

COMBUSTION OF VOLATILE ORGANIC COMPOUNDS OVER MONOLITHIC CATALYSTS

Anna Musialik-Piotrowska and Krystyna Syczewska
Institute of Environment Protection Engineering,
Technical University of Wroclaw
50-370 WROCLAW, Poland

ABSTRACT

The Research Group of Ecological Catalysis, Technical University of Wroclaw, concentrates on the preparation of monolithic catalyst on metal foil supports (Al-Ti or steel). Five noble metal catalysts, platinum and palladium (and two of them with Rh ingredient), were prepared for the laboratory tests. They were tested for combustion of four different species - toluene, n-heptane, acetone and ethanol. The results of laboratory tests were of utility in the preparation of the catalytic monolith for a lacquer drier (SEM 300). Activity tests were carried out under normal conditions of drier operation and they corroborated the expected high activity of the catalyst. The compact unit (drier and catalyst) allowed also for energy savings during the whole drying cycle. High activity of the monolithic catalyst in this process allows us to assume that it will be applicable to the combustion of other organic polluting species, replacing traditional granular catalysts.

INTRODUCTION

Solvent vapours form a major group of organic pollutants emitted to the atmosphere. They come predominantly from varnishing and enamelling processes. Typical solvent are a mixture of hydrocarbons (benzene, toluene, xylene, styrene) and their oxy derivatives - alcohols (ethanol, butanol), esters (ethyl acetates, butyl acetates), ketones (acetone, methyl-ethylketone), glycols, etc.

In terms of economy, the most efficient method for treating such flue gases is catalytic oxidation [1]. In the past few years, there has been growing interest in the development and application of platinum- or palladium based monolithic catalysts on ceramic supports [2 to 9]. For economic reasons, the use of metal supports is far less frequent in engineering (they weigh more and are more expensive than the ceramic ones). It is generally believed that Fe-Cr-Al or Ti-Al alloys are best suited for being used as catalyst supports. The active ingredient is deposited on the support, covered with the washcoat (generally $\gamma\text{-Al}_2\text{O}_3$ in the presence of rare earth).

In Poland, attempts to prepare a monolithic ceramic support of the parameters desired have failed so far. For this reason, the Research Group of Ecological Catalysis, Technical University of Wroclaw, concentrated on the preparation and manufacture of a monolithic catalyst on a metal-foiled support.

AIM AND SCOPE OF THE STUDY

At the Laboratory of Ecological Catalysis a number of cata-

lyst samples were prepared on a noble metal basis (Pt, Pd or Rh) and deposited onto metal supports (Ti-Al or steel foils). Preliminary tests were run to optimize the thermal and chemical processing of the support, as well as the method of depositing the washcoat and active layers, so as to provide a durable attachment of the active ingredient and the supporting material.

The investigations of the monolithic catalysts involved two steps:

- laboratory tests (catalytic activity was tested in the oxidation of selected solvent vapours), and
- full-scale tests (catalytic activity was tested in the oxidation of the polluting species emitted by an industrial SEM-300 type lacquer drier).

In the laboratory tests use was made of five catalysts. As the testing results were satisfactory, a catalytic block was prepared and placed in a prototype lacquer drier of a 300 m³/h performance.

DESCRIPTION OF CATALYSTS

The catalysts were obtained by deposition of aluminium oxides, lanthanum compounds, and the active ingredients - platinum, palladium or rhodium - onto an aluminium-titanium or a steel foil which was 0.3 mm thick and had been etched superficially. The catalysts were then formed appropriately, to become cylindrical or rectangular in shape, by alternate arrangement of even and pleated foils. The foils arranged in this way provided passages which were equilateral triangles in their cross-sections.

According to the scale of the test, the catalysts were varied in size. More details on the contacts used are gathered in Table 1.

Table 1.

Description of catalysts

Catalyst	Support	Active ingredient	Surface area, m ²
M-15	Al-Ti foil	0.02% Pt, 0.01% Pd, La	0.15
M-17	steel foil	0.06% Pt, 0.025% Pd La	0.15
M-18	Al-Ti foil	0.05% Pt, 0.02% Pd, La	0.15
M-19	Al-Ti foil	0.05% Pt, Pd, Rh, La	0.15
M-21	Al-Ti foil	0.04% Pt, 0.01% Pd, La	0.15
ZUGIL	Al-Ti foil	0.13% Pt, 0.06% Pd, La	16.50

METHODS

Laboratory tests were run in a throughflow reactor. The laboratory catalysts were tested in the oxidation of four compounds which differed in chemical structure: toluene, n-heptane, acetone and ethanol. The concentration of each component was ca. 1 mg/dm³. Oxidation efficiency was investigated at temperatures ranging from 200 to 500°C and a space velocity of 20,000 h⁻¹.

Full-scale tests made use of a prototype drier with a monolithic catalyst included in the gas circulation system, designed and manufactured by Techma-ZUGIL, Wielun (Poland). According to the technological diagram, the gas stream is sucked in from the drier by a fan and then pumped to provide contact with the catalytic monolith. The catalyst is heated by the air coming from the drier and reheated by electric heaters. The clean air stream is returned from the catalyst block to the drier chamber. The temperature in the chamber amounts to at least 100°C and varies from one lacquer type to another. The temperature of gases before passage through the catalyst block should not be lower than 280-300°C. Space velocity approached 20,000 h⁻¹.

The drying process ran in three stages:

- I (up to ten minutes) intensive evaporation of the solvent;
- II (about 20 minutes) final evaporation of the solvent;
- III (about 30 minutes) surface hardening.

Investigations of the prototype were carried out for three types of paint:

- phtalocarbamide paint with relevant diluent (SWW 1318-124),
- phtalic paint modified with white spirit diluent (SWW 0246-320),
- chlorinated rubber paint for general purposes, with relevant diluent (SWW 1318-152).

RESULTS OF INVESTIGATIONS

ACTIVITY TESTS FOR LABORATORY CATALYSTS

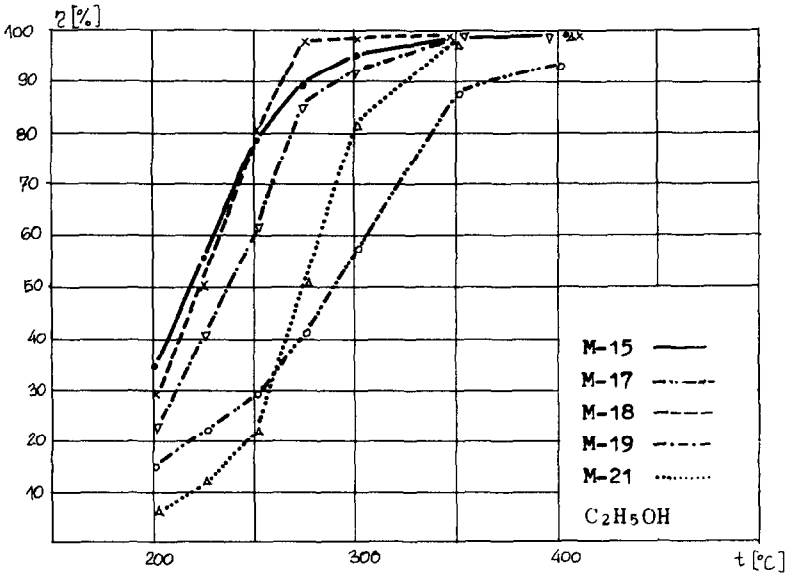
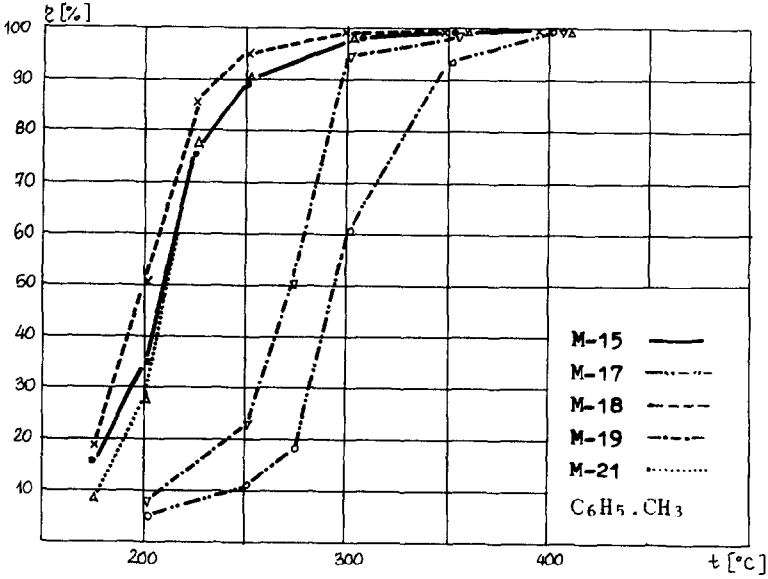
The results are plotted in Figs. 1 to 4.

The catalytic reactivity of the compounds to be oxidized is shown in decreasing order:

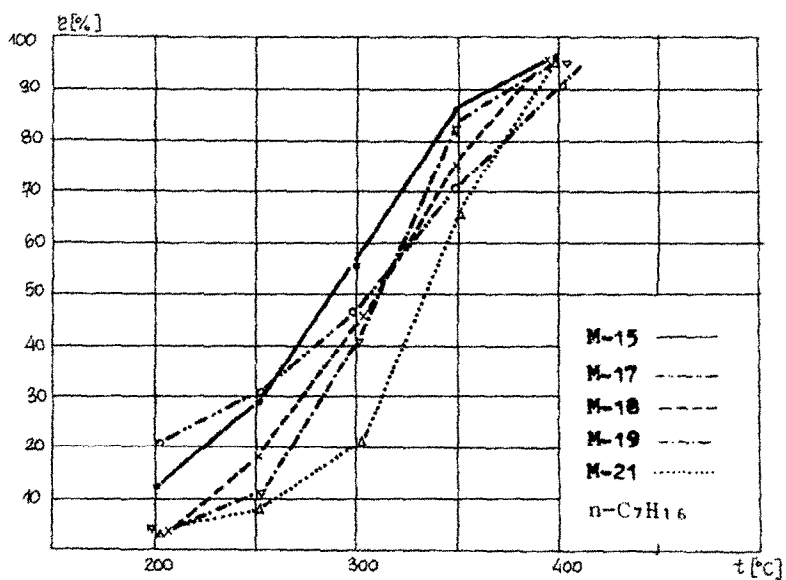
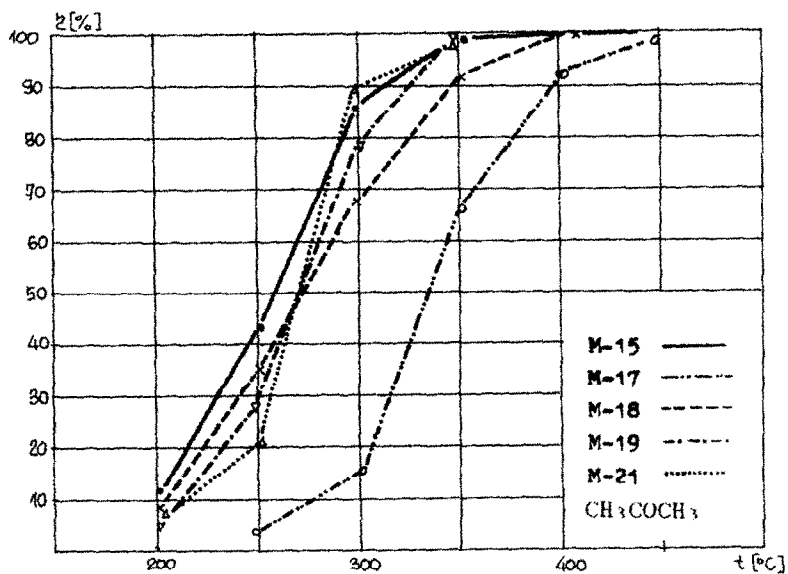
toluene > ethanol > acetone > n-heptane

Toluene was oxidized most effectively over each of the catalysts tested. M-18, M-15 and M-21 were the most active catalysts, and 90% oxidation efficiency for M-18 was achieved at a temperature of 230°C. 90% oxidation efficiency over the less active catalyst, M-19, was achieved at a temperature by 65 deg higher than that over M-18. The catalyst M-17 was found to be the least active contact. In the presence of M-17, 90% oxidation efficiency was achieved at 340°C, a temperature which yields over 98% efficiency in the presence of the other catalysts.

The M-18 catalyst also showed the highest activity in ethanol oxidation, 90% efficiency was achieved at 260°C (Fig. 2). At 350°C,



Figs 1 and 2. Combustion efficiency of toluene and ethanol vapours over laboratory monolithic catalysts. Concentration of the pollutant 1 g/m^3 , space velocity $20\,000 \text{ h}^{-1}$



Figs 3 and 4. Combustion efficiency of acetone and n-heptane vapours over laboratory monolithic catalysts. Concentration of the pollutant 1 g/m^3 , space velocity $20\,000 \text{ h}^{-1}$

oxidation of ethanol vapours was complete. In terms of their activity, M-15, M-19 and M-21 ranked second, third and fourth, with 90% efficiency at 275, 290 and 325°C, respectively. Like in toluene oxidation, M-17 was found to be the least active contact.

Acetone oxidation (Fig. 3) ran at the fastest rate in the presence of M-15. Over M-19 or M-21 the oxidation rate was only slightly slower. Thus, at 320°C, the efficiency of acetone oxidation amounted to 94% when M-15, M-19 or M-21 was present. For comparison, at the same temperature oxidation efficiency was 78% and (only) 34% in the presence of M-18 and M-17, respectively.

Of the compounds tested, n-heptane was found to be the most resistant to catalytic oxidation (Fig. 4). Below 250°C, M-17 was the most active contact; above 250°C it was also M-15. However, 90% efficiency of n-heptane oxidation was not achieved until the temperature rose to 365°C.

As shown by the results obtained, the highest activity was that of M-15 and, also, that of M-18. The catalyst on the steel foil support, M-17, was found to be the least active contact.

RESULTS OF FULL-SCALE TESTS (DRIER WITH CATALYST)

The results are listed in Tables 2, 3 and 4.

Preliminary test of the drier showed that solvent evaporation was most intensive during the first 5 to 10 minutes of the drying process. Owing to the exothermic character of the catalytic oxidation reaction, the temperature of the gases after passage through the catalyst block increased by some 50 degrees to return to its initial value after 10 minutes (this temperature was then kept constant throughout the process).

Table 2.

Average efficiencies of solvent vapour oxidation during drying of phtalocarbamide paint coatings (space velocity, 13,000 h⁻¹; temperature of gases before the catalyst, 330°C)

Pollutant	Stage 1		Stage 2	
	Enter. concentration, g/m ³	Oxid. effic. %	Enter. concentration, g/m ³	Oxid. effic. %
acetone	85 - 108	100	not detected	-
ethyl acetate	72 - 94	90	16 - 30	90
benzene	8 - 14	99	traces	100
decane	traces	100	traces	100
toluene	660 - 950	99.5	10	93
butyl acetate	340 - 430	99.5	16 - 20	100
butanol	1320 - 1550	100	94 - 100	93
xylene	470 - 520	98	32 - 42	98
dodecane	1020 - 1290	99.5	54 - 56	100

Table 3
Average efficiencies of solvent vapours oxidation during drying of modified phthalic paint coatings (space velocity, 19,000 h⁻¹; temperature of gases before the catalyst, 320°C)

Pollutant	Stage 1		Stage 2	
	Enter. concentration, g/m ³	Oxid. effic. %	Enter. concentration, g/m ³	Oxid. effic. %
acetone	42	96	traces	100
ethyl acetate	61 - 100	94	traces	100
MEK	120 - 150	95	traces	100
benzene	115 - 119	96	0 - 1	100
decane	337 - 372	97	21 - 73	98
toluene	277 - 327	99	11 - 16	100
undecane	245 - 261	99	19 - 23	100
ethyl benzene	traces	100	traces	100
xylylene	173 - 243	100	7 - 26	100
dodecane	88 - 109	100	8 - 9	100
cyclohexanone	23 - 24	100	1 - 4	100

Table 4
Average efficiencies of solvent vapour oxidation during drying of chlorinated-rubber paint coatings (space velocity, 19,000 h⁻¹; temperature of gases before the catalyst, 320°C)

Pollutant	Stage 1		Stage 2	
	Enter. concentration, g/m ³	Oxid. effic. %	Enter. concentration, g/m ³	Oxid. effic. %
acetone	90 - 104	96	not detected	-
ethyl acetate	150 - 187	91	1 - 3	100
MEK	65 - 78	91	traces	100
benzene	140 - 160	96	1 - 2	100
decane	245 - 270	98	6 - 8	91
toluene	187 - 190	99	7 - 9	100
undecane	113 - 131	100	10 - 12	100
ethyl benzene	245 - 273	100	4 - 6	100
xylylene	250 - 290	100	12 - 28	100
dodecane	316 - 365	100	3 - 5	100
butyl acetate	130 - 157	100	not detected	-
cyclohexanone	21 - 24	100	0 - 2	100

Under routine operation conditions, the activity of the catalyst was found to be very high in the oxidation of each solvent vapour tested. Only ethyl acetate and acetone were more resistant to oxidation, yet their oxidation efficiency exceeded 90%. The oxidation of the remaining components was almost complete.

SUMMARIZING COMMENTS

The investigations corroborated the high activity of the monolithic catalysts on metal supports which had been developed by the Ecological Catalysis Research Group, Technical University of Wrocław. The contacts had a high resistance to chemical and thermal stress, and no losses were found in the active ingredient as a result of exposure. The application of monolithic catalysts on metal supports accounted for considerable pressure drop (from about 100 mm H₂O in the presence of a granular catalyst to 10 mm H₂O in the presence of catalytic monolith).

As the results of laboratory tests were promising, it was designed and constructed a lacquer drier integrated with the catalytic oxidation of the solvent vapours emitted in the course of the process. The design of the drier meets the pollution control standards, eliminates the need of releasing excess air outside the chamber, and allows energy savings.

The results obtained in this study make us believe that our metal-supported monolithic catalyst may successfully replace conventional granular catalysts in the oxidation of organic air pollutants emitted from various sources.

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