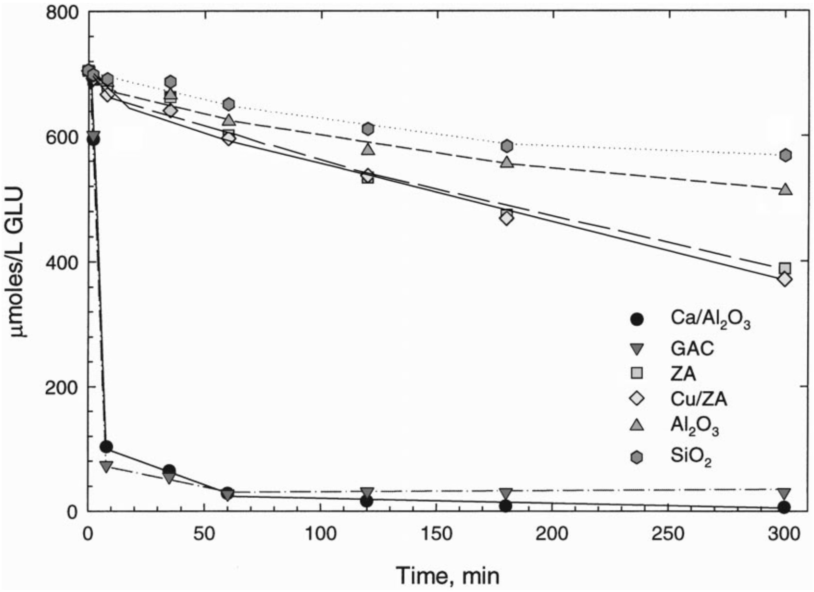

Fig. 1. Adsorption of sodium-gluconate (GLU) as a function of time in batch reactor tests on a series of mixed oxides and, for comparison, of a granular active carbon (GAC).

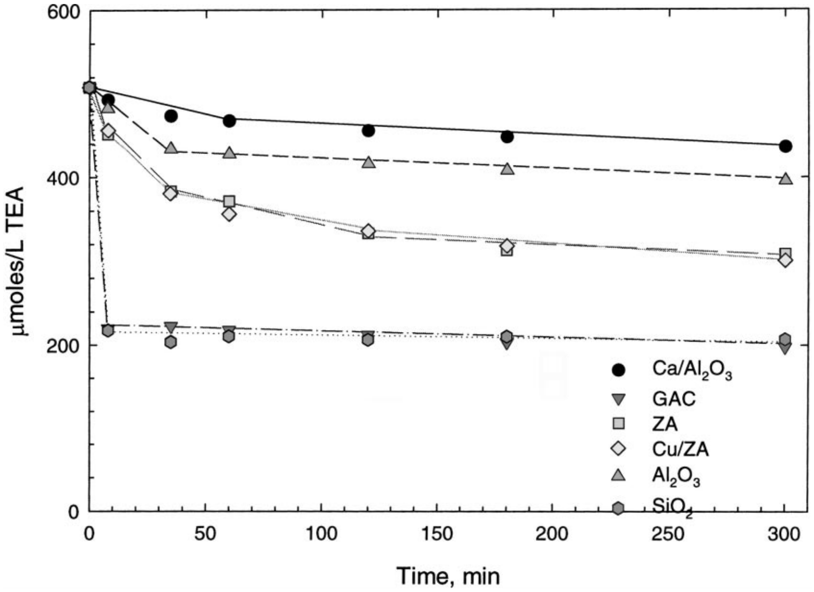

Fig. 2. Adsorption of triethanolamine (TEA) as a function of time in batch reactor tests on a series of mixed oxides and for comparison of a granular active carbon (GAC).

because it was previously verified that behavior does not significantly change in further consecutive adsorption-regeneration cycles. Temperatures of 250 and 450°C were selected for the oxidative treatment, because the first one is roughly the temperature limit that must be observed to avoid combustion of the active carbon and to make comparison of the regenerability of the oxide adsorbent with that of the active

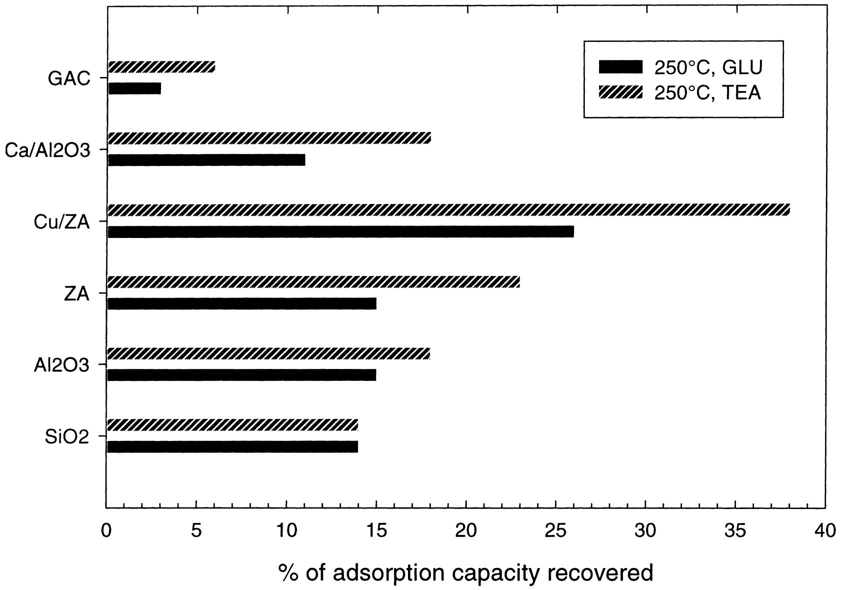

Fig. 3. Percentage of the adsorption capacity (with respect to the initial sample in tests as in Figs. 1 and 2) recovered in the case of GLU and TEA adsorption after regeneration in dry conditions at 250°C. Data refer to behavior during the third cycle of reaction-regeneration.

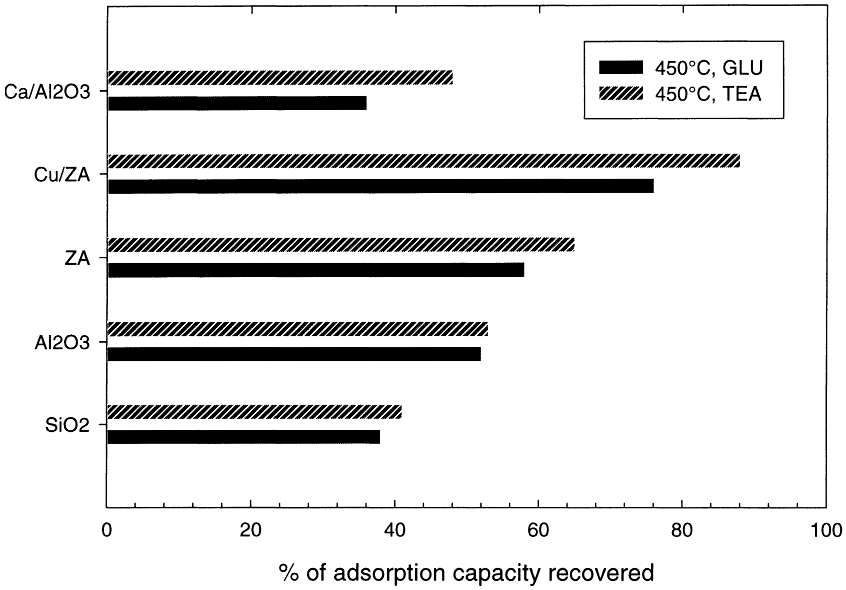

Fig. 4. Percentage of the adsorption capacity (with respect to the initial sample in tests as in Figs. 1 and 2) recovered in the case of GLU and TEA adsorption after regeneration in dry conditions at 450°C. Data refer to behavior during the third cycle of reaction-regeneration.

carbon possible. The higher regeneration temperature was selected as appropiate for high temperature oxidative treatments, in conditions in which the possible thermal sintering of the oxide adsorbents during oxidative regeneration (also taking into account possible local overheating) can be avoided. As expected, no substantial decrease in surface area was observed after regeneration. 450°C oxidative treatment was not possible for GAC, due to combustion of the active carbon.

After oxidative regeneration at 250°C it was possible to recover a low fraction of the adsorption capacity, although generally the fraction recovered by oxides is significantly higher than that of the active carbon. It may be also noted that, while there are minor differences between the various oxides in terms of the fraction of adsorption capacity recovered, significant enhancement is shown by the sample containing copper, due to the role of copper in catalyzing the combustion of the adsorbed substances. It can be also noted that recovery of adsorption capacity after TEA adsoption is sligthly higher than after GLU adsorption.

After oxidative regeneration at 450°C the fraction regenerated increases more than twofold, although in all cases regeneration is not complete here too. The copper containing sample shows a significant increase in the regenerability with respect to undoped oxide.

Since zirconia-alumina samples show a better compromise between the adsorption behavior of both TEA and GLU as well as good regenerability, further investigation of the role of copper as a catalytic element for promoting the combustion of the adsorbed substances was focused on ZA and Cu/ZA samples.

In Fig. 5 the TPO results for ZA after adsorption of TEA, as for the tests reported in Fig. 2, are reported. After adsorption, the solid was recovered by filtration and simply dried overnight at room temperature before being loaded in the reactor for the TPO experiments. Three peaks of carbon oxides formation, centred at about 120, 350 and 500°C were detected (Fig. 5). This suggests the presence of different TEA species on the surface of ZA characterized by different strength/oxidizability. In fact, the formation of ethanol (a product desorption must be (a product probably derived from the hydrolysis of adsorbed TEA) and of NO_x (probably deriving from the oxidation of amino group) also closely follows that of CO_2·CO formation, on the otherhand, occurs mainly at the higher temperatures. Traces of methanol and of monethanolamine were also detected in the 100–200°C range. No desorption of TEA as such was detected however, suggesting that the rate of its transformation (by oxidation or hydrolysis, as indicated by the detection of ethanol) is faster than that of its desorption.

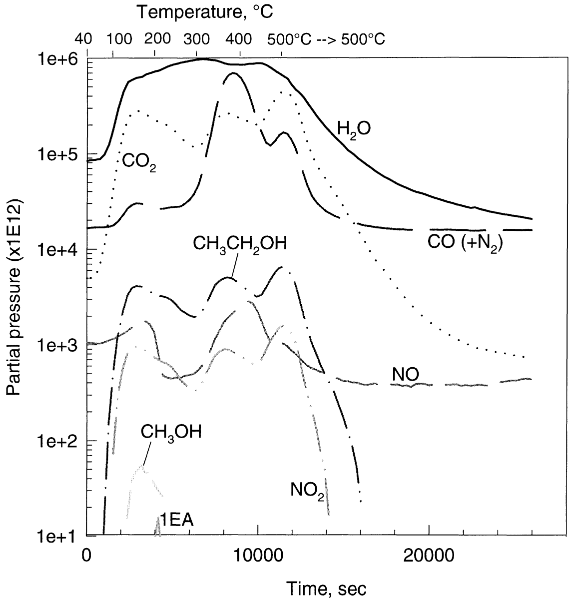

Fig. 5. Temperature programmed oxidation (TPO) tests using ZA after adsorption of TEA in conditions as for Fig. 2.

The ammonia signal (mass 17) is covered by the very intense fragmentation of water at the same mass, but the intensity ratio between the peaks at mass 18 and 17 is very close to that expected for water only. This indicates that ammonia formation should be not very significant, although it is not possible to rule out low ammonia desorption. Due to the detection of relatively large amounts of NO_x, however, it is reasonable to assume that adsorbed ammonia (deriving from TEA hydrolysis) is primarily oxidized to NO_x.

TPO results for Cu/ZA are shown in Fig. 6. Several significantly different features are present as compared with TPO data for the copper-free ZA sample (Fig. 5):

The formation of carbon oxides is shifted to lower temperatures, and in particular the formation of CO_2 and CO in large amounts occurs below about 450°C, although some residual CO_x formation was also detected at 500°C during the isothermal run following maximum temperature in the TPO experiment being reached. This indicates that copper effectively catalyzes the oxidation of adsorbed substances, although in this case too, adspecies that are quite resistant towards oxidation are present. These adspecies only slowly oxidized even at 500°C in a flow of air.

The ratio between CO_2 and CO is higher than in the case of the ZA sample, confirming the improved oxidation characteristics of the sample containing copper.

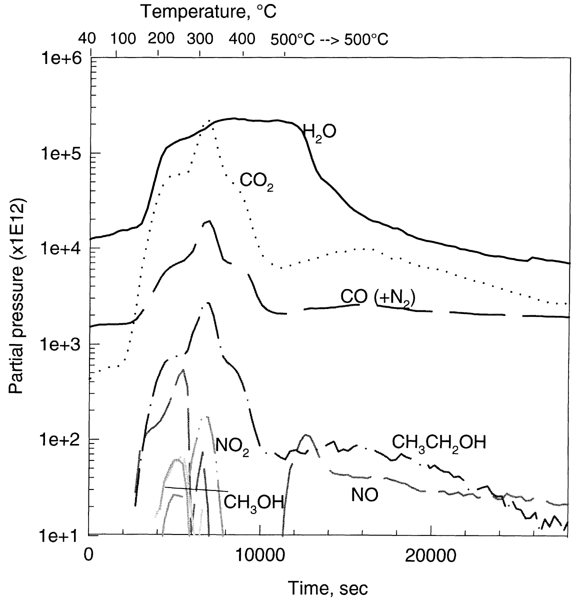

Fig. 6. Temperature programmed oxidation (TPO) tests using Cu/ZA after adsorption of TEA in conditions as for Fig. 2.

The formation of NO_x is significantly reduced in comparison to the ZA sample. It is known that copper ions catalyze both the direct selective oxidation of ammonia to N_2 and the reaction of NO_x with adsorbed ammonia [11]. It is thus reasonable to assume that the presence of copper catalyzes these reactions, thus leading to lower formation of NO_x.

It should also be noted that, as observed for Fig. 5, in Cu/ZA (Fig. 6) the formation of ethanol and NO_x also closely follows that of carbon oxides, indicating that the first step of TEA transformation is probably the hydrolysis connected to the presence of large amounts of adsorbed water on the sample.

As discussed for the ZA sample, the presence of different desorption peaks in CO_x and in the fragmentation products in the case of Cu/ZA suggests the presence of TEA adspecies with different adsorption strengths and reactivity towards O_2. However, during the TPO run the continuous increase in temperature does not provide clear evidence that this phenomenon is apparent, due to insufficient time for complete conversion. Therefore, a second set of TPO experiments were performed on Cu/ZA. During a first run the temperature is raised to 200°C only, then isothermal temperature is maintained for about 8 h (Fig. 7A). Then, after cooling to room temperature, the same sample was analyzed again in TPO experiments from room temperature to 500°C (Fig. 7B). It can be noted that the overlap in the desorption curves for the two cases roughly describes the TPO data obtained in direct heat-

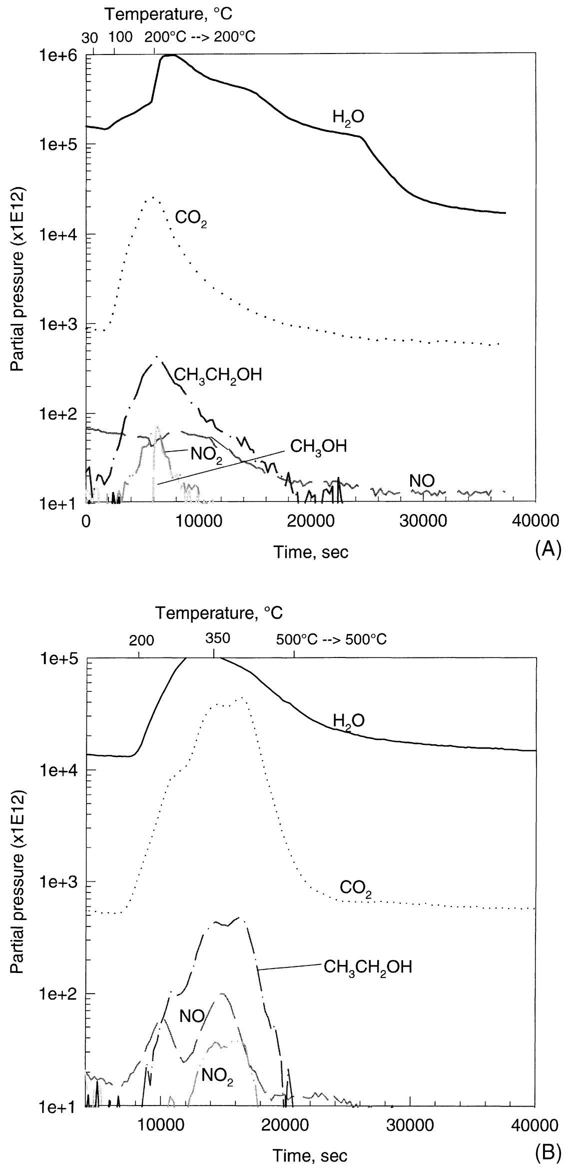

Fig. 7. (A) Temperature programmed oxidation (TPO) tests up to 200°C using Cu/ZA after adsorption of TEA. After reaching the temperature of 200°C, the sample was kept at the same temperature for about 8h in the flow of air, prior to cooling. (B) TPO tests up to 500°C on the same sample after the TPO tests in Fig. 7A.

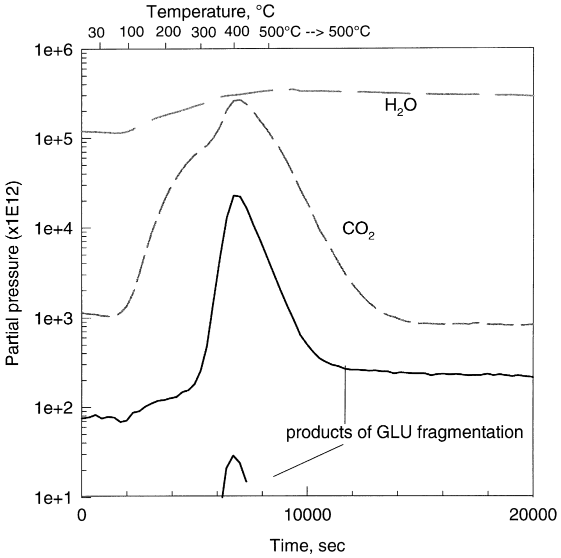

Fig. 8. Temperature programmed oxidation (TPO) tests using Cu/ZA after adsorption of GLU in conditions as for Fig. 1.

ing from room temperature to 500°C (Fig. 6). This suggests that the results observed are not masked by kinetic effects, but are really due to the formation of quite unreactive TEA adsorbed species on the oxide. These adspecies need a temperature in the 300–500°C range to be hydrolyzed and oxidized: this explains why regeneration by oxidative treatment in mild conditions is not effective, even in the presence of components which catalyze the reaction of oxidation such as copper.

Copper, on the other hand, is necessary not only to promote the combustion of adsorbed species and thus allow better regenerability (Figs. 3 and 4), but also to lower the formation of NO_x and CO. A secondary catalytic post-treatment, however, would be probably necessary in the event of application of the technology.

The TPO curves for GLU adsorbed on Cu/ZA are reported in Fig. 8. Oxidation of adsorbed GLU occurs in two steps, centred at about 250 and 400°C, giving mainly CO_2 (CO formation was very low). Concomitantly with the higher temperature desorption peak of CO_2, the formation of GLU fragmentation products (at mass 85 and 43) was also observed, suggesting that in this case the hydrolysis of adsorbed GLU also leads to partial desorption of GLU itself. Using ZA, analogous TPO curves were observed, but the higher temperature CO_2 peak shifts to about 500°C.

3.3. *Regeneration by wet air oxidation*

In dry oxidative regeneration, combustion is not complete and there are competitive fragmentation/desorption reactions which indicate the need for a secondary catalytic treatment to purify the gas emission. Therefore, an alternative means of regeneration of the exhausted adsorbent by wet air oxidation was also evaluated. The results of the fraction of adsorption capacity (with respect to fresh initial samples) recovered by wet air oxidation treatment at different temperatures is shown in Fig. 9 in the case of TEA and GLU adsorbed on Cu/ZA and ZA.

For reaction temperatures below about 200°C, low regenerability of the samples was observed, but above this temperature good regenerability was observed especially for the sample containing copper. The presence of copper to catalyze wet oxidation is not only necessary to improve adsorbent regenerability, but in general to increase the oxidizability of adspecies, as suggested by the lowering of the amount of products of partial oxidation detected in the aqueous solution after the wet air oxidation tests (Table 1).

The promoting role of copper in enhancing the regenerability of oxide-type adsorbents is probably related to its redox properties and thus to an enhancement of the rate of oxidation of the adsorbed substances by a Mars-van Krevelen type mechanism in which the adsorbed substances are oxidized by the copper which is then reoxidized by the oxygen dissolved in water. However, it may be also observed that due to the radical-type mechanism prevailing during the non catalytic wet air oxidation, a second possible mechanism of the action of copper is to activate the oxygen which is adsorbed on the catalytic surface by electron transfer, generating negatively charged oxygen species which are known to possess higher oxidation power.

It may finally be noted that some leaching of the copper is observed especially in the samples treated at the higher temperatures (Table 1), indicating potential problems in the deactivation of the samples using this procedure, although the amount of copper leached is of the order of a few percent with respect to the total amount of copper in the sample and thus up to five cycles of reaction-regeneration no deactivation was noted.

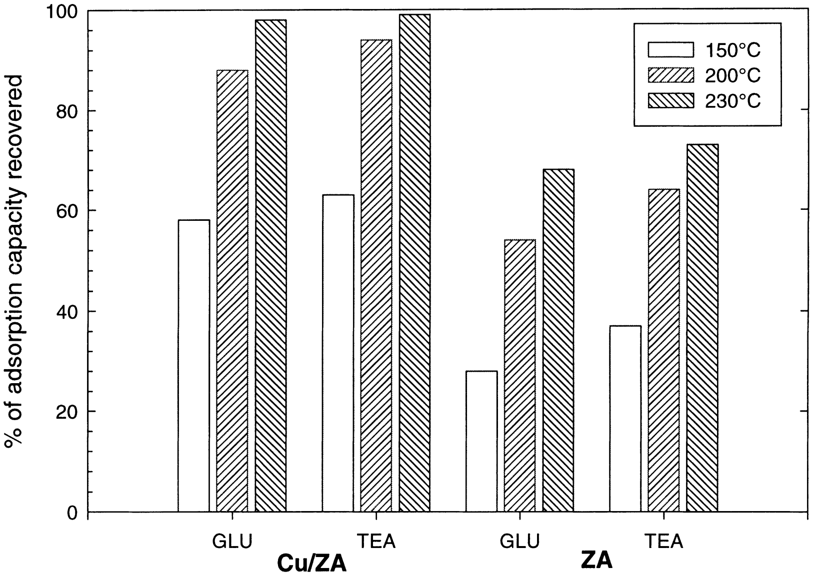

Fig. 9. Percentage of the adsorption capacity of ZA and Cu/ZA (with respect to the respective initial samples in tests as in Figs. 1 and 2) recovered in the case of GLU and TEA adsorption after regeneration by wet air oxidation at increasing reaction temperatures (3 h, 20 bar of oxygen partial pressure). Data refer to behavior during the third cycle of reaction-regeneration.

Table 1
Amount of acetate and formiate ions and of copper leached from the catalyst detected in the aqueous solutions after wet air oxidative regeneration as indicated for Fig. 9

Sample	Temp. (°C)	By products in solution		Copper leaching (ppm)
		Acetate (ppm)	Formiate (ppm)	
ZA	150	84.3	38.4	–
	200	121.5	42.2	–
	230	116.5	40.8	–
Cu/ZA	150	30.3	13.7	8
	200	44.5	21.6	11
	230	39.8	11.6	13

4. Conclusions

The addition of a catalytic element such as copper to solid oxide-type adsorbents considerably promotes their regenerability either by dry or wet air oxidation, but temperatures above 450°C in dry conditions and above 200°C in wet conditions are necessary to reach good levels of regenerability. With respect to active carbon, the use of oxide-type adsorbents containing copper as a catalytic element allows regeneration in mild conditions, but performances in adsorption are much lower especially when the oxide-type adsorbent is not tailored to absorb a specific class of chemical.

The drawback in dry regeneration is the partial desorption of the products of fragmentation, the formation of carbon monoxide and, in the case of chemicals containing amino groups the formation of NO_x. A secondary catalytic post-treatment may be thus necessary. The use of copper-modified adsorbents reduces these drawbacks, but does not eliminate them completely.

In wet air oxidation one drawback is the partial leaching of the copper, although this phenomenon is limited to a small percentage of the total copper amount in the adsorbent/catalyst. Small amounts of the products of partial oxidation are also detected in the aqueous solution used for wet air oxidative regeneration. The presence of copper significantly reduces this phenomenon.

The addition of copper as a catalytic element to improve the regenerability of oxide-type adsorbents promotes the behavior of regenerable adsorbents, but does not completely eliminate some of the drawbacks in the use of this technological solution for the purification of water streams. A further effort is thus necessary to improve the regenerability of these materials which should also parallel an effort to develop materials with better adsorption rates and properties, especially using complex mixtures of different classes of chemicals.

Acknowledgements

Financial support of this work from the EC Brite-III programme (contract BRPR-CT95-0034) is gratefully acknowledged.

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