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Comparison of precious metals and base metal oxides for catalytic deep oxidation of volatile organic compounds from coating plants: test results on an industrial pilot scale incinerator

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Abstract

For the coating application case, base metal oxides catalysts (Cu/Cr, Cu/W or Cu/Mn) are not more resistant to poisoning than PGM catalysts, the best results being obtained for a Pt/Pd (1:5) catalyst formulation. Furthermore, the cleaning of aged PGM catalyst is easy and efficient whereas their degree of compactiveness is very high.

Keywords: Volatile organic compounds; Oxidation; Industrial pilot scale incinerator; Metal oxides

1. Introduction

1.1. Case study

This paper gives some results concerning a study dealing with catalytic oxidation feasibility to reduce volatile organic compounds (VOC's) emissions from a coil-coating work, pre-lacquering application. The organic coating used in this application can involve a large phase of organic solvents, between 20 and 60 % of their initial volume [1]. However, poisons can be suspected: metals, silicium and silicone components in the paint, Zn and Cr from the steel preparation steps.

For paint application gaseous effluents are characterised by a great number of compounds, changing in nature and in concentration. Up to 20 components can be identified in the solvent phase of a paint. They can be classified into 4 main families: aromatics, alcohols, esters and ketones. Because of the relatively low concentrations resulting of such a process (3.5 g/m^3 STP) and because of the curing temperatures (250–300°C), catalytic incineration appears as a very interesting technique to purify gaseous effluent at low energy cost. Important advantages can also be seen in the limited NO_x formation and for discontinuous processes.

PGM catalysts were firstly tested; improvements to increase its span life were assessed. A second way to allow higher life span was to use different kinds of catalysts, the based metal oxides (BMO). As a matter of fact, they are said to be more poisons resistant. Furthermore, it was hoped that their apparent oxidation order with respect to the hydrocarbon was different than with the precious metal one so that an optimal reaction could be reached by using two stages of oxidation: a first

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one with a BMO operating at the highest concentrations of VOC's and a second one operating at the lowest residual concentrations. It is pointed out that PGM catalysts present an apparent zero reaction order with respect to the hydrocarbon for a majority of the organic solvents used in coatings [2–4]. A Langmuir–Hinshelwood mechanism is suggested (see for example Frost et al. [5]). The base metal oxides stage must present, ideally, a first order of reaction with respect to the hydrocarbon.

1.2. Experimental section

Pilot scale incinerator description

A bench test (see Fig. 1) for the various catalysts was designed to operate directly under industrial conditions with a by-passed flow-rate of the outlet oven effluents (in parallel to a thermal incinerator). This oven ensured the drying and the curing of a top layer paint. Firstly a fan sucks the effluent from the coating oven through a flowmeter and electric heaters.

For ageing tests, the coating oven effluent can be by-passed so that the ventilator sucks only fresh air. The reference component (liquid phase) is delivered from a syringe pump to the heated air flow, where it is flashed by means of a heated injector.

The contaminated and heated air passes across the catalytic reactor where the VOC's are destroyed. A thermal insulation of the reactor is made to provide nearly adiabatic conditions. The temperatures at both sides of the catalyst are measured by means of platinum probes.

The gas to be analyzed was systematically sampled at the reactor inlet and outlet.

The effluent sampler analysis was mainly supplied by a gas chromatograph (GC) working in gas phase through a capillary column and equipped with a flame ionization detector (FID).

The overall bench test was under computer control to monitor 24 h tests.

Methods of assessment

The full detailed explanations of the method used to assess the catalyst life time can be found in a previous publication of the authors [6] but they can be summarized as:

1. continuous data acquisition of operating parameters like inlet and outlet temperatures, temperature raising, flow-rate, operating conditions of the coil-coating process;
2. periodic measurement of the catalytic incineration effectiveness to abate VOC's emissions from the coating oven;
3. periodic plotting of the ageing curve of the catalyst;
4. analyses of the catalyst at the end of the test.

This paper characterizes mainly the quality of the catalysts tested by comparing the evolution of ageing curve versus the total operating time. It must be said that the plotting of ageing curves is not sufficient to characterize the catalyst resistance even if chemical analyses of the catalyst are made after the test. Continuous data acquisition

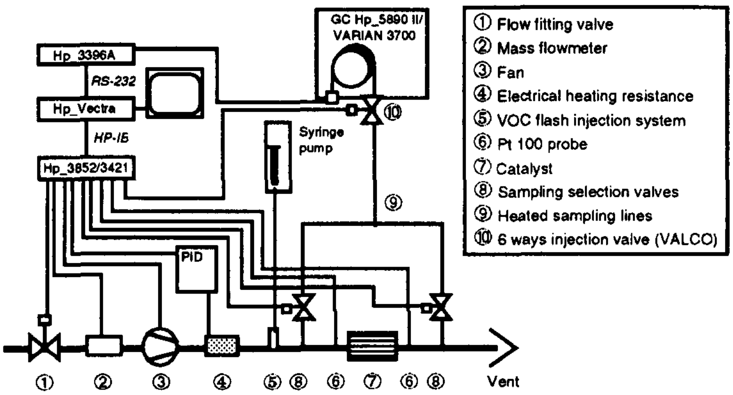

Fig. 1. Bench test unit diagram.

Table 1
Description of the catalysts tested

Sampling	Catalyst	Support	Shape	Cells density	Active metals	Loading	GHSV[a] (h^{-1})
#1	PGM	keramic	monolith	200	Pt	30 g/ft^3	20000
#2	PGM	metallic	corrugated	200	Pt/Pd	120 g/ft^3	20000
#3	metal oxides	TiO_2	pellets	–	Cu/Cr	29.2%/3.5%	10000
#4	PGM	metallic	corrugated	400	Pt	30 g/ft^3	20000
#5	metal oxides	TiO_2	monolith	100	Cu/W	1.22%/7.1%	7000
#6	metal oxides	Al_2O_3	pellets	–	Cu/Mn	9.2%/19.2%	3000

[a] Nominal values.

monitoring is the only way to point out the reversible poisoning effects.

Toluene was chosen as the representative compound of the VOC's blend and therefore it was used as the reference compound for the plotting of ageing curves. For all catalysts, the used toluene concentration for ageing curves was 1 g/m^3 (STP).

Catalysts tested

The six tested catalysts are described in Table 1. Operating conditions during the ageing tests respect the nominal space velocity of the catalyst given by the manufacturer. In order to abridge the duration of the tests, ageing was accelerated by increasing the nominal velocity by a factor of 2.5 during the continuous test monitoring.

2. PGM catalysts

2.1. Pt catalyst on a monolithic ceramic support (#1 catalyst)

The #1 catalyst was used in the industrial pilot catalytic incinerator at its nominal space velocity. The inlet temperature was in the range of 250–350°C.

Fig. 2 shows the evolution of the ageing curves of this catalyst which was tested over 18 weeks (1600 operating h), the curve of week 18 being the last one before stopping the test.

Fig. 3 shows the comparison between the three states of the catalyst: fresh, aged and washed by a 5% NaOH solution.

The incineration curves of the figure represent the ethene efficiency versus the feed temperature of the catalyst obtained for an ethene concentration of 1000 ppm and a GHSV of 50 000 h^{-1}. Those different conditions are justified by the fact that the use of ethene is easier than toluene in a laboratory bench test (results are more accurate) whereas the use of a higher space velocity is necessary to observe significantly the poison phenomena.

It can be pointed out from Fig. 2 that a reversible poisoning occurs between the weeks 16 and 18. This phenomenon was confirmed by the continuous data acquisition. Elemental chemical analyses with plasma torch reveal the presence of

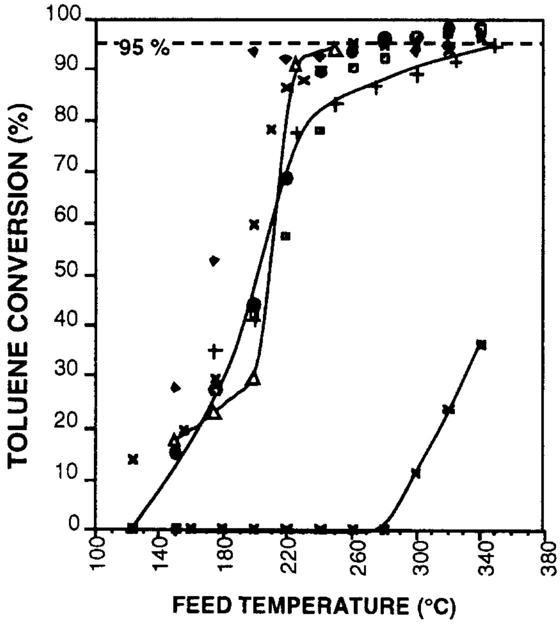

Fig. 2. Ageing curves of the #1 catalyst: (Δ) fresh; aged, weeks: (●) 2, (♦) 4, (□) 6, (×) 10, (∗) 16, (+) 18.

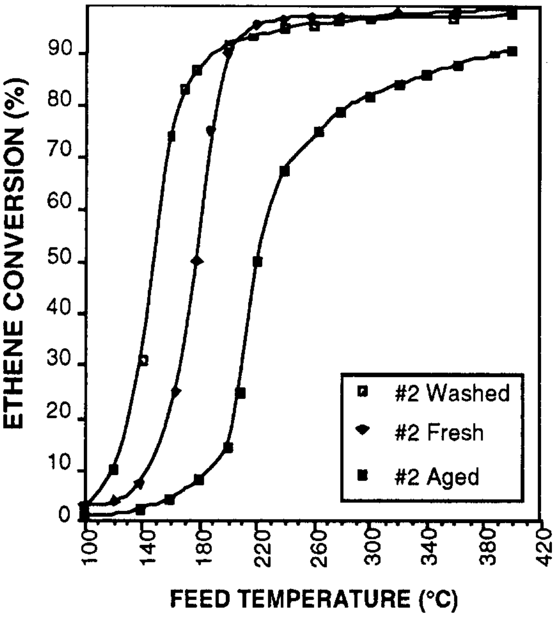

Fig. 3. Washing of the #1 catalyst.

$BaSO_4$ (Ba: 0.7% and S: 0.2%). If the action of sulphur as reversible poison is known, it is not still established that the $BaSO_4$ can present the same effects. The nature of the catalyst support does not allow to reveal the presence of silicone compounds; X-rays diffraction analyses suffer the same limitation but they could show the presence of silicone compounds without the possibilities of quantification.

2.2. Pt/Pd catalyst on a corrugated metal support (#2 catalyst)

The #2 catalyst was developed as a conclusion of the results obtained thanks to #1 catalyst. As a matter of fact, one thing to do when strong site adsorption or masking occurs is to increase the number of active sites by increasing the active metal loading. To keep the price of the catalyst constant it was suggested to add palladium at the formulation as the main compound; a ratio of 1:5 between Pt and Pd allows to keep an equal cost with a precious metal loading of 120 g/ft^3. The corrugated metal support was useful to realize chemical analyses after the test.

Test conditions were set at 350°C and the space velocity was 42 500 h^{-1}, around two times the nominal velocity, in order to accelerate the ageing.

Fig. 4 shows the evolution of the ageing curves of this catalyst which was tested over 30 weeks (2160 operating h). The results obtained with this catalyst are better because the effects of reversible poisoning cannot be observed and especially the efficiency after the 2160 operating h is not bad. Because the space velocity, during the continuous test, matches more than 2 times the nominal value, the life time of the catalyst can be assessed up to 4000 h.

Fig. 5 shows the comparison between the three states of the catalyst: fresh, aged and washed during 16 h respectively by a 5 and 25% NaOH solution.

In regard to Fig. 2 and Fig. 4, the poisoning effect is attenuated on the #2 catalyst. This effect is not so evident in regard to Fig. 3 and Fig. 5 but it can be seen that the oxidation of ethene is less efficient on the #2 catalyst (effect of Pd). The washing was repeated with a 25% NaOH solution.

Cleaning at an inlet temperature of 600°C was tried in order to observe the eventual impact of possible high molecular weight VOC's which could be condensed at the surface. Little improve-

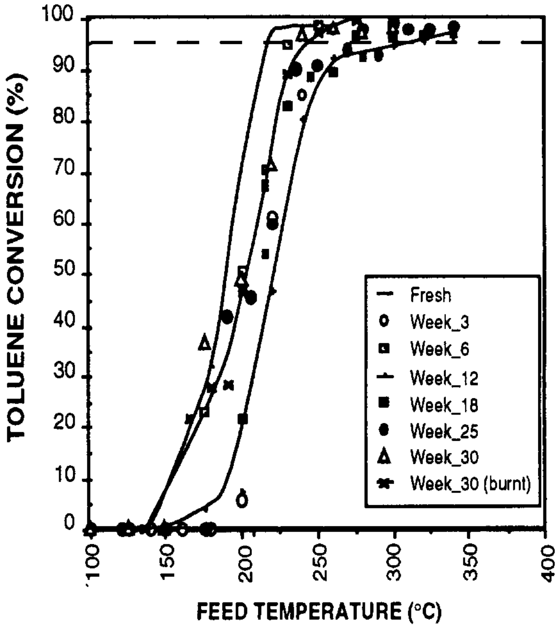

Fig. 4. Ageing curves of the #2 catalyst.

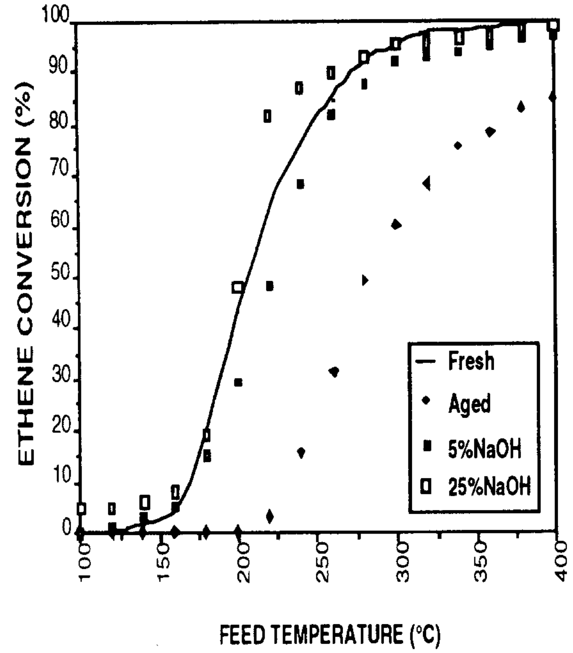

Fig. 5. Washing of the #2 catalyst.

ment has been observed (see Fig. 4, week 30 'burnt').

The results of the chemical analyses, thanks to the use of a metallic support, let to appear a significative presence of silicone compounds which is the main detected poison (2% in weight).

Following the results of the catalyst washing, silicone compounds can not be qualified as irreversible poisons; the term of semi-reversible poisoning is more adequate. Such results can be found in the literature [7].

2.3. *Pt catalyst on a corrugated metal support (#4 catalyst)*

The development of the #4 catalyst was made in order to observe the effect both of increasing the cell density and of the support changing, keeping constant the Pt loading in relation with the #1 catalyst.

Test conditions were set at 350°C and the space velocity was fixed at 45 000 h^{-1}.

This catalyst was only tested over 8 weeks. After 4 weeks, its activity fell drastically (see Fig. 6).

No washing results were available because the catalyst was damaged during the high temperature cleaning (mistake in the cleaning procedure led to a temperature of 850°C). The support and the catalyst melt literally.

From a practical point of view, it can be pointed out that such an incident can not only damage the catalyst but also the catalytic system because of the metal melting.

3. Cu/Ti catalysts

Base metal oxides catalysts are generally claimed more resistant to poisoning. As a matter of fact, this quality can be explained by the larger surface developed by the catalyst because the needed quantity of catalyst material is bigger than for PGM catalysts. On the other side, base metal oxides are cheaper but from a practical point of view it can be affirmed that the final cost of an incinerator is equal. Base oxide metal can be made in the bulk. This section relates the results of the test on #3 and #5 sampling, respectively, Cu-Cr/W catalysts available in pellets and with a monolithic shape.

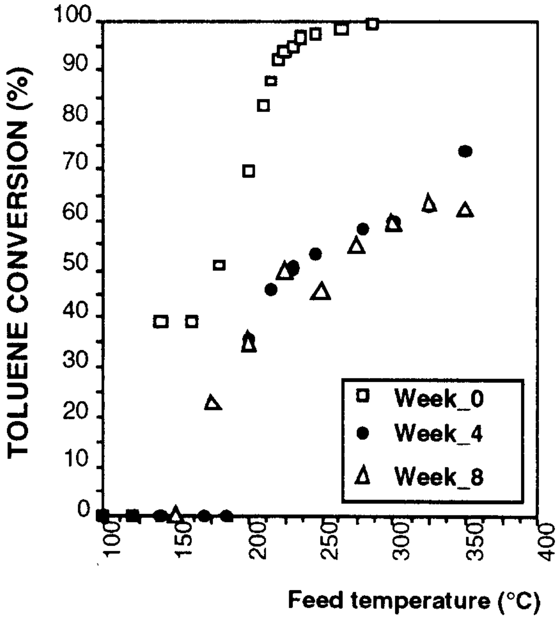

Fig. 6. Ageing curves of the #4 catalyst.

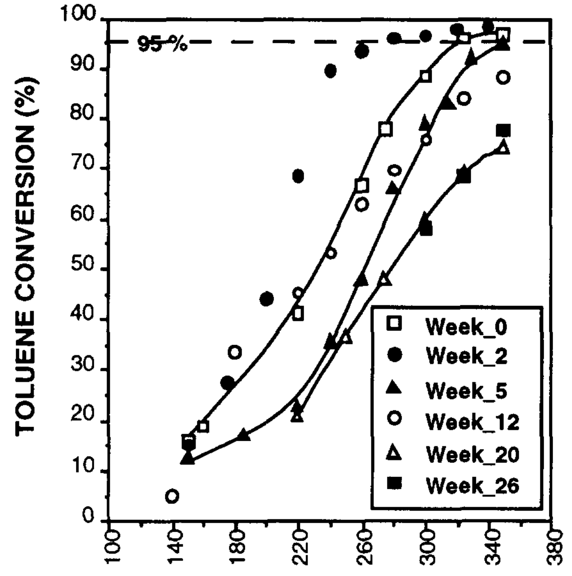

Fig. 7. Ageing curves of the #3 catalyst.

3.1. Pellets shape (Cu/Cr)

The #3 catalyst was used in the industrial pilot catalytic incinerator at its nominal space velocity (flow-rate of 30 m^3/h STP). The inlet temperature was set at 350°C.

Fig. 7 shows the evolution of the ageing curves of this catalyst which was tested over 26 weeks but the efficiency of the catalyst fell to an unacceptable value after only 5 weeks.

When removing the catalyst from the incinerator, it was established that its volume had strongly decreased. It has been concluded at this moment that a mechanical problem occurred, accelerated by the fact that the direction of the flow was scheduled down to up.

Chemical elemental analyses were made by comparison of a sampling from the fresh catalyst and samplings of the aged one. No significative poisoning was detected; only the content in Zn had increased (from 0.03 to 0.09%).

3.2. Monolithic shape (Cu/W)

An attempt to use the same catalyst as #3 but with a monolithic shape was made. The ageing curves are not related here because the catalyst activity fell drastically after only one week. The removal of the catalyst allows to show that the catalyst was literally blown up.

The analyses of data coming from the continuous data acquisition and monitoring system revealed a phenomenon such as shown in Fig. 8. Laboratory tests allow to reproduce the phenomenon with the same effect (blowing up); the oxidised compound was toluene at 2 g/N m^3.

The explanation is found in the high adsorption capacity of the catalyst for toluene as shown at Fig. 9. The evolution of the incineration curve as

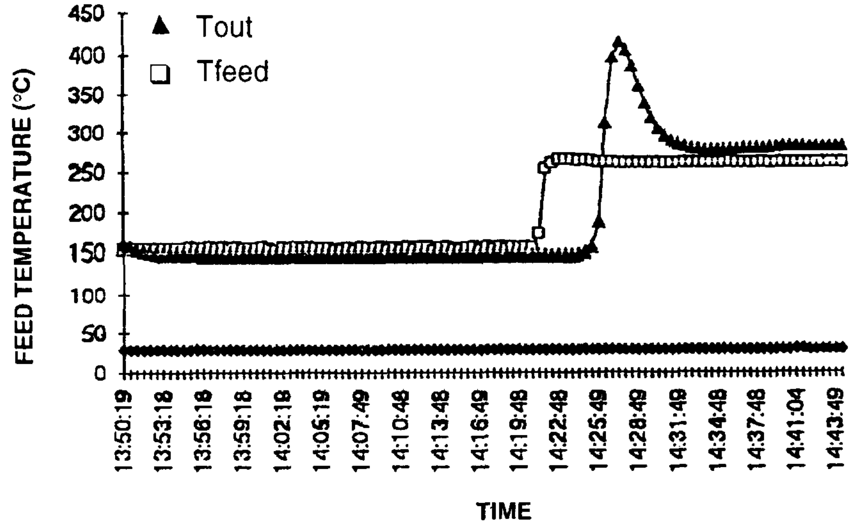

Fig. 8. Temperature peak when changing the feed temperature.

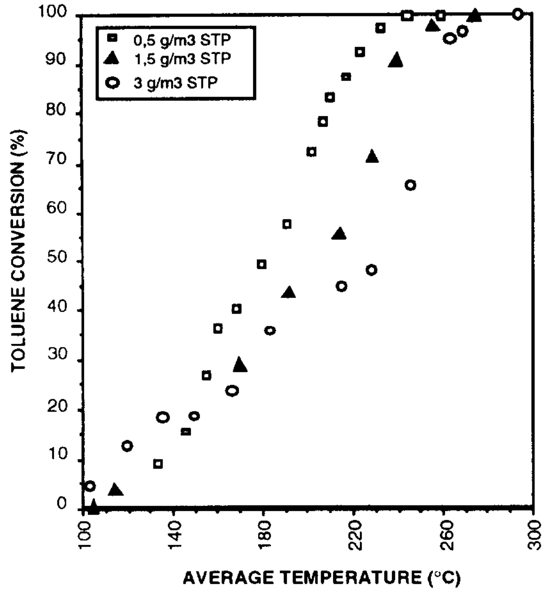

Fig. 9. Oxidation curve of toluene over a Cu/Cr catalyst at different concentrations.

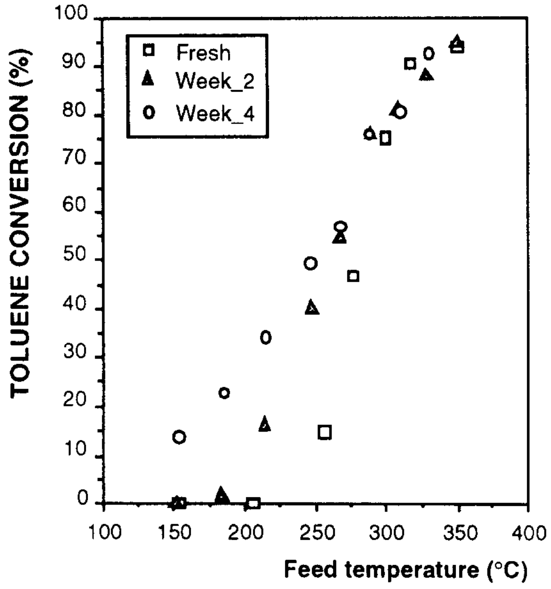

Fig. 10. Ageing curves of the Cu/Mn catalyst.

a function of the toluene concentration fits with an $a \leq 0$ order of reaction.

So the problem of blowing up occurs during a displacement of the adsorption equilibrium when increasing the temperature. The desorbed toluene increases fast the temperature of the oxidation during a short period of time. This thermal stress is fatal for the catalyst.

Finally, the same explanation can be given for the #3 catalyst from which the apparent effects were not so evident.

4. Cu/Mn catalyst

Fig. 10 shows the test of the ageing for this catalyst. The trends for the Cu/Mn catalyst is a similar behaviour to the best tested PGM (#2 catalyst). With such a supported catalyst, effects like reported for the #5 catalyst are avoided.

To conclude about the BMO tested catalysts during the present study, it must be said that the difference pointed out between this catalyst and the PGM one in the chemical reaction order of the oxidation (with respect to the hydrocarbon) is not sufficient to justify the use of this catalyst as an optimising first stage of oxidation. Indeed it can be shown, within the range of the tested concentrations, that this reaction order trends to zero for toluene over the PGM catalyst [4] whereas it is matching 0 for the #5 catalyst and 0.65 for the #6 catalyst (see respectively Fig. 8 and Fig. 11). Furthermore the BMO catalyst activity is too low in order to justify a BMO/PGM combination.

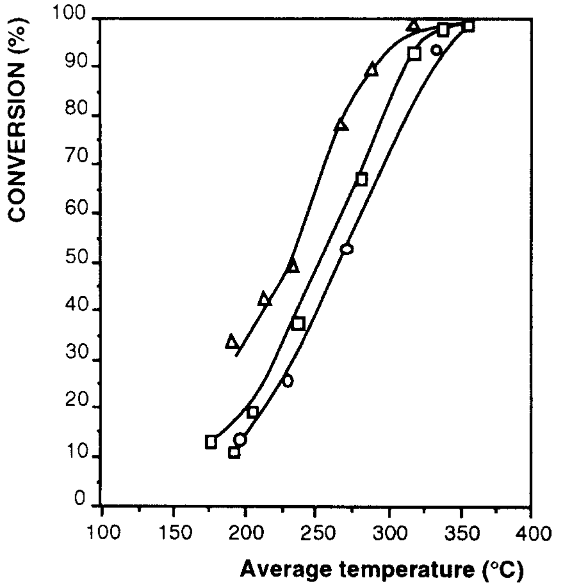

Fig. 11. Oxidation curve of toluene over the Cu/Mn catalyst at 0.5 Δ, 1.5 □ and 3.0 g/N m^3 ○.

5. Discussion

In the scope of this study, base metal oxides catalysts are not found to be better than PGM catalysts from the point of view of their silicones resistance.

Tested Cu/Cr catalysts are not recommended for the application case in coil-coating. The best catalyst found is an overloaded PGM (#2 catalyst). The problem of a possible cost over is solved by using palladium preferentially to platinum. The behaviour of the tested Cu/Mn catalyst is similar to the previous catalyst but the required volume is 6 to 8 times bigger than for PGM.

Even if the BMO catalysts present a lower cost, the price for the complete catalytic system may be equal or even higher than a system using a PGM one.

Maintenance aspects are shown to be very important. The tested PGM catalysts have shown to be very successfully cleaned by a NaOH solution. From this point of view, monolith PGM catalysts are very easy to remove out of the system for cleaning. In this case the silicone poisoning can be considered as semi-reversible.

Preventive techniques can be useful to prolong the service time of the catalyst; trials have shown that the service time was inversely proportional to the space velocity when poisons are present. Hence, it is possible to increase the life span by increasing the catalyst quantity or the surface in order to trap poisons. That can be reached by using an inert mass before the catalyst.

It is suggested by some system suppliers to put a catalytic bed with based metal oxides before the PGM catalyst as a pre-oxidation step, the ideal being that this pre-oxidation step exhibits an opposite oxidation order than the main stage. This behaviour was not pointed out for the BMO catalyst tested in this study.

References

[1] S. Vigneron and J. Hermia, Rapport final de la recherche CECA No. 7261-04/441/02, Louvain-la-Neuve, Mai 1992.
[2] A.A. Barresi and G. Baldi, Chem. Eng. Sci., (1992) 1943.
[3] I. Mazzarino and A.A. Barresi, Catal. Today, 17 (1993) 335.
[4] S. Vigneron and J. Hermia, Catal. Today, 17 (1993) 349.
[5] A.C. Frost, J.E. Sawyer, J.C. Summers, Y.T. Shah and C. Dassori, Environ. Sci. Technol., 25 (12) (1991) 2065.
[6] S. Vigneron, J. Hermia and J. Gillaux, Studies Environ. Sci., 61 (1994) 445.
[7] J. Chen, R.M. Heck and R.J. Farrauto, Catal. Today, 11 (1992) 517.