applied
catalysis B

Causes of deactivation and regeneration of an industrial Pt–NiO/Al₂O₃ nitrogen oxides reduction catalyst

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Abstract

The deactivation mechanism and regeneration of spent industrial Pt–NiO/Al₂O₃ catalysts used for NO$_x$ reduction was studied by means of SEM–EDS, chemical analysis and kinetic measurements It was found that the main cause of deactivation under industrial operating conditions is fouling due to carbonaceous and ZnO deposits Various contaminant removal procedures (calcination, wet screening and acetic acid leaching) were tested and the influence of these procedures on contaminant removal and the catalyst activity were investigated Regeneration of the spent industrial catalyst using inexpensive processes was shown to be feasible

1. Introduction

Industrial catalyst deactivation is usually due to poisoning, inhibition, fouling, sintering, chemical reactions and restructuring of the surface [1]

Ideally the characterization of catalysts with respect to deactivation should involve four types of information [1]

1 The nature of the deactivating substances
2 The relation between the quantity of deactivating substances and catalytic properties

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3 The relation between surface changes and catalytic properties

4 The effect of the removal of deactivating substances or active phase redistribution on the total or partial recovery of the catalytic properties

The performance of deactivated catalysts can often be improved by regeneration Deactivation results from inhibition, fouling or sintering and all of these may be reversed —at least in part— with some catalysts Regeneration may consist of either (i) removal of deactivating substances (sometimes poisons, most often inhibitors or fouling agents), e g , coke in hydrogenation catalysts, or (ii) redispersion of the active phase (platinum catalysts) or (iii) both of them (hydrodesulphurization or catalytic reforming catalysts)

Coke removal and active phase redistribution are used extensively in industrial practice and adequate information exists about the conditions and the mechanism of these processes [2–4] Removal of metallic inhibitors or fouling agents is more complicated and difficult, since it involves conditions that may affect the presence of the catalyst's active species Information in the open literature is limited and refers mainly to hydroprocessing catalysts [5–8] Various weak acids and complexing reagents are used in order to dissolve selectively the contaminants without affecting the active components

The main effort of this study was to determine the causes and the type of deactivation as well as the possibility of regeneration of an industrial platinum–nickel–alumina catalyst using simple analytical and deactivating substances removal techniques

2. Experimental

Spent Pt–NiO/γ-Al$_2$O$_3$ nitrogen oxides reduction catalyst (C53-1, Catalysts and Chemicals Europe S A) was obtained from the nitrogen production unit of the EKO petrochemical plant in Thessaloniki, Greece A simplified flowsheet of the nitrogen production unit is shown in Fig 1 Nitrogen is produced through air combustion by LPG (mainly propane), followed by cleaning of the product gases The catalyst was in the form of pellets (diameter 6 5 mm and height 6 5 mm) Chemical analysis of the spent catalyst after dissolution and concentrations determination by Atomic Absorption Spectrophotometry (AAS, Perkin Elmer 2380) gave the following results 0 125% Pt, 2 5% Ni, 0 28% Zn, 0 05% Fe, 0 02% Cu, 5% humidity (measured by catalyst heating at 120°C for 24 h) and 2 8% carbon (measured by thermal gravimetric analysis, TGA), the balance being mainly alumina and traces of other elements

Scanning electron microscopy (SEM) was used for surface optical observations and energy dispersion system (EDS) analysis for the determination of the near-surface elemental composition Although EDS analysis is not precise for small concentrations and does not measure carbon, it gives valuable information about
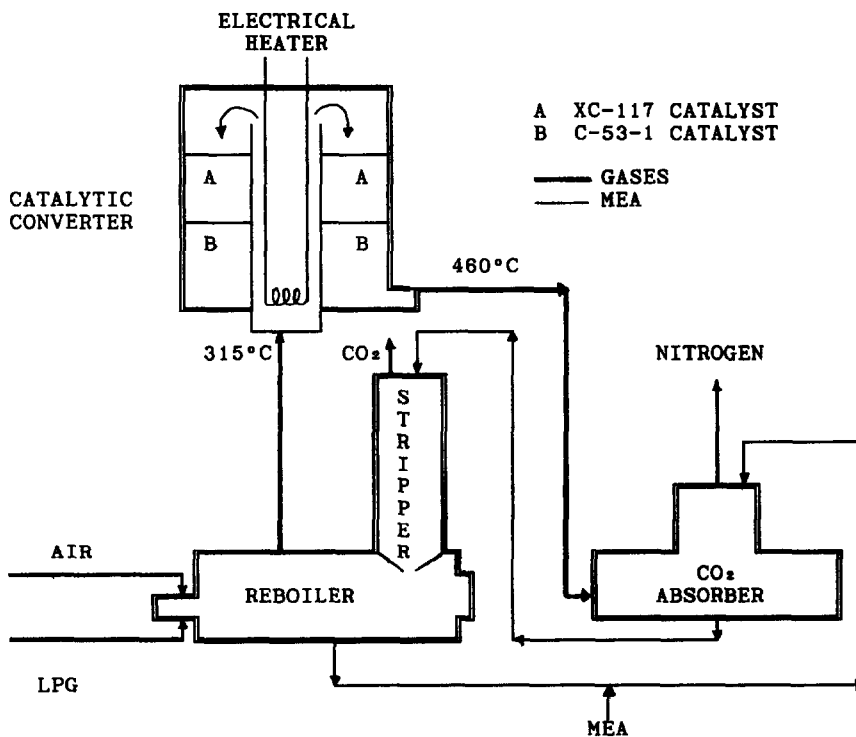
Fig 1 A simplified flowsheet of the nitrogen production unit (blower, pumps, heat exchangers, gas–liquid separators and instrumentation are not included)

the relative elemental composition of the near-surface region where deactivated substances are normally found

Total surface area of the catalyst was determined by nitrogen adsorption (BET method, Micrometrics AccuSorb 2100E)

Bulk chemical analysis for metals concentration determination was made by atomic absorption spectrophotometry (AAS)

In order to remove carbon and organic compounds, calcination was carried out in the laboratory on a static surface under natural airflow

Wet screening was carried out on a screen by thoroughly washing with fresh water, followed by deionized water washing

The acetic acid leaching procedure was carried out using a fixed-bed laboratory glass reactor as described by Hernandez [9] The leaching solution was pumped continuously through the catalyst bed from the bottom of the reactor (up-flow)

Analytical grade reagents were used for all chemicals

Activity tests were conducted in a fixed bed microreactor using a charge of 62 pellets Analytical grade nitrous oxide (6% in helium) was used as feed gas The catalyst bed was conditioned with helium at 250°C for $\frac{1}{2}$ h, then the catalytic surface was reduced by hydrogen at 400°C for 2 h and cleaned by helium for $\frac{1}{2}$ h After that, nitrous oxide was fed at a rate of 200 ml/min When the reactor temperature

stabilized at the predetermined value, residual nitrous oxide in the product was determined using gas chromatography (Perkin Elmer-Sigma 300)

3. Results and discussion

3 1   Causes of deactivation

SEM–EDS analysis gives valuable information about the surface condition and the near-surface chemical composition of catalysts In the photographs of Fig 2 a
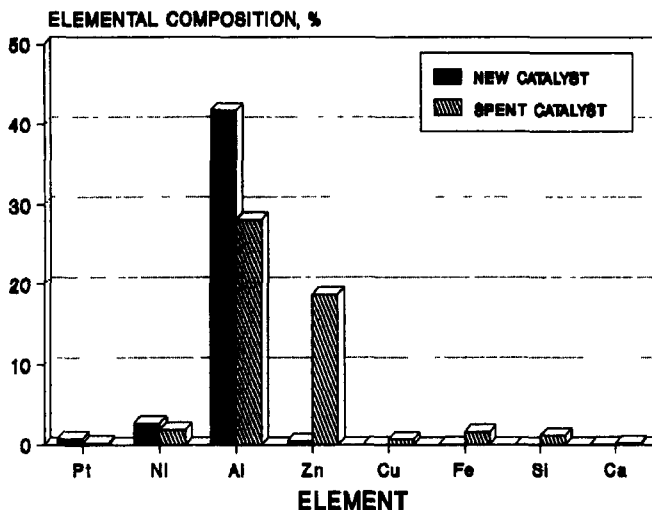
ELEMENTAL COMPOSITION, %
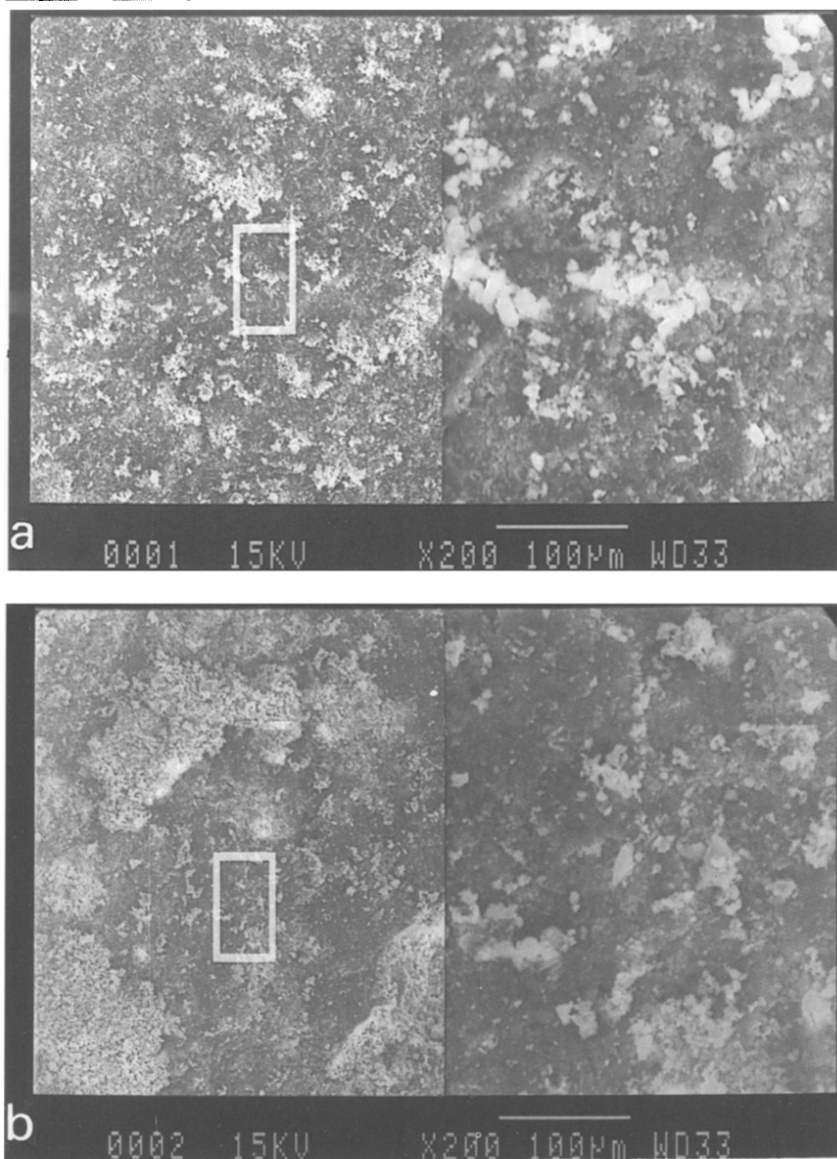
Fig 3 EDS near-surface composition analysis of the new and spent catalyst

comparison is made between the surfaces of new and spent catalysts It is obvious that the surface of the spent catalyst is smoother than that of the new catalyst, due to the coverage by foreign solid matter This is in agreement with the total surface measurements by the BET method which was 165 m^2/g for the new and 126 5 m^2/g for the spent catalyst, respectively The results of the near-surface analysis by EDS for new and spent catalysts are shown in Fig 3 The elements detected in the new catalyst were aluminium from the γ-alumina substrate, the active constituents (platinum and nickel) and trace quantities of contaminants such as, silicon, iron, copper and calcium The spent catalyst contained surprisingly high zinc quantities (more than 20%), as well as silicon, calcium, iron, and copper in quantities considerably higher than the ones present on the new catalyst surface The other main
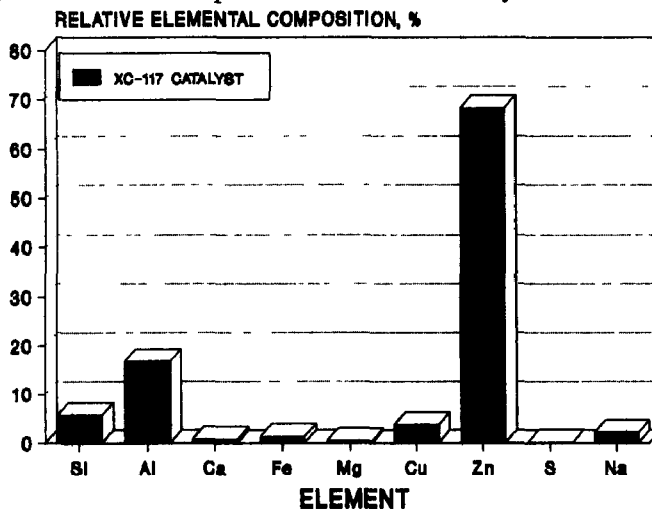
RELATIVE ELEMENTAL COMPOSITION, %

Fig 4 EDS near-surface relative composition analysis of the carbon monoxide oxidation catalyst

constituent of the spent catalyst was carbon (2 8%) as determined by TGA

In order to determine the possible source of zinc contamination, a rough description of the actual industrial unit is made in Fig 1 The gases produced by air–LPG combustion pass through a catalytic converter consisting of two catalyst beds The first one contains a CuO–ZnO, XC-117 (Chemetron Chemicals S A) carbon monoxide oxidation, sulphur resistant catalyst The second one contains, the C-53-1 Pt–NiO/γ-Al$_2$O$_3$ catalyst for NO$_x$ reduction The produced gases, mainly nitrogen and carbon dioxide, pass through the MEA (monoethanolamine) absorption unit for carbon dioxide separation The EDS analysis of the spent CuO–ZnO is shown in Fig 4 Zinc and copper are the main active constituents, while aluminium and silicon are possibly contaminants from the dust carried by air in the industrial unit It is obvious that zinc oxide as well as copper oxide dust produced by erosion of the easily eroded XC-117 catalyst is transferred by the gas flow onto the surface of the C-53-1 catalyst, covering its surface and reducing its activity Silicon and calcium, as well as iron, determined on both spent catalysts, may be attributed to dust transferred by the atmospheric air used in the process

Carbon determined in the catalyst is probably formed during the starting of the unit when it does not work at normal combustion and catalytic conversion conditions

The nature of the deactivating constituents (metal oxides and carbon) show that the more probable deactivation mechanism is fouling

3 2 Procedures and activity tests

To confirm the above proposed fouling deactivation mechanism and to examine the possible rejuvenation technique of the catalyst, a series of experiments were carried out The main effort was to remove the contaminants and to compare the activity of the treated catalyst with the activity of the new and the spent catalyst Wet screening, calcination and acetic acid leaching in various combinations were used

The procedures applied were

Procedure 1 Wet screening

The weak forces by which the metals and silicon oxides dust are attached on the catalyst surface, permit the removal by washing

A spent catalyst sample (100 pellets) was placed on a screen and then thoroughly washed with fresh water for 1 h Then it was washed for another $\frac{1}{2}$ h with deionized water to remove any residuals from fresh water and was dried by heating at 120°C for 24 h

Procedure 2 Wet screening and acetic acid leaching

Zinc oxide is easily soluble even in a weak acid environment [10] Wet screening followed by weak acid leaching is expected to improve the removal of metallic oxide contaminants without affecting the active species of the catalyst Acetic acid, being a rather strong organic acid, was selected as leaching agent
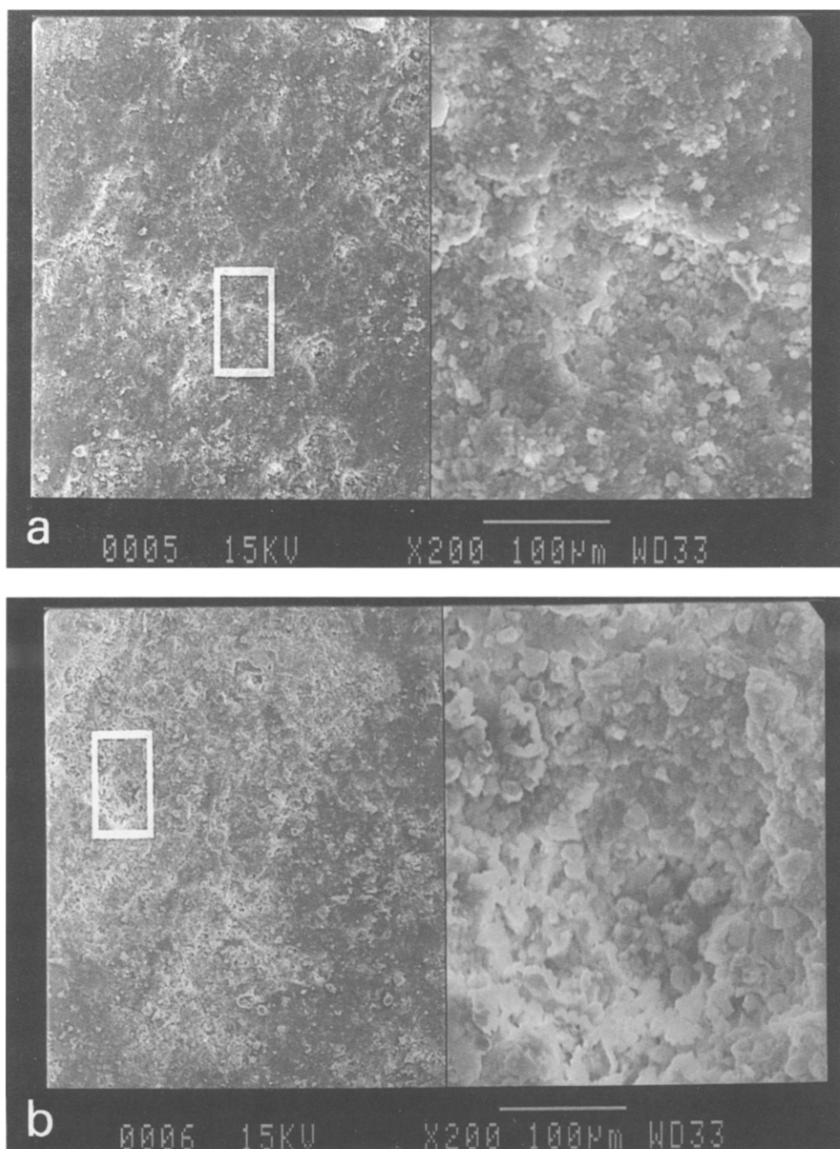
Fig 5 SEM photographs of the catalyst surface treated by Procedure 1 (wet screening) (a) and Procedure 3 (calcination, wet screening) (b)

A spent catalyst sample (100 pellets) was treated according to the wet screening procedure and then placed in a static-bed glass reactor 1 l of a 1 *M* acetic acid solution was heated in a water bath at 40°C and was pumped continuously through the catalyst bed at a rate of 10 ml/min The leaching procedure was stopped when a constant zinc concentration was achieved in the leaching solution (3 h) After acid leaching the catalyst bed was washed with deionized water pumped through the bed to remove the acetic acid that remained in the catalyst (until neutral reaction of the exiting water, 2 h) Finally the catalyst pellets were dried for 24 h at 120°C
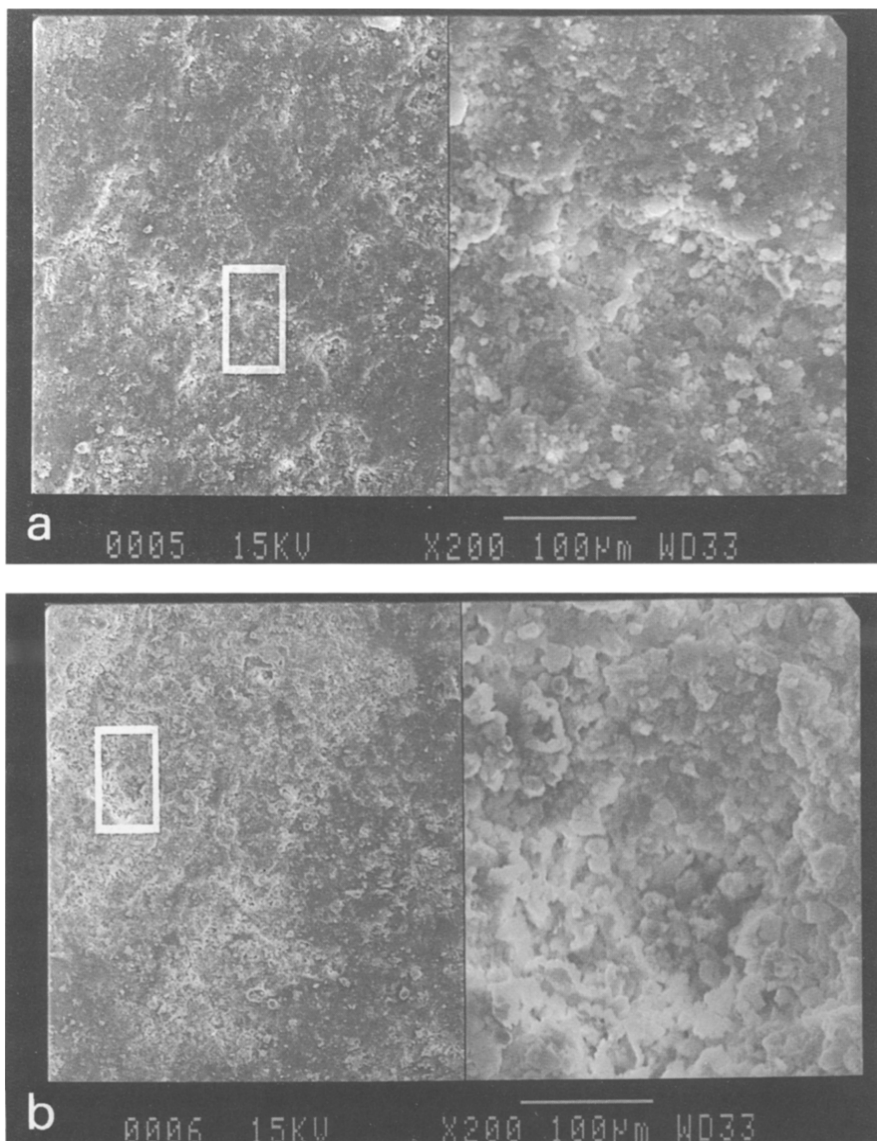
Fig 6 SEM photographs of the catalyst surface treated by Procedure 2 (wet screening–acetic acid leaching) (a) and Procedure 4 (calcination, wet screening and acetic acid leaching) (b)

Procedure 3 Calcination and wet screening

Wet screening was combined with calcination to remove carbon contaminants and to compare the relative influence of the main contaminants on the catalysts' activity

A spent catalyst sample (100 pellets) was calcined in a furnace at 550°C under natural airflow until constant weight was achieved (2 h), and then was treated according to the wet screening procedure
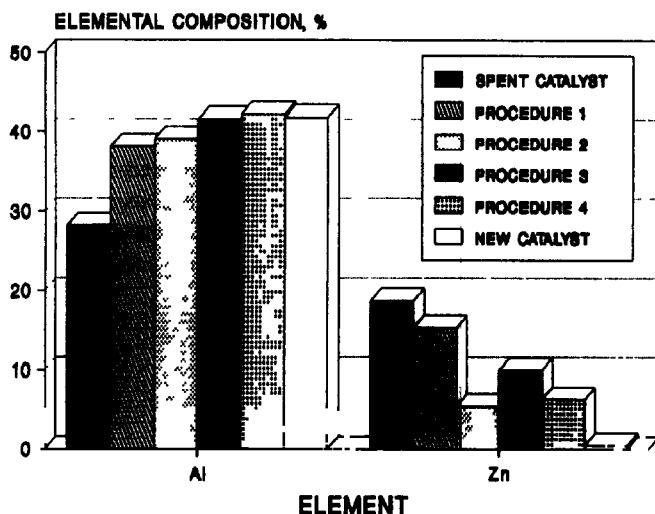
ELEMENTAL COMPOSITION, %

Fig 7 EDS near-surface composition analysis for aluminium and zinc before and after the regeneration treatment

Procedure 4 Calcination, wet screening and acetic acid leaching

The procedure was the same as Procedure 2 with the difference that before wet screening the catalyst sample was calcined for 2 h at 550°C

After each procedure the catalyst samples were subjected to

— Surface observations by SEM The results are shown in the photographs of Figs 5 and 6 The improvement of the surface condition is obvious compared with the surface of the spent catalyst (Fig 2), although acid leaching seems to affect the catalyst surface by alumina and possibly nickel oxide dissolution

— EDS analysis The results for the near-surface elemental composition are shown in Fig 7 (for aluminium and zinc) and in Fig 8 (for iron, copper and
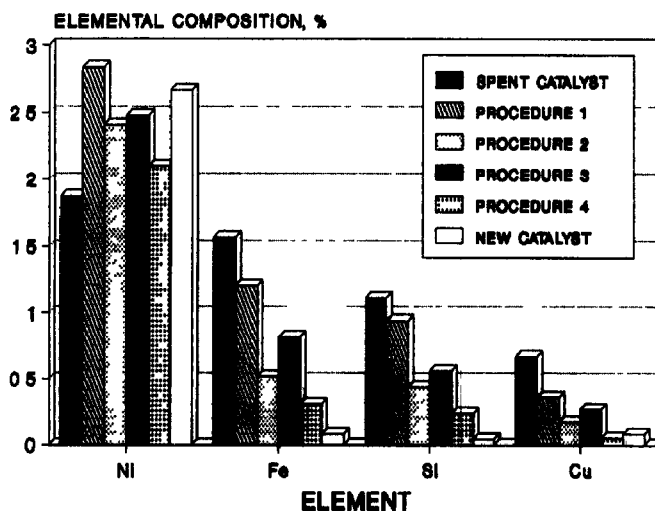
ELEMENTAL COMPOSITION, %

Fig 8 EDS near-surface composition analysis for nickel, iron, silicon and copper before and after the regeneration treatment
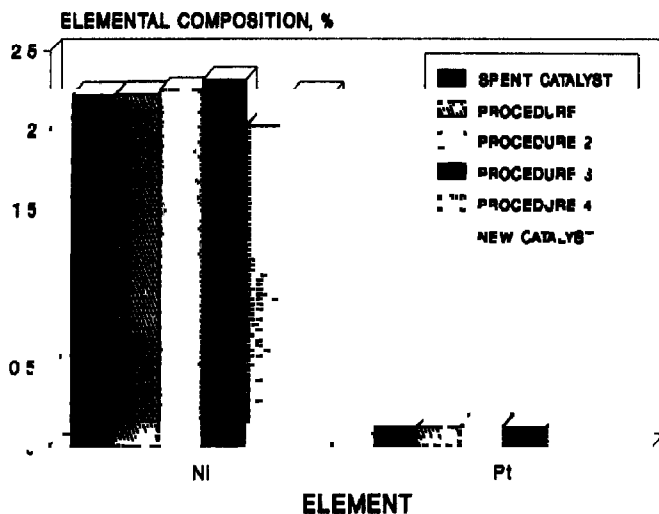
Fig 9 Bulk chemical analysis results for the catalyst's active components before and after the regeneration treatment

silicon) The concentration of all contaminants at the surface is minimized and reaches that of the new catalyst Acid leaching seems to remove greater quantities of metallic oxide contaminants from the surface

— Bulk chemical analysis The results concerning the catalyst active species (platinum and nickel) are shown in Fig 9 and those concerning the main metallic contaminants (zinc, iron and copper) in Fig 10 Considerable nickel dissolution was observed during Procedure 4
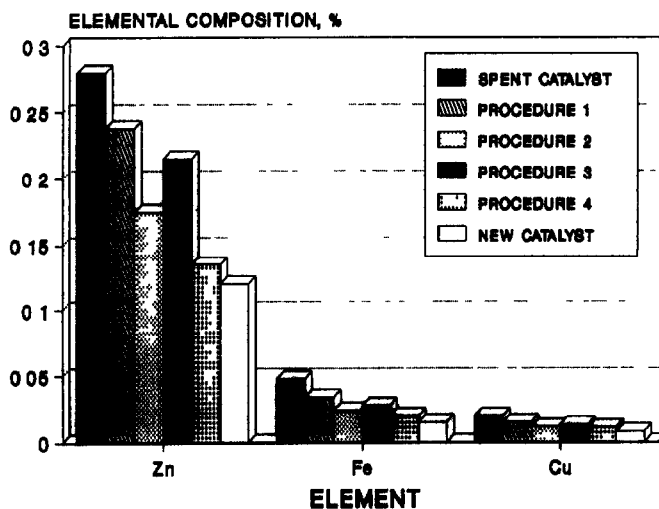

Fig 10 Bulk chemical analysis results for the main metallic contaminants (zinc, iron and copper) before and after the regeneration treatment
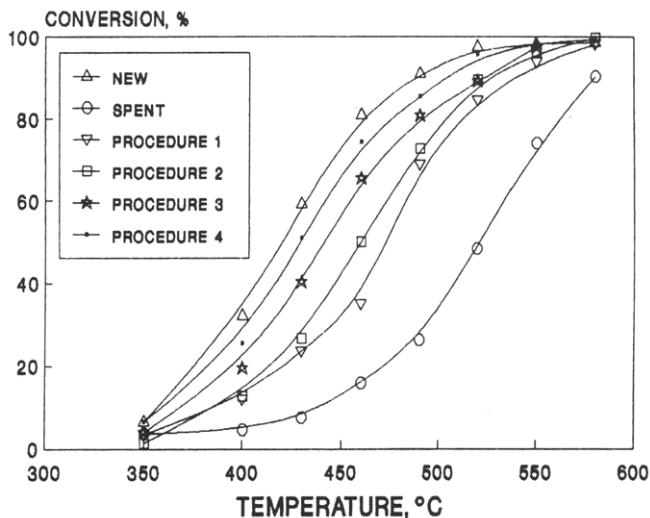
Fig 11 Activity tests (N_2O conversion, %) at various temperatures for catalyst before and after treatment

— Activity tests were conducted in a microreactor under the conditions described in the experimental procedure The yield of nitrous oxide reduction for various temperatures is shown in Fig 11 and for the temperature used by the industrial unit (460°C) in Fig 12

In Table 1 the results of the above observations from bulk chemical analysis and activity tests are quantified and summarized to facilitate comparison between the experimental procedures used It is obvious that the catalyst subjected to wet screening combined with calcination gains 80% of the new catalyst activity Acid
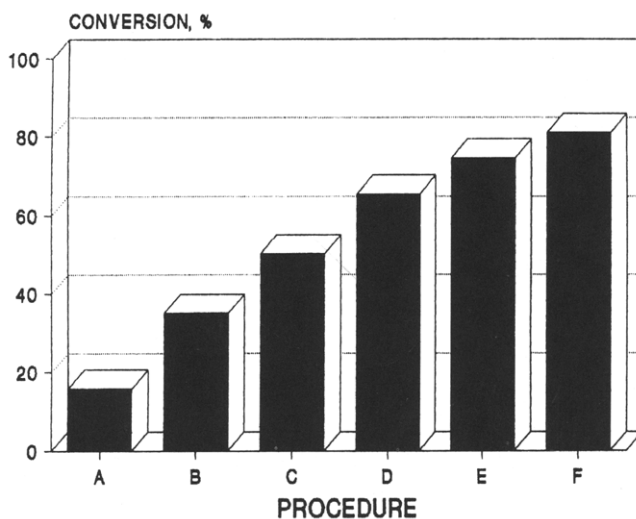

Fig 12 Activity tests results at 460°C (A spent catalyst, B wet screening, C wet screening and acetic acid leaching, D calcination and wet screening, E calcination, wet screening and acetic acid leaching, F new catalyst)

Table 1
Comparison of the main metallic contaminants removal yield and catalytic activity of the applied regeneration procedures[a]

Removal (%)	Procedure 1	Procedure 2	Procedure 3	Procedure 4
Zinc	26 3	65 6	40 6	90 6
Iron	42 4	72 7	60 6	84 8
Copper	41 7	66 7	58 3	75 0
N_2O	43 2	62 0	80 7	92 0

[a] Metallic contaminants removal yield calculations are based on the added by contamination quantity, since a considerable quantity of these elements exist in the new catalyst N_2O reduction yield calculation is given as a percentage of the respective value for the new catalyst

leaching further improves the catalyst activity but possibly dissolves active species (nickel oxide) A further improvement of the calcination procedure (proper regulation of temperature and atmosphere) and the wet screening procedure (proper washing time, washing water pressure and the use of a vibrating screen), may increase further removal of contaminants, alleviating the need for the problematic acid leaching stage

4. Conclusions

A spent $Pt–NiO/Al_2O_3$ nitrogen oxides reduction catalyst was examined concerning the causes of deactivation and the possibility of regeneration Various techniques (SEM, EDS, TGA and chemical analysis) were used to define the contaminants causing deactivation The so collected information combined with information of the active industrial conditions were adequate for establishing that the deactivation is caused by fouling Substances causing fouling were found to be carbon and metallic oxides (mainly zinc oxide) A combination of contaminants removal procedures (calcination, wet screening and acetic acid leaching) results in a considerable increase in activity of the spent catalyst, confirming the above proposed deactivation mechanism The applied procedures establish a regeneration treatment that makes the spent catalyst reusable Further kinetic studies are needed to optimize the regeneration system conditions

Acknowledgements

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