Deactivation and Characterization of SCR Catalysts Used in Municipal Waste Incineration Applications

Jan G. M. Brandin¹ · C. U. Ingemar Odenbrand²

Received: 6 July 2017 / Accepted: 17 October 2017 / Published online: 6 November 2017
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Abstract Catalysts used for selective catalytic reduction were deactivated for various times in a slipstream from a municipal solid waste incineration plant and then characterized. The activity for NO reduction with NH₃ was measured. The Brunauer–Emmett–Teller surface areas were determined by N₂ adsorption from which the pore size distributions in the mesopore region were obtained. Micropore areas and volumes were also obtained. The composition of fresh and deactivated catalysts as well as fly ash was determined by atomic absorption spectroscopy and scanning electron microscopy with energy dispersive X-ray analysis. The

changes in surface area (8% decrease in BET surface area over 2311 h) and pore structure were small, while the change in activity was considerable. The apparent pre-exponential factor was 1.63×10^5 (1/min) in the most deactivated catalyst, compared to 2.65×10^6 (1/min) in the fresh catalyst, i.e. a reduction of 94%. The apparent activation energy for the fresh catalyst was 40 kJ/mol, decreasing to 27 kJ/mol with increasing deactivation. Characterization showed that catalytic poisoning is mainly due to decreased acidity of the catalyst caused due to increasing amounts of Na and K.

✉ Jan G. M. Brandin
Jan.Brandin@lnu.se

¹ Department of Built Environment & Energy Technology,
Linnaeus University, SE-351 46 Växjö, Sweden

² Department of Chemical Engineering, Lund University,
P.O. Box 124, SE-221 00 Lund, Sweden

Graphical Abstract

Keywords Deactivation · Characterization · SCR catalysts · Municipal solid waste incineration

1 Introduction

In a recent study, selective catalytic reduction (SCR) was compared to selective non-catalytic reduction (SNCR) for the reduction of nitrogen oxides (NO_x) [1]. The authors reported that in order to reduce the NO_x level emitted by municipal waste incineration (MSWI) plants to 100 mg/ Nm^3 SCR it may be necessary to replace SNCR with SCR. In our view, in new installations, the catalyst should be placed after the boiler in a high-dust position. However, deactivation of the catalyst by compounds in the fly ash will then become a serious problem. Fly ash contains many potentially poisonous compounds, of which alkali metals are of the greatest concern [2–4]. These will cause deactivation of the catalysts, by blocking the Brønsted acid sites, as in the case of the burning forest residues [3, 5]. In a previous study, we investigated the effect of impregnation with lead nitrate on the activity of SCR catalysts, and found it to be large [6]. We have also reported on the deactivation of SCR catalysts after use for 2000 h in the treatment of flue gases from a MSWI plant [7]. In this latter study, alkali metals and some other metals were shown

to deactivate the catalyst to a high degree. The components of fly ash determine the degree of the deactivation of the catalyst.

A number of studies have been published recently regarding the fly ash from MSWI plants [8–11]. Some are concerned with the stabilization of the ash for use in construction works [8], while others deal with the recovery of, e.g., Zn from the ash [9], tailoring catalyst for simultaneous abatement of polychlorinated dibenzodioxins (PCDD) and NO_x [10] or developing a better catalyst for MSWI applications [11]. There is also a vast amount of information on the deactivation of SCR catalysts in general [12–20]. Li et al. [12] presented a review on the topic in 2016, where they discussed the deactivation and possible regeneration of the catalyst. The deactivating compounds mentioned are alkali metals, alkaline earth metals, SO_2 , HCl , P_2O_5 and heavy metals such as Pb, As, and Zn. Alkali metals deactivate catalysts by neutralizing the Brønsted acid sites. Alkaline earth metals cause moderate deactivation, compared to K and Na. SO_2 has a dual effect, causing deactivation by ammonium bisulphates at low temperatures, and activation at temperatures between 350 and 450 °C. Activation is caused by formation of sulphate groups on the TiO_2 support. The possible deactivating effect of CaSO_4 is also noted. Pb has been reported to cause serious catalytic poisoning by either chemical reaction, or by the introduction of a barrier between the

gas phase and the active sites. Zn has been found to cause about the same degree of deactivation as K. Wu et al. [13] found strong deactivation (a 65% decrease in conversion) in the presence of both K and Cl between 300 and 400 °C. Lei et al. [18] studied different deactivation methods and their effects when using KCl as deactivating agent. The three methods studied were: wet impregnation, solid diffusion and vapour deposition. The method chosen was found to mainly effect the rate of deactivation. The observed decay rates were 1.9, 3.0 and 12.3%/day for wet impregnation, solid diffusion and vapour deposition, respectively.

In this study, we have determined which of the components of the fly ash from a MSWI plant deactivate a commercial SCR catalyst. The activity of the SCR reaction was correlated to the contents of the elements in the catalyst, measured by atomic absorption spectroscopy (AAS). The thermal stability of the fly ash and the fresh catalyst was studied separately in order to explain the results obtained from the poisoned catalysts.

2 Methods

2.1 Deactivation of the Catalyst

The type of catalyst studied was a commercial V_2O_5/WO_3 on TiO_2 catalyst strengthened by silica fibres. The manufacturer cannot be given because of confidentiality agreement. A total of seven 200-mm long, 150 mm × 150 mm monoliths with a wall thickness of 1.1 mm and a pitch of 7.5 mm were used [7]. Four of them were placed in a deactivation chamber in a slipstream from the main flue gas channel, with gas flowing from top to bottom. The conditions in the deactivation chamber were: temperature 230 °C, NO_x 60 mg/ Nm^3 and NH_3 20 mg/ Nm^3 (45 and 26 ppm respectively), O_2 2% and space velocity 5000 h^{-1} . SO_2 was also present at 50 to 200 ppm [21].

The monoliths were subjected to these conditions for various times. When one monolith was removed, a new one was inserted in its place and placed in the slipstream for a new period of deactivation. This procedure was repeated until seven monoliths had been deactivated for various amounts of time. The deactivated monoliths and a new, unexposed monolith were analysed using the methods described below.

2.2 Measurement of Catalyst Activity

The activity of samples taken from the fresh and deactivated monoliths was determined as described previously [6]. Samples (one monolith channel including walls, 60 mm long) were cut from the front of the full monoliths and tested for activity, for surface area, pore structure and for chemical composition. A Balzer QMG 311 mass spectrometer was

used for gas analysis. The temperatures used in the test for activity in the reduction of NO were from 260 to 400 °C at 20 °C intervals, with 40 minutes' equilibration time at each temperature. The gas stream contained about 600 ppm NO, 700 ppm NH_3 , and 2% O_2 , with He as the carrier gas, containing about 3000 ppm Ar which was used as an internal standard. The flow rate was 900 Ncm^3/min , the space velocity was 12,800 h^{-1} , and the pressure was kept at around 1.25 bar. The analysis set-up is shown in Fig. 1.

The activity is presented as an apparent rate constant determined from the following equations:

$$x = \text{conversion of NO} = (CNO_{in} - CNO_{out}) / CNO_{in}$$

where CNO_{in} is the concentration of NO in inlet to reactor (mol/cm^3), CNO_{out} is the concentration of NO in outlet from reactor (mol/cm^3).

r_{NO} = rate of disappearance of NO

$$= -k_{NO} \times [NO]^1 \times [NH_3]^0 \text{ (mol/cm}^3_{cat} \text{, min)}$$

$$k_{NO} = -F_{NOin} / (CNO_{in} \times V_{cat}) \times \ln(1 - x) \text{ (cm}^3_{gas} / \text{(cm}^3_{cat} \text{, min)})$$

$$k_{NO} = k_{NO0} \times \exp(-E_a / (R \times T))$$

where k_{NO} is the first order rate constant (1/min), based on catalyst volume, F_{NOin} is the molar flow of NO into the reactor (mol/min), k_{NO0} is the pre-exponential factor (1/min), E_a is the activation energy (J/mol), R is the universal gas constant (J/mol/K), T is the temperature (K).

$$V_{cat} = L \times A_{wall} = 6 \times 0.33 = 1.98 \text{ (cm}^3\text{)}$$

where V_{cat} is the volume of catalyst wall (cm^3), calculated from the dimensions of the 60 mm long channel used, L is the length of the monolith = 6 cm in the majority of the experiments, A_{wall} is the cross sectional area of the monolith wall = $0.86^2 - 0.64^2 = 0.33 \text{ (cm}^2\text{)}$, Area inside

Fig. 1 Experimental set-up used to analyse the activity of the catalyst samples. 1, 2, 3, and 4: Gas cylinders for He, O_2 , NO and NH_3 , respectively. 5 Rotameters, 6 Flow regulators, 7 Pressure sensors, 8 Preheating quartz glass tubes, 9 Oven with temperature regulator, 10 Quartz glass reactor, 11 3-way valves for selection of gas to the analyser, 12 Mass spectrometer, 13 Computer

wall = $4 \times 0.64 \times \text{length} = 15.36 \text{ (cm}^2\text{)}$, Vol/Area inside wall = $1.98/15.36 = 0.1289 \text{ (cm)}$.

$$r\text{NO}_{\text{obs}} = F_{\text{NOin}}(\text{mol/s}) \times x/V_{\text{cat}}$$

kmt is the mass transfer coefficient from Sherwood number [22] (cm/s), Shav is the average Sherwood number = $2.696(1 + 0.139/z')^{0.81}$, z' is the non-dimensional length = $L \times D_{\text{NO}}/(dh^2 \times u)$

$$\text{kmt} = \text{Shav} \times D_{\text{NO}}/dh \text{ (cm/s)}$$

dh is the hydraulic diameter = 0.64 (cm), D_{NO} is the molecular diffusivity of NO in He (cm²/s), D_{NOeff} is the effective diffusivity of NO in pores (cm²/s), twall is the wall thickness = 0.11 (cm).

The length of the mini-monoliths varied somewhat from sample to sample. Therefore, the measured values of concentrations and monolith length were used in the calculation of the rate constants. To determine the presence of mass and temperature gradients in the catalyst the criteria presented by Ramirez were used [23]. For mass gradients inside the monolith wall we used criterion number 7:

$$r\text{NO}_{\text{obs}} \times \text{twall}^2 / (D_{\text{NOeff}} \times C_{\text{NOin}})$$

and for external mass transport criterion number 5 was used:

$$r\text{NO}_{\text{obs}} / (A_{\text{wall}} / \text{Vol}_{\text{cat}} \times \text{kmt} \times C_{\text{NOin}}).$$

2.3 Measurements of the Catalyst Composition

There is a distribution of the poisonous compounds in and on the surface of the monolithic catalyst wall. SEM is used to study the surface of the catalyst but also the penetration of the poisons into the monolith wall. To study the composition of the bulk of the catalyst the surface layer was removed. AAS, which is a more exact method, was used in order to quantify the amount of poisons and determined the content in the whole piece used for analysis.

2.3.1 Analysis Using AAS

The equipment used was a GSM atomic absorption spectrometer. The catalyst samples were crushed and finely ground in a mortar. Known weights were dissolved in 25 ml 40% HF. The solution was diluted with distilled water to the concentration required for analysis. All analyses were performed on duplicate or triplicate samples to reduce the influence of analytical errors. The results given are the mean values of the experimental ones in weight percent (wt%).

2.3.2 Analysis Using SEM-EDAX

The catalyst samples and the fly ash were analysed using a JEOL JSM-840A scanning electron microscope with a Link

AN 10000 energy-dispersive X-ray analyser. Various elements were determined quantitatively on the surface, and in the bulk when a 0.4 mm layer scraped off the surface. The concentrations of elements across the catalyst wall were also mapped to determine whether there was a concentration gradient. The components of the catalyst: Ti, Si, W, V and Al, were determined as well as the catalyst poisonous compounds. The results are given as atom %.

2.4 Analysis Using N₂ Adsorption

The surface area and the pore size distribution of fresh and deactivated catalysts as well as the fly ash were determined by physisorption of N₂ at − 196 °C. For catalysts, this study of the pore system was performed on a piece of the wall of the monolith using a Micromeritics ASAP 2400 system. Outgassing was performed at 0.04 mm Hg and 90 °C for 1 h and at 400 °C for 24 h to a final pressure of 10^{−3} torr before the adsorption study. The BET surface area was calculated as described by Brunauer et al. [24]. The accuracy of this method was better than 1%, according to separate measurements for the experimental conditions used. The mesopore size distribution was calculated using the method described by Barrett et al. [25]. The total pore volume is given for pores smaller than 3000 Å in diameter.

The micropore volume and the micropore surface area were calculated using the t-plot method of Harkins and Jura [26]. Samples of the fresh catalyst were also submitted to sintering for up to 288 h at 400 °C to study the stability of this material. To study the melting or removal of poisonous compounds from the deactivated monoliths the degassing temperature, before measurement of surface area, was varied between 100 and 450 °C in 50 °C intervals. The degassing was performed for 24 h at each temperature. The fresh catalyst was also treated at 400 °C for various lengths of time to study possible sintering.

3 Results

3.1 Fly Ash

The ash was crushed and freshly ground in a mortar and was dark grey.

3.1.1 Surface Area and Pore Structure

The BET surface area (SBET) as well as the micropore surface area (Smicro) are constant at about up to a degassing temperature of 300 °C after which they decrease sharply (Fig. 2). The BET area decreases from 5.26 to 2.95 m²/g between 250 and 400 °C and does not decrease further at 450 °C, i.e. a decrease of 44%. The micropore area

Fig. 2 Surface areas of the fly ash as a function of the degassing temperature

decreased from 2.06 to 0.29 m²/g, i.e. by 86%. These results indicate that the fly ash contains one or more compounds that decrease access to the micropores above 300 °C.

It can be seen from Fig. 3 that the total pore volume seems to be more or less independent of the degassing temperature. However, the volume of the micropores decreases sharply at temperatures above 300 °C from 9 to 1.2 × 10⁻⁴ cm³/g, i.e. by 87%, similar to the decrease in the micropore surface area.

Figure 4 shows the cumulative surface area (Scum) distribution for small mesopores (down to 17 Å) at various degassing temperatures. The curves for 150, 200 and 300 °C show very similar behaviour. At 350, 400 and 450 °C the cumulative surface area (Scum) is constant below 35 Å, meaning

that only a small fraction of pores is in the region 17–35 Å. At diameters above 35 Å all the curves overlap.

3.1.2 Chemical Composition of the Fly Ash

Fly ash contains many elements known to be poisonous to the catalyst (Mg, K, Na, P, Zn and Ca) [4]. It can be seen from Table 1 that some components are evenly distributed (small standard deviations) over the surface (Mg, Na, K and Si) while others vary between sampling points (P, Ti, Fe, Zn, Al, S, Cl and Ca). Large amounts of Cl and S were found in the fly ash. However, Pb was not detected, which is strange as it was detected in poisoned catalysts using AAS (see below).

Fig. 3 Total volume and micropore volume of the fly ash as a function of the degassing temperature

Fig. 4 Cumulative pore area distribution (Scum) for fly ash **Table 1** Composition (atom %) on two points on the surface of the fly ash as determined by SEM-EDAX

Element	Sample 1	Sample 2	Mean	SD
P	1.02	2.25	1.64	0.50
Ti	1.63	2.70	2.16	0.44
Fe	2.33	1.79	2.06	0.22
Mg	3.85	3.03	3.44	0.33
Zn	3.87	6.53	5.20	1.09
Na	3.98	4.43	4.21	0.18
K	4.27	4.49	4.38	0.09
Al	9.20	11.93	10.56	1.11
S	11.87	8.95	10.41	1.19
Cl	12.22	11.32	11.77	0.37
Si	14.91	14.83	14.87	0.03
Ca	30.87	27.77	29.32	1.27

S.D. standard deviation

3.2 Fresh Catalyst

3.2.1 Surface Area and Pore Structure

Table 2 presents the effect of degassing temperature on the pore structure of the fresh catalyst. It can be seen that there is almost a 5% increase in BET surface area (from 62 to 65 m²/g) when the temperature is increased from 100 to 400 °C (Table 2). The total pore volume does not seem to be dependent on degassing temperature, and shows a maximum of 0.271 cm³/g at 400 °C. The micropores open up increasing the area from 3.1 to 7.5 m²/g at 400 °C. At 450 °C the value falls to 6.3 m²/g indicating instability at this high temperature (as discussed below). The micropore volume increases up to 400 °C and then decreases at 450 °C. The micropore volumes are very small compared to the total pore volumes, being between 0.44 and 1.03% of the total pore volume. The average pore diameter increases from 148 to 180 Å as the temperature increases.

The accuracy of the measurements of the BET surface area and the micropore surface area was determined by

Table 2 Effect of degassing temperature on pore structure of the fresh catalyst degassed for 24 h at the given temperature

Temperature (°C)	SBET (m ² /g)	V _{tot} (cm ³ /g)	S _{micro} (m ² /g)	V _{micro} (cm ³ /g)	D _{pore} (Å)
100	62.0	0.224	3.1	0.0010	148.1
150	62.1	0.218	4.3	0.0015	145.6
200	63.4	0.240	5.1	0.0018	158.7
250	64.7	0.222	6.1	0.0023	144.9
300	63.7	0.235	6.4	0.0024	158.8
350	65.6	0.229	6.9	0.0026	150.7
400	65.0	0.271	7.5	0.0028	179.7
450	64.9	0.269	6.3	0.0023	177.9

measuring four samples of the reference material degassed at 400 °C. The values obtained were $\pm 1\%$ for the BET surface area and $\pm 5\%$ for the micropore volume.

3.2.2 Chemical Composition

The results of the elemental analysis of the fresh catalyst using SEM-EDAX and AAS are given in Table 3. The most abundant element in the surface as in the bulk is Ti at 87 atom % as expected since TiO_2 is the catalyst support. The silicon (5 and 4% respectively) probably arises from silica in the glass fibres identified by SEM. Wolfram is present at 3 atom % and is a common component of modern SCR catalysts. Vanadium is present at 1.9 and 1.6 atom % in the

surface and in the bulk. The atomic ratio between aluminium and calcium is about 2 in the surface, and closer to 3 in the bulk for the fresh catalyst. This could indicate that Ca-aluminate cement (forming CaAl_2O_4) has been used as a binder in the catalyst, and the composition may vary somewhat depending on the mixing in the manufacture of the catalyst.

The values measured using AAS, recalculated to give the percent by weight and assuming oxides, were 0.91% vanadium pentoxide, 8.45% tungsten trioxide on 78.27% titanium dioxide and 11.03% silica as mechanical reinforcement. A binder, CaAl_2O_4 , is present at a level of about 1.03%. AAS analysis also showed the presence of iron (probably hematite) at below 0.2%. Minor amounts of Na and K oxides were also found, together constituting about 0.1%.

3.2.3 Stability of the Fresh Catalyst at 400 °C

All samples have been degassed at 400 °C for 24 h before the start of the sintering process. The sintering was performed in an oven in air at 400 °C for the time given. It is obvious that there is a, after some instabilities below 72 h, decrease of BET surface area from 69.9 to 62.1 m^2/g (by 7.8 m^2/g) after 288 h (Fig. 5). The accuracy in the surface area is better than 1% so the drop (11.1%) is noticeable. The area in the pores smaller than 17 Å (Smicro) drops from a value of 8.9–2.1 m^2/g (by 6.8 m^2/g) at 288 h. Thus, most of the decrease in area takes place in the smallest pores.

We studied the mesopore size distribution in order to find a correlation to the loss in surface area. There is no systematic difference in the mesopore size distribution for the sintered samples (not shown here).

It can be seen from Fig. 6 that the total pore volume increases very little, from 0.270 cm^3/g before sintering, to 0.277 cm^3/g after sintering for 288 h. However, there is some

Table 3 Results of SEM-EDAX analysis (atom %) and AAS (wt%) of the fresh catalyst

Element	Surface	Bulk	By AAS
Al	1.27	1.60	0.53
Si	5.27	4.29	8.61
W	2.92	3.02	7.00
Ti	86.41	87.57	49.00
V	1.93	1.57	0.535
S	1.52	1.42	
Cl	0	0	
Ca	0.62	0.54	0.17
Na			0.026
K			0.056
Zn			0.008
Fe			0.137
Pb			0.011
Total	99.94	100.01	66.08

Fig. 5 The effect of sintering time on the pore surface area of the fresh catalyst

Fig. 6 The effect of sintering time on the pore volume of the fresh catalyst

Table 4 The effect of deactivation time on surface area and pore structure

Deactivation time (h)	SBET (m ² /g)	V _{tot} (m ³ /g)	S _{micro} (cm ³ /g)	V _{micro} (cm ³ /g)
0	65.0	0.2684	7.5	0.0028
360	62.4	0.2742	2.9	0.0008
403	62.4	0.2647	1.7	0.0002
853	63.1	0.2680	4.3	0.0015
1458	63.1	–	4.6	0.0016
1908	58.6	–	3.7	0.0014
1951	60.4	–	4.3	0.0016
2311	60.0	–	3.5	0.0010

instability in the data at sintering times below 72 h, similar to that seen in Fig. 5. In contrast, the micropore volume decreased from 0.0034 before sintering to 0.0017 cm³/g after 4 h, after which it increased to 0.0024 cm³/g at 72 h. The final micropore volume after 288 h was 0.0003 cm³/g, which corresponds to a 91% decrease compared with the fresh material.

3.3 Deactivated Catalysts

3.3.1 Surface Area and Pore Structure

The deactivated samples have BET surface areas, when degassed at 400 °C for 24 h, which decrease with deactivation time (Table 4). The decrease is 65 to 60 m²/g (about 8%) over 2311 h. The total pore volume remains unchanged at 0.27 cm³/g independent on deactivation time. There is a large decrease in micropore surface area from 7.5 to 1.7 m²/g for the sample used for 403 h. At longer times of exposure,

the surface area remains constant at 4.1 m²/g with a standard deviation of 0.5 m²/g, which is within the accuracy of these measurements. Thus the drop in micro pore surface area is 45%.

There is an increase in the micropore volume for the fresh catalyst at increasing degassing temperatures as could be expected as water is removed from the small pores (not shown here). After an initial drop of micropore volume from 0.0028 cm³/g by 71% during the first 360 h there seems to be an almost constant value of 0.0014 cm³/g with a standard deviation of 0.0002 cm³/g at longer times i.e. a final drop of 50%.

From studies of the pore size distribution (not shown here), there is no difference between the fresh catalyst and the catalyst used for 2311 h in the mesopore region from 17 to 500 Å pore diameter.

3.3.2 Chemical Composition

The contents of Na, K, Zn, Fe, Ca and Pb were measured by AAS, and the results are shown in Figs. 7 and 8.

The two alkali metals, Na and K, and Zn showed a linear increase with deactivation time, reaching contents of 0.20, 0.26 and 0.36 wt%, respectively (Fig. 7). It should be noted that these values represent the average contents of these metals as the whole wall of the monolith was dissolved before analysis by AAS.

Figure 8 shows the corresponding results for Ca, Pb and Fe.

The contents of Ca and Pb vary dramatically over time (Fig. 8). The maximal value for Ca is about 0.9 wt%, while the highest values for Pb range from about 0.2–0.3 wt%. The fresh catalyst contained some Ca (0.17 wt%) and only very little (0.011 wt%) Pb. The content of Fe decreased slightly

Fig. 7 Contents of Na, K, Zn, measured by AAS in deactivated catalysts, as a function of exposure time

Fig. 8 Content of Ca, Pb and Fe, measured by AAS, in deactivated catalysts as a function of exposure time

with exposure time from 0 to 2311 h, its maximum being 0.15 wt%.

The results of the SEM-EDAX analysis of two different areas of the catalyst are given in Table 5.

SEM-EDAX analysis of the sample exposed for 1908 h showed that the bulk of the catalyst (after the top 0.4 mm had been removed) did not contain any Pb, Zn or Cl, and only small amounts of Ca and S (Table 5). The components on the outer surface of the catalyst must thus arise from the fly ash. Ca, Pb and S are also largely the result of exposure to the fly ash. The composition varies considerably between the two points of the surface which were analysed, especially in the cases of Pb and Ca. Surface 1 is much more contaminated, while the amounts of the catalyst components V, W and Ti are much lower than in the bulk. V varies from 0.31

Table 5 Results of SEM-EDAX analysis on two points on the surface and in the bulk of the catalyst used for 1908 h (atom %)

Element	Surface 1	Surface 2	Bulk 1	Bulk 2
Al	2.04	1.29	0.98	1.27
Si	5.60	4.15	4.81	4.42
W	0	2.38	3.09	3.37
Ti	39.52	63.23	86.76	86.49
V	0.31	1.20	1.46	1.62
S	24.46	12.80	2.43	2.34
Cl	0.98	0.35	0	0
Ca	7.41	2.42	0.46	0.49
Zn	4.62	4.27	0	0
Pb	15.06	7.90	0	0
Total	100.00	99.99	99.99	100.00

atom % on Surface 1, to 1.20% on Surface 2. The amounts of V, W and Ti are very similar in the two bulk samples. It can thus be concluded that layers of sulphates and chlorides of Pb, Ca and Zn may cover the sample exposed to flue gases/fly ash for 1908 h.

Figure 9 shows the ratios of various metals to V on the surface of the catalyst as a function of exposure time. The maximal coverage (Me/V) for each metal, after 2311 h deactivation, was 0.84 for Na, 0.64 for K and 0.53 for Zn.

The data for each metal were fitted to a straight line.

Table 6 gives the values of the parameters, intercept and slope, with 95% confidence intervals, for the linear fits of metal coverage presented in Fig. 9, together with the coefficients of determination (R^2) for the fits. The value of R^2 for the Na/V data was quite low, so the correlation coefficients, R , were tested using a t test. All the correlations were found to be significant at the 95% level. The coverage rates, given by the slopes of the fits, are similar for all three metals, taking the 95% confidence interval into account.

3.4 Catalyst Activity

3.4.1 Activity of the Fresh Catalyst After Sintering

The rate constants for the fresh and sintered catalysts increased in a regular fashion with temperature, as expected (data not shown). The apparent activation energy of the sintered samples was 33–34 kJ/mol, compared with 35.5 kJ/mol for the non-sintered samples. The pre-exponential factor decreased from 1.35×10^6 1/min to about $8e \times 10^5$ 1/min after 32 h sintering, and then remained constant. The decrease in the pre-exponential factor is 40%.

Table 6 The parameters obtained from linear regression of the metal coverage (Me/V) vs time data

Metal ratio	Intercept (10^2)	$\pm$ (10^2)	Slope (10^4 1/h)	$\pm$ (10^4 1/h)	R^2
Na/V	3.73	12.8	2.96	0.91	0.64
K/V	10.94	5.46	2.10	0.39	0.83
Zn/V	9.83	3.35	1.94	0.24	0.91

3.4.2 Activity of the Deactivated Catalysts

The catalysts have been exposed to flue gases from 36 to 2311 h. The apparent rate constants have been measured and the results are given in Fig. 10.

It can be seen from Fig. 10 that the rate constants vary with exposure time. In our previous study [7], we found parallel processes of deactivation by metals (Na, K and Zn) and activation by sulphate groups created on the catalyst surface. The initial increase in the rate constant is due to sulphation. The rate constant reaches a maximum sometime between 403 and 853 h exposure. The pattern of increase and decrease was similar for all the temperatures investigated. However, the smallest rate constant occurs at different times for different temperatures. At 260 °C the minimum is at 1458 h, while at 400 °C it is at 1951 h. The value of the rate constant for the catalyst deactivated for 1908 h deviates from the expected value. It is much higher than the rate constant for the sample deactivated for 1951 h, especially at the highest temperature. The cause will be discussed below.

Activation energies were determined in the temperature range 260 to 340 °C (from plots of $\ln(k)$ vs. $1/T$) and are shown in Fig. 11 for all catalysts.

Fig. 9 The increase in coverage of the V atoms, with the metals Na, K and Zn (Me/V atom ratio), as a function of exposure time

Fig. 10 The effect of exposure time on the rate constant at different temperatures

Fig. 11 The dependence of the activation energy on the K/V ratio for all the catalysts

The activation energy decreases linearly with the exposure time, i.e., on the degree of contamination of the catalyst. In the present study, the activation energy decreased from 40 kJ/mol in the fresh catalyst to 28 kJ/mol in the catalyst exposed for 2311 h, where the K/V ratio was around 0.64.

Pre-exponential factors were also determined in the temperature range 260 to 340 °C (from the same plots used in Fig. 11) and are shown in Fig. 12 for all catalysts.

Figure 12 shows that the pre-exponential factor decreased to very low values (around 1.6×10^5 1/min) after long exposure times.

The pre-exponential factor for the fresh catalyst is 2.65×10^6 (1/min), while for the catalyst exposed for 1951 h it is about 1.63×10^5 , i.e., a decrease of 94%.

3.4.3 Effect of Mass and Temperature Gradients

In our experiments, the SCR reaction rate is limited by diffusion in the pores of the catalyst. We calculated the criteria for the absence of internal (criterion 7) and external (criterion 5) mass transport, according to Ramirez [23]. Table 7 presents the results for the fresh catalyst, where it can be seen that criterion 7 must be less than 0.15, and criterion 5 less than 0.05 to ensure the absence of gradients.

At the lowest temperature, criterion 7 is just fulfilled. This means that the effectiveness factor for internal diffusion is just above 0.95, and limitation due to internal diffusion is minimal. Criteria 7 and 5 are not met at any other temperature. Thus, both external mass transfer limitations and internal mass transfer limitations can be expected. These criteria

Fig. 12 The dependency of the pre-exponential factor on the K/V ratio for all the catalysts

Table 7 Estimation of mass transfer limitations according to Ramirez [23]

T (K)	$r_{\text{NO}_{\text{obs}}} \text{ (mol/cm}^3_{\text{cat}}/\text{s)}$	$D_{\text{effNO}} \text{ (cm}^2/\text{s)}$	$C_{\text{NOin}} \text{ (mol/cm}^3)$	Criterion 7	Criterion 5
533	5.824×10^{-8}	0.473	1.414×10^{-8}	0.145	0.098
553	7.009×10^{-8}	0.500	1.363×10^{-8}	0.171	0.116
573	8.556×10^{-8}	0.532	1.315×10^{-8}	0.203	0.140
593	1.004×10^{-7}	0.563	1.271×10^{-8}	0.233	0.162
613	1.141×10^{-7}	0.590	1.229×10^{-8}	0.261	0.180
633	1.235×10^{-7}	0.630	1.191×10^{-8}	0.274	0.192
653	1.314×10^{-7}	0.660	1.154×10^{-8}	0.287	0.202
673	1.368×10^{-7}	0.693	1.120×10^{-8}	0.293	0.211

Criterion 7 Internal diffusion limitations are negligible when the criterion is < 0.15 , *Criterion 5* External (film) diffusion limitations are negligible when the criterion is < 0.05

have also been calculated for the catalyst exposed for 1951 h. The values obtained were somewhat higher, so this sample will also be limited by mass transfer. All the other samples will be limited by external and internal mass transfer since their observed rates of NO reduction were higher.

The external and internal temperature gradients (calculations not shown) were small and would not have any significant effect on the results. The rate of the SCR reaction is so high that a temperature gradient of 6.3 °C can be expected along the reactor axis. The internal temperature gradient inside the catalyst wall is below 0.035 °C, thus the catalyst is isothermal over its cross section, but not along its axis.

4 Discussion

In this study, a commercial $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ SCR monolith was subjected to long-term exposure to flue gas containing fly ash from a municipal waste incineration plant. Analysis of the composition of the fly ash showed the presence of P,

Ti, Fe, Mg, Zn, Na, K, Al, S, Cl, Si and Ca. Unfortunately no Pb was detected in our fly ash sample but the deactivated catalyst contained Pb. On the other hand Eigmy et al. [27] analysed fly ash from a waste incinerator using neutron activation and inductively-coupled-atomic emission spectroscopy (ICP-AES) for Pb. They reported the following elemental contents (wt%): Cl (23.2), K (10.9), Zn (10.4), Na (8.4), Ca (4.6), Si (3.8), Pb (2.7) and Al (2.1) (they did not analyse the S content). Some of the compounds they found were NaCl, K_2ZnCl_4 , CaAl_4O_7 , K_4PbO_4 and CaSiO_3 . The Pb was found to exist in the forms Pb, PbO, PbCl_2 and PbSO_4 . Our analysis of the catalyst used/exposed for 1908 h (using SEM-EDAX) showed the same elements. The ash must have been subjected to temperatures much above 300 °C in the incinerator before reaching the catalyst. The presence of components in the ash that melt at 300 °C shows that salts precipitate from the hot flue gas when it cools down. The precipitated salts form aerosol particles in the flue gas, which are captured by the fly ash. Our analysis of the micropore volume and pore area distribution of the fly ash

showed that the volume of pores below 30 Å decrease above 300 °C. We believe that the fusible compound in the fly ash may be ZnCl_2 (melting point 290 °C), and the decrease in the number of small pores of the fly ash is due to their being filled with molten Zn salts (i.e. ZnCl_2 , or molten K Zn double salts).

The surface area with (65 m²/g at 400 °C degassing temperature) and the pore structure of the fresh catalyst are in agreement similar catalysts [28]. The total pore volume and the micropore volume, 0.271 and 0.0028 cm³/g are also in agreement with similar catalysts.

The fresh catalyst was sintered at 400 °C in dry air in an oven for various amounts of time. The BET area decreased rapidly during the first 4 h from, 70 to 62 m²/g. After some instability up to 72 h, the BET area remains at 62 m²/g up to the final time at 288 h (Results not shown here). This change in area is quite unlike that we observed in a previous study at 20 wt% V_2O_5 , [29], where the BET area followed the general power law expression (GPLe) [30]. The GPLe model for sintering is based on the differential equation: $dS/dt = -k \times (S - S_{eq})^n$. The surface area approaches a constant value, S_{eq} , at long times. The exponent n is usually 2. A gradual decrease in the area with time was seen, especially in the presence of water [29]. The time in the deactivation unit does not affect the surface area to the same extent as the activity decrease. Therefore, deactivation is of a chemical nature.

The amount of V^{5+} deposited on the catalyst surface in the present study was 1.75 μmol/m². This can be compared to 13 μmol/m² for a monolayer catalyst [31]. The active vanadia sites are isolated VO_4 units with one $\text{V}=\text{O}$ bond and three $\text{V}-\text{O}-\text{Ti}$ bonds. The WO_3 is a non-interacting additive and does not influence the structure of the vanadia species unless the content of vanadia is above one monolayer. Water has an effect at low temperatures, but not above 300 °C where the vanadia retains its structure.

The fly ash contains compounds that poison the catalyst, which accumulate on the outer surface and in the pore system. The most detrimental components are K and Na, which directly neutralise the $\text{V}-\text{O}-\text{H}$ groups, the sites on the catalyst for the adsorption of NH_3 , thus leading to rapid deactivation of the original sites. In parallel to this deactivation, we have formation of new Brønsted acid sites from sulphate groups, as described in [7]. The ammonia adsorbed on these sites serves as a depot of ammonia needed for the reduction of NO.

Chemical analysis by SEM-EDAX showed that the fresh catalyst contained the components expected in a commercial SCR catalyst. The accumulation of poisons on the outer surface of the catalyst used for 1908 h, was revealed using EDAX. The contents of Na, K and Zn increased linearly with exposure time. Most of the poisons were found on the outer surface, and Zn, Cl and Pb did not penetrate into the bulk of

the catalyst. More S was present in the bulk of the used catalyst than in the fresh one. The S/Ti ratio was 0.0275 in the bulk of the catalyst used for 1908 h, compared to 0.0163 in the fresh catalyst, and is an effect of creation of new sulphate groups on the surface. The SEM analysis of the catalyst used for 1908 h showed that compounds covered two different areas on the surface to much different degrees. The contents of elements in the interior of the used catalyst and the bulk of the fresh catalyst were very similar. The catalyst used for 2311 h had a surprisingly low content of both Pb (0.16 wt%) and Ca (0.04 wt%). This could be explained by some of the Ca and Pb deposited as a surface layer on the outside of the monolith falling off before analysis, or if the flow distribution in the deactivating unit was such that this position did not have as high a flow as the others. This particular sample was at the same position in the deactivating unit through all 2311 h of deactivation.

The results for Na are more scattered than those for K and Zn, probably because of the higher diversity of food waste than other types of waste that are mixed for combustion. However, the deposition rates are constant over time (Fig. 7) so the long-term composition of the feed is constant. This also agrees well with verbal information from the personnel at the plant that the fuel (waste from different origins) is mixed to obtain a uniform composition to avoid problems during combustion.

The activity changed (apparent 1st order rate constant) with time-on-stream. The rate constant first increased by 46% at 853 h, and then decreases by 17% at 1951 h, compared to the fresh sample. At longer exposure times, the rate constant is almost constant, being 91% of the value for the fresh sample after 2311 h of use. The rate constant at 1908 h of use is higher than expected. The low values of both K and Na in this sample can explain this result. We observed a trend of decreasing activation energy with increasing degree of contamination. The activation energy decreased from 40 kJ/mol for the fresh catalyst, to 28 kJ/mol in that used for the longest time. The pre-exponential factor decreased by 92% for the most deactivated sample. Thus, this method of analysis, using pre-exponential factors instead of rate constants, gives a clearer picture of the deactivating effect. Others [1, 2] have also observed similar trends.

It should be noted that the deactivating effects measured in this study are the combined effects of K, Na and possibly Zn, and it is not possible to distinguish the effect of one component only from our data. In this study it was found that the apparent activation energy decreased with increasing deactivation. We have interpreted this as being the result of an increase in diffusion resistance. If the catalyst is deactivated by deposition of poisons first on the outer surface, the poisons have to diffuse into the catalyst. This should result in a gradient of poisons from the outer surface towards the centre of the catalyst. The

catalyst activity will mirror this gradient; low activity at the outer surface and gradually increasing activity in the central parts. This means that the reactants have to diffuse through a gradually growing porous layer of more or less inert material. The same could apply when fouling the outer surface with a porous layer of inert, small particles.

Tokarz [4] studied a $V_2O_5/TiO_2/SiO_2$ catalyst with a surface area of about $200 \text{ m}^2/\text{g}$ and a pore volume of $1 \text{ cm}^3/\text{g}$ for applications in flue gas cleaning in waste incineration, both in the lab and in the plant. The particle size used in the lab studies was $60\text{--}80 \text{ }\mu\text{m}$. An impregnated catalyst was used to study the effect of each element on 1 and 3 wt% basis of the added element. Their values of the ratio of the rate constant for the catalyst in question to the rate constant for the fresh catalyst (k/k_{fresh}) were 0.822 for Fe, 0.708 for Zn, 0.657 for Ca, 0.473 for Na and 0.144 for K, at $180 \text{ }^\circ\text{C}$ and 3 wt% of the metals. This gives an indication of the degree of poisoning resulting from the elements studied. The metal contents determined in this study at $400 \text{ }^\circ\text{C}$ were: 0.36 wt% for Zn, 0.26 wt% for K and 0.2 wt% for Na after 2311 h deactivation. Therefore, the effects should be smaller by a factor of at least 10. However, it is difficult to compare the values of activities at two such different temperatures.

Kröcher and Elsener [32] studied compounds present in catalysts used in treatment of exhausts from diesel engines and their effect on the catalytic activity. They found similar compounds to those in the present study, so their findings are discussed here, despite the fact that the application is different. They reported a linear decrease in the rate constant with the ratio of potassium to vanadium to the value 0.1, where the decrease in activity was about 80%. Thereafter, the decrease was smaller, but at the ratio of potassium to vanadium (K/V) = 0.2 the decrease in activity was 98%. We also observed a similar levelling-off of the effect of poisons at high metal to vanadium ratios.

Larsson et al. [33] studied the effects of impregnation and aerosol deposition on activity. When KCl was impregnated into the catalyst to a concentration of 0.2 wt% (fresh catalyst 0.05%), the decrease in activity at $300 \text{ }^\circ\text{C}$ was 22.4%. Aerosol deposition led to a deactivation of only 6.7%. When using $ZnCl_2$ the effects were 24.1% for impregnation and 32.4% for aerosol deposition. Aerosol deposition with K_2SO_4 showed lower values than with $ZnCl_2$, while impregnation with K_2SO_4 had the same effect as with $ZnCl_2$ showing that aerosol particles do not enter the catalyst pores. The activation energies reported for the fresh and the particle-deposited samples were constant, but decreased with contamination in the impregnated samples, to 12.2 kJ/mol , for the sample with the lowest amount of K. Their reported activation energies were so low that they might be strongly effected by diffusion processes, and some of the poisoning effects could thus be disguised. Nonetheless, this comparison is interesting as we

believe that the deactivation process in the present study was of the particle deposition type.

It is common to study the catalytic activity as a function of degree of coverage of the catalyst's active sites by poisons. Results are usually given for only one poison at a time. Tang et al. [34] showed that Na deactivates a V_2O_5/TiO_2 catalyst. The rate constant measured at $310 \text{ }^\circ\text{C}$ decreased from 97.1 to $35.0 \text{ (cm}^3/\text{g/s)}$, i.e. by 64%, when the Na/V molar ratio increased from 0 to 0.2. Deng et al. [35] have studied the effects of the introduction of alkali during entrained-flow combustion. We believe that comparison with their results could be interesting as the mode of introduction of the poison is similar to ours. After 5 h exposure to KCl, the value of k/k_{fresh} was 0.35 (measured at $400 \text{ }^\circ\text{C}$). The content of K was then 0.0659 wt%. This is at a value of wt% K where we observed an increased rate of reaction as a result of activation by new sulphate groups on the surface. During the first 500 h on-stream our values of (k/k_{fresh}) increased by a factor of 1.4, at $340 \text{ }^\circ\text{C}$, instead of decreasing. In the presence of SO_2 and O_2 , SO_3 is formed at the vanadia sites at a low reaction rate [36]. This takes place in the deactivation unit in the current study, at $230 \text{ }^\circ\text{C}$, where the gas contained 50 to 200 ppm SO_2 , 2% O_2 , 45 ppm NO, 25 ppm NH_3 as well as nitrogen, water and fly ash. Under these conditions, sulphate species are formed that are bound to the TiO_2 support, increasing the Brønsted acidity of the catalyst.

Yu et al. [37] investigated fresh and poisoned (by KNO_3 impregnation) commercial $V_2O_5\text{--}WO_3/TiO_2$ honeycomb catalysts, and obtained similar results. They reported an increase in the conversion from 40 to 70% by the addition of 1500 ppm SO_2 to the gas flowing over a K-poisoned (K/V = 0.77) catalyst. Chen and Yang [38] also reported a similar increase in conversion using SO_2 for catalysts deactivated by Ca and Li. Their reported rate constants were $0.4 \text{ cm}^3/\text{g/s}$ for K/V = 0.53 and $10 \text{ cm}^3/\text{g/s}$ for the fresh catalyst, at $300 \text{ }^\circ\text{C}$. Our values were 4.96 and $4.95 \text{ cm}^3/\text{g/s}$ at K/V = 0.58. This demonstrates the effect of activation by surface sulphation. Klimczak et al. [39] studied the deactivation of a $V_2O_5\text{--}WO_3/TiO_2$ catalyst using both impregnation and aerosol exposure. The deactivating effect was greater at temperatures above $350 \text{ }^\circ\text{C}$, as was observed in the present study. KNO_3 aerosols caused a decrease in the conversion of NO from 62 to 17% at $350 \text{ }^\circ\text{C}$. The corresponding values for aerosols of $NaNO_3$ and $CaNO_3$ were to 20 and 49%, respectively. They also found good correlations between the experimental activity and that calculated with contributions from single poisons, as well as interactions between several poisons. Furthermore, they demonstrated the positive effect of sulphur on the activity of poisoned catalysts, as in the present study.

No correlation of activity with concentration of poisons were observed for Fe, Pb and Ca. The Pb/V ratio in the fresh catalyst was only 3.7% of the K/V ratio. Thus, only the effect

is foreseen to be largest for the alkali metals in the fresh material at least. Even at higher degrees of deactivation, the K/V ratios are about four times higher than the Pb/V ratios. The Ca/V ratio ranged from 0.1 to 2.0 (probably only on the surface meaning a low effect on the activity). The Fe coverage ranged from 0.15 to 0.25 and was fairly constant over time. For comparison, the K coverage varied from 0.135 to 0.636.

Kamata [3] impregnated a commercial catalyst of the same type as in the present study containing 1% V_2O_5 with up to 2 wt% K in the form of KNO_3 . They used small particle sizes of 0.10 to 0.18 mm. We calculated the apparent values of the activation energy and pre-exponential factor from their data. The result was an activation energy of 76.7 kJ/mol for the fresh catalyst and 3.81×10^{11} (1/min) for the pre-exponential factor. At a degree of poisoning of K/V = 0.2 the activation energy was almost unchanged, while the pre-exponential factor was 2.42×10^{11} (a decrease of 36%). We obtained values of the activation energy and the pre-exponential factor of 40.2 kJ/mol and 2.65×10^6 (1/min), respectively, for the fresh catalyst. When K/V was 0.2 we obtained values of 36.3 kJ/mol for the activation energy and 1.68×10^6 for the pre-exponential factor. The decrease in the pre-exponential factor is 37% for our values, which is in excellent agreement with the results of Kamata. At 260 °C, the rate constant for the fresh catalyst calculated from data given by Kamata was 1.16×10^4 (1/min), whereas our value was 320, i.e. a factor of 36 lower. At 400 °C the corresponding values were 1.39×10^5 (Kamata) and 1.72×10^3 (the present study), i.e. they differ by a factor of 81. This indicates much greater limitation by internal diffusion in our study than in that of Kamata.

In the case of potassium, Chen and Yang [38] reported a 34.6% decrease in the rate constant at 300 °C, at a K/V coverage of 0.2. We found a 48% decrease in the pre-exponential factor at K/V = 0.2 for the fitted values. It should be noted that our results are the combined effect of several poisons, and effect will thus be greater than for a single poison.

Lisi et al. studied the combined deactivating effects of alkali metals and HCl [40]. For a catalyst with 1.88 wt% V they observed an exponential decrease in the pre-exponential factor, from 85.5 for the fresh material, to 36.8 L (h/g), at 0.18 wt% Na. For K the value of the pre-exponential factor at 0.3 wt% was 35.9 L (h/g). In their experiments, the activation energy was constant at 58.6 kJ/mol. The wt% used for Na and K should represent equal molar ratios for Me/V. The degree of deactivation was reported to be almost identical at 0.18 wt% Na and 0.3 wt% K. A levelling off of the factor was seen at higher degrees of poisoning. These results are similar to those obtained in the present study.

Mass gradients limit the rate of reaction, but not to a very high degree. The apparent activation energy of 40 kJ/mol for the fresh catalysts indicates mass transfer limitations

since the intrinsic activation energy is around 85 kJ/mol. We have found one other paper [41] reporting the gradients in a 3.45% V_2O_5/TiO_2 catalyst measured at 300 °C. The concentration of NO at the centre of the fresh catalyst was reported to be 20% of the value at the monolith wall (internal gradient, wall thickness of 0.38 mm). When it was poisoned with 0.85 wt% K_2O the concentration of NO at the centre increased to 83% of its surface value. The value of K_2O used in the present study was 0.26 wt% at the highest degree of poisoning so the effect should be smaller. This agrees with our conclusions, that our experiments are limited by internal as well as external mass transfer. Since the gas flows only inside the monolith in our experiments, we used the whole wall thickness as the characteristic length, which could cause some errors in the calculations. We have found no publications on the mass transfer conditions in one-sided flow in a monolith.

5 Conclusions

It is clear from the results of this study that there is no significant change in the mesopore system of the SCR catalyst as a result of the accumulation of poisons. However, some poisons cause the volume and area of the micropores to decrease significantly. Since the reaction rate is not strongly affected by internal diffusion limitations, all parts of the catalyst will contribute to the activity. As the changes in surface area and pore structure are minimal, the effects seen on the activity are mainly caused by chemical deactivation. Many poisons were accumulated in the deactivated catalysts, which will decrease the activity; the strongest being K and Na, but Zn will also decrease the activity. No such effect was observed for Pb, Fe or Ca. The high content of Cl in the fly ash could contribute significantly to the deactivation process, but was not studied separately in this work.

The results of this investigation show an increase in catalytic activity due to SO_2 (as sulphates) up to 853 h on-stream, at which the maximum activity is reached. This is an important result, since on-stream activation actually prolongs the lifetime of the catalyst. Thereafter, a rapid decrease is observed in the contents of Na and K especially. Zn also lowers the activity of the catalyst, but the effect starts at higher coverage of the vanadium atoms.

The results presented here are important, not only for waste incineration, but also for incineration in general, since they show how deactivation proceeds when the catalyst is deactivated by fly ash components.

Acknowledgements We wish to thank Johan Janner who measured the rate of reduction NO_x . Birgitta Lindén helped us with the nitrogen adsorption measurements and the SEM analysis. The Swedish waste incineration plant is acknowledged for allowing us to use their facilities to expose the catalyst samples.

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