

ANNA MUSIALIK-PIOTROWSKA*,
KRYSTYNA SYCZEWSKA*

METAL OXIDE CATALYSTS FOR OXIDATION OF SOLVENT VAPOURS

Organic air pollutants are emitted predominantly during enamelling or varnishing processes and generally include aromatic hydrocarbons (xylene, toluene), alcohols, esters and ketones. The objective of our study was to develop an oxide catalyst cheaper than traditional platinum-based catalyst for treatment of flue gases from tractor chassis drier. Three metal oxide catalysts (Cu-Cr-Co, Cu-Cr-V, Cu-Cr-Mn) on γ -Al₂O₃ were prepared and tested in the oxidation process of toluene, *n*-heptane and ethanol mixture in air. They exhibit high activity comparable to that of 0.05% Pt catalyst. An industrial batch of Cu-Cr-Mn catalyst on γ -Al₂O₃ in the form of Raschig rings was produced and tested in the large laboratory scale. The results were used for the design and construction of catalytic reactor with the Cu-Cr-Mn catalyst for treating exhaust gases from drier in the URSUS factory.

1. INTRODUCTION

Solvents constitute a major group of organic pollutants entering the atmosphere. They come predominantly from enamelling or varnishing processes. Solvent vapours generally include aromatic hydrocarbons (toluene, xylene), alcohols, esters and ketones, but they rarely contain typical catalyst poisons (sulphur or chlorine compounds). In developed industrial countries, the catalysts with noble metal as an active phase (platinum or palladium) are applied to air pollution control. The widespread use of such catalysts should be attributed not only to their high activity, but to their processing stability as well. But the ever increasing noble metal prices cause many scientists to transfer their attention to oxide catalysts. Thus, KARNAUKHOV [1] suggests that catalysts should be selected according to the following rules:

less active and cheaper oxide catalysts are applicable when the polluting species are not too toxic and their admissible values are not too rigorous;

* Institute of Environment Protection Engineering, Technical University of Wrocław, pl. Grunwaldzki 9, 50-377 Wrocław, Poland.

when the polluting species are highly toxic and the removal efficiency required is very high, it is economically advisable to make use of platinum catalyst with noble metal content sufficient to provide the oxidation efficiency desired.

In fact, the only criterion for the choice of the metal oxide ingredient when preparing a catalyst is the presence of weakly bound oxygen on its surface. Such oxygen can readily react with gaseous organic compound to form CO_2 and H_2O . But once its bonding energy with respect to metal surface exceeds 250 kJ/mol, the reactivity of oxygen will drop rapidly. According to BORESKOV [2], reactivity of hydrocarbons (particularly light hydrocarbons) in the presence of oxide catalysts varies in the following descending order:

alkines > alkenes > aromatics > paraffines.

Thus, for hydrocarbons with six carbons in the molecule the relative rate of the oxidation reaction increases as follows:

n -hexane < benzene < 1-hexene < 1-hexyne.
(1) (1.8) (3.9) (5.0)

It has also been found that, depending on the compound to be oxidized, there might be only a slight difference in specific activity of noble metal-based catalysts and oxide catalysts. This finding holds, e.g., for the oxidation of methane or acetone, but if olefins are to be oxidized, the difference in catalytic activity may approach two orders of magnitude.

Today the majority of oxide catalysts are being prepared on the basis of copper, chromium, cobalt, manganese, iron or nickel oxides [3]–[5].

2. AIM AND SCOPE OF INVESTIGATIONS

The objective of the investigations was to develop an oxide catalyst for the treatment of flue gases from a tractor chassis drier (Tractor Manufacturing Plant URSUS, Warsaw). An oxide catalyst was proposed because of two reasons: the price of platinum is high and still increasing and the polluting species are readily oxidizable.

For the purpose of preliminary tests three oxide catalysts were prepared according to our own recipe: Cu–Cr–Co (A), Cu–Cr–V (B) and Cu–Cr–Mn (C); all of them on the $\gamma\text{-Al}_2\text{O}_3$ support. Their catalytic activities were tested in the oxidation of the three-component mixture (toluene, *n*-heptane and ethanol) in air.

On the basis of the catalyst (C), which had been prepared from domestic, easily available species, an experimental industrial batch of the catalyst on $\gamma\text{-Al}_2\text{O}_3$ support in the form of Raschig rings was produced (C–T). The catalyst was tested on a laboratory scale in the oxidation of a reaction mixture simulating the composition of the drier flue gases. As the oxidation efficiency was high, the catalyst was then tested in a mobile apparatus for the combustion of solvent vapours released by the chassis varnishing drier. Control tests were carried out with real flue gases from the URSUS factory.

Making use of the results obtained, a mathematical model of the oxidation in the presence of the C-T catalyst was constructed, and a catalytic system of 3600 Nm³/h for the oxidation of organic pollutants emitted by the chassis drier for the URSUS factory was designed.

3. CATALYSTS

In the table there are presented the catalysts used during investigations. Except for TUD-2924, each catalyst was prepared according to our own recipe by impregnation of γ -Al₂O₃ support of varying shapes. For laboratory tests, C-T was broken up to an equivalent diameter of 2-2.5 mm. Owing to the deep impregnation of the catalyst, even the internal surfaces were covered by the active metal oxides.

Table

Characteristics of the catalysts

Catalyst	Active ingredient	Support
(A)	Cu-Cr-Co	γ -Al ₂ O ₃ , 2 mm spheres
(B)	Cu-Cr-V	γ -Al ₂ O ₃ , 2 mm spheres
(C)	Cu-Cr-Mn	γ -Al ₂ O ₃ , 2 mm spheres
(E)	Pt, 0.05 wt.%	γ -Al ₂ O ₃ , 2 mm spheres
TUD-2924	Cu-Cr-Al 5 × 4 mm pellets	prepared at TU of Dresden (Germany)
C-T	Cu-Cr-Mn	16 × 16 × 4 mm, Raschig rings
Pt-T	Pt, 0.05 wt.%	16 × 16 × 4 mm, Raschig rings

4. METHODS

Laboratory tests were carried out in a flow glass reactor in which 10 cm³ of catalyst was placed. Oxidation efficiency was investigated at the temperatures ranging from 200 to 500°C and the space velocities of 10,000 and 20,000 h⁻¹. The components of the reaction mixture were produced in separate dosers by evaporation and diluted with air to the concentrations desired. The laboratory catalysts (A), (B), (C), (E) and TUD-2924 were tested in the oxidation of a toluene, *n*-heptane and ethanol vapour mixture in air at the space velocity of 20,000 h⁻¹. The concentration of each component was ca. 1 mg/dm³. Laboratory tests were also carried out in the presence of the C-T catalyst in the oxidation of four-component vapour mixture (xylene, toluene, butanol, ethyl acetate) in air, simulating the composition of

the drier flue gases. The main polluting species released with the solvent vapours from the drier are xylene, toluene, butanol and minute quantities of ethyl acetate. Because of the varying concentrations of the pollutants emitted by the drier, the investigations were carried out for the concentration of 0.3 mg/dm^3 , which approached the real value, but was lower than that of the laboratory test reactions.

Large laboratory scale investigations were carried out in a mobile apparatus of a performance from 20 to $120 \text{ m}^3/\text{h}$, which made it possible to test up to 10 dm^3 catalyst portion of industrial grain size. In such an apparatus, the activity of the C-T catalyst was investigated in oxidation of the solvent vapours emitted by the chassis varnishing drier in the URSUS factory.

Control tests involved oxidation of real gases, released by the URSUS, in the presence of the following catalysts: C-T, Pt-T and two-layer bed (with $3/4$ of C-T and $1/4$ of Pt-T). Control test was carried out for the C-T catalyst at the space velocity of $15,000 \text{ h}^{-1}$. Tests involving real industrial gases were carried out at selected temperatures.

The concentrations of particular air pollutants were analyzed by means of gas chromatograph with FID detector in the column packed with Apiezon L on Chromosorb W. Conditions of analysis were determined in such a manner as to obtain a distinct peak for each pollutant. During the tests on real gases the samples for analysis were concentrated on activated carbon and extracted with CS_2 (Polish Standard PN-78/Z-04119).

5. RESULTS OF INVESTIGATIONS

5.1. ACTIVITY TESTS FOR LABORATORY CATALYSTS

The results were plotted in figures 1-3. They led to conclusion that the activities of the three oxide catalysts (A), (B) and (C) were similar and high in the oxidation of the test mixture. Only in the oxidation of ethanol the catalyst (A) was found to be more active than the remaining two; 90% oxidation efficiency in the presence of the (A) catalyst was achieved at 275°C , whereas the same efficiency in the presence of the (B) or (C) catalyst was observed at 315°C . The catalyst (A) yielded also smaller amounts of acetaldehyde, a product of incomplete ethanol combustion. 90% oxidation efficiency of toluene and *n*-heptane was achieved at 360°C and 390°C , respectively, in the presence of both, (A) or (C) catalysts. The catalyst (B) was found to be slightly less active.

The activity of the platinum catalyst (E) was noticeably higher than that of the oxide catalyst only in the oxidation of toluene (with a 90% efficiency at 300°C). Oxidation of *n*-heptane and ethanol was even more effective in the presence of oxide catalysts. TUD-2924 was found to be the least active catalyst under study.

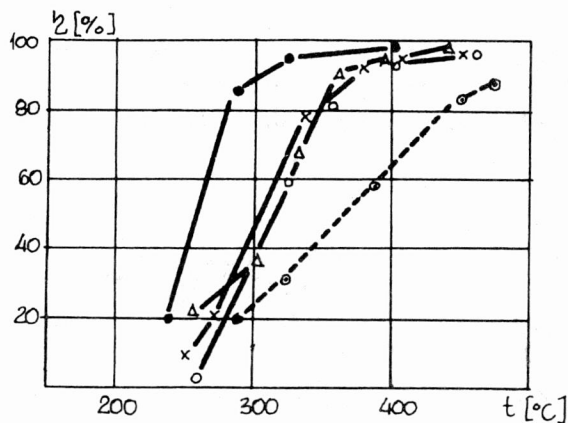


Fig. 1. Combustion efficiency of toluene in the mixture with *n*-heptane and ethanol in air in the presence of the following catalysts: × (A), ○ (B), Δ (C), • (E) and ◊ TUD-2924

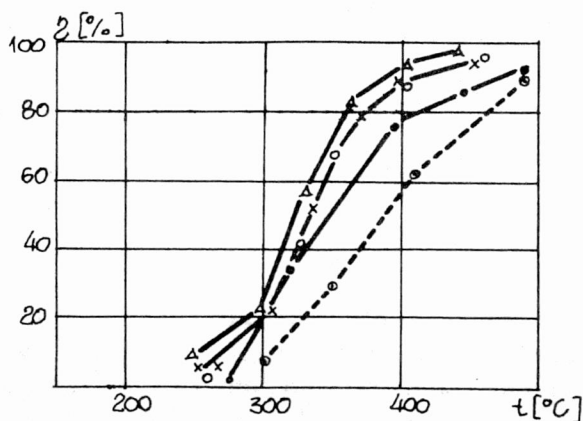


Fig. 2. Combustion efficiency of *n*-heptane in the mixture with toluene and ethanol in air in the presence of the following catalysts: × (A), ○ (B), Δ (C), • (E) and ◊ TUD-2924

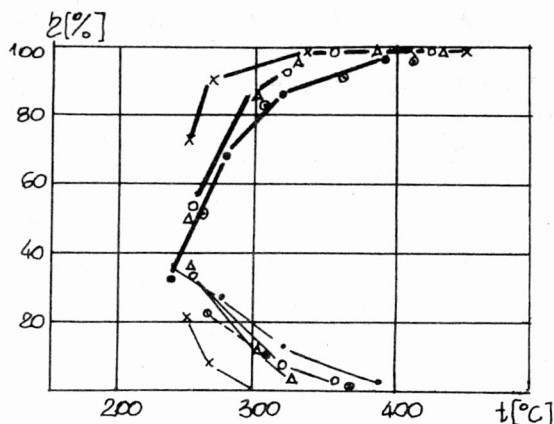


Fig. 3. Combustion efficiency of ethanol in the mixture with toluene and *n*-heptane in air (and the contribution of acetaldehyde in the off-gases) in the presence of the following catalysts: × (A), ○ (B), Δ (C), • (E) and ◊ TUD-2924

Considering the slight differences between the activities of oxide catalysts, the composition of the catalyst (C) (Cu–Cr–Mn oxides) was selected for further studies. An experimental industrial batch of the catalyst on γ - Al_2O_3 support in the form of Raschig rings (C–T) was produced for that purpose. In figure 4, the results of laboratory

tests on the oxidation of the reaction mixture simulating the emission from the chassis varnishing drier are presented. Of the polluting species under study, butanol was the most readily oxidizable (with a 90% oxidation efficiency at 300°C). The same efficiency for ethyl acetate, xylene and toluene was achieved at 330°C, 360°C and 420°C, respectively.

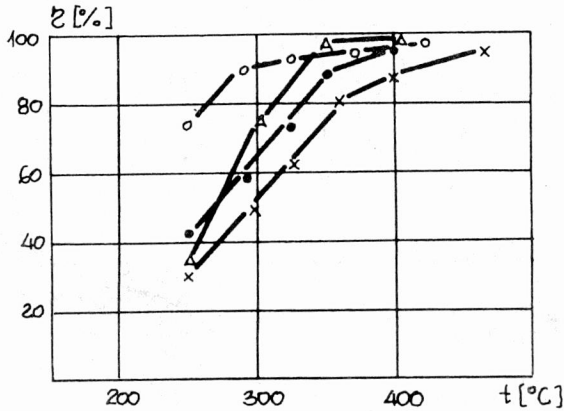


Fig. 4. Combustion efficiency of the mixture simulating the typical solvent vapour emission in the presence of C-T: • xylene, × toluene, o butanol, Δ ethyl acetate. Space velocity 10,000 h⁻¹

5.2. ACTIVITY TESTS FOR MOBILE APPARATUS

The results of solvent vapour oxidation in the presence of the C-T catalyst at the space velocity of 10,000 h⁻¹ are shown in figure 5. In that test, solvent vapours contained predominately toluene, xylene and butanol. Ethyl acetate evaporated very quickly. Under real conditions its presence can be identified only at the stage of varnishing; at the stage of drying some heavier components are emitted. Analysis of solvent vapours showed the presence of a number of species occurring at noticeably lower concentrations, often in trace amounts only. These compounds

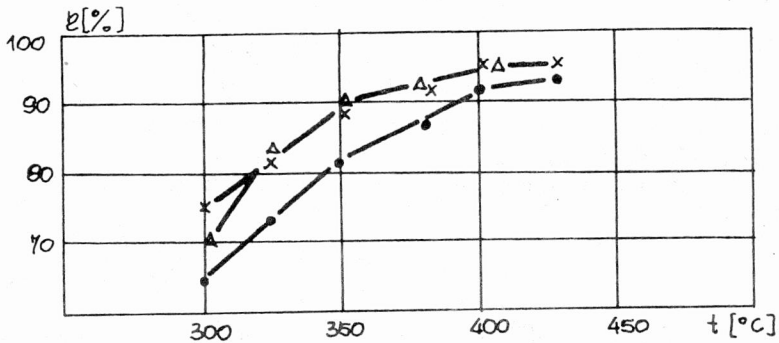


Fig. 5. Combustion efficiency of the solvent vapours in the presence of C-T catalyst in the mobile apparatus: Δ xylene, • toluene, × butanol. Space velocity 10,000 h⁻¹

were expressed in terms of decane, undecane and dodecane. They were completely oxidized at 300°C, the lowest investigated temperature. Butanol and xylene were oxidized with a 90% efficiency at 360°C, and toluene at 395°C.

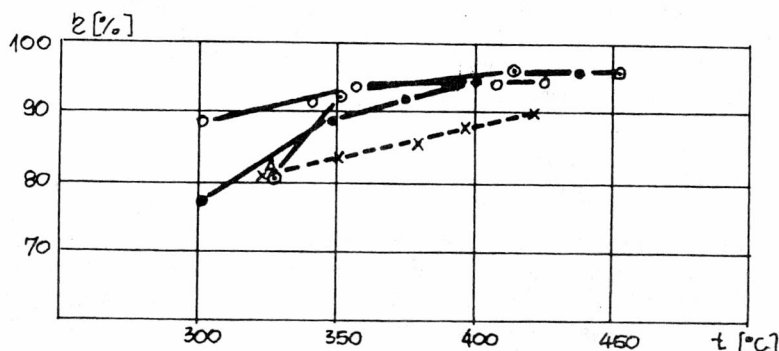


Fig. 6. Combustion efficiency of the solvent vapours emitted from the chassis drier in the URSUS factory (mobile apparatus):
 ○ Pt-T, ○ 3/4 C-T + 1/4 Pt-T, • C-T (10,000 h⁻¹), × C-T (15,000 h⁻¹)

Figure 6 shows the results of oxidation tests carried out on the real flue gases from chassis drier. The platinum catalyst Pt-T was found to be more active than the oxide catalyst. In the presence of Pt-T, a 90% oxidation efficiency for the sum of pollutants was obtained at 330°C. In the presence of the two-layer catalyst bed (3/4 of C-T and 1/4 of Pt-T) and the catalyst C-T, the temperatures required for 90% efficiency were by 16 deg and by 30 deg higher, respectively. Increase in the space velocity for the catalyst C-T up to 15,000 h⁻¹ is not recommendable, its activity had a tendency to decrease considerably.

Analysis of the results and economic consideration support the usefulness of the Cu-Cr-Mn oxide catalyst when applied to the oxidation of flue gases from chassis drier in the URSUS factory.

7. SUMMARIZING COMMENTS

The metal oxide catalysts, cheaper than the platinum ones, were found to have a high activity comparable to that of a platinum catalyst with reduced content of noble metal (to 0.05 wt.%).

Oxide catalysts can be successfully applied to the treatment of solvent vapour emissions, specifically those where oxyderivatives are dominant. When aromatic hydrocarbons are prevalent, it is advisable to make use of a two-layer catalyst bed (3/4 oxide catalyst and 1/4 platinum catalyst).

The space velocity of 10,000 h⁻¹ was found to be optimal for metal oxide catalyst. Increase in the space velocity can decrease considerably the oxidation efficiency.

REFERENCES

- [1] KARNAUKHOV N.A., DORONIN V.P., CYRULNIKOV P.G., *Khimicheskaya Promyshlennost*, 1 (1988), pp. 55–57.
- [2] BORESKOV G.K., *Catalysis – Science and Technology*, Akademie Verlag, Berlin, 3 (1983), pp. 40–137.
- [3] TOROPKINA T.N., VOLODINA L.I., *Lakokrasochnye Materialy i ikh Primenenie*, 5 (1988), pp. 64–67.
- [4] PRIGENT M., *Revue L'Institut Francais du Petrole*, Vol. 40, 3 (1985), pp. 393–409.
- [5] DECELLES R.E., *Industrial Heating*, 11 (1985), pp. 28–34.

KATALIZATORY Z TLENKÓW METALI W UTLENIANIU PAR ROZPUSZCZALNIKÓW

Organicznymi gazowymi zanieczyszczeniami powietrza są przede wszystkim pary rozpuszczalników organicznych, w skład których wchodzi węglowodory aromatyczne (głównie ksylen i toluen), alkohole, estry, ketony itp. Celem pracy było otrzymanie katalizatora tlenkowego, tańszego niż tradycyjne platynowe, służącego do unieszkodliwiania gazów odlotowych z suszarki podwozi traktorów w Zakładach URSUS. Wykonano trzy laboratoryjne katalizatory tlenkowe na bazie mieszanych tlenków metali (Cu–Cr–Co, Cu–Cr–V i Cu–Cr–Mn) naniesionych na $\gamma\text{-Al}_2\text{O}_3$ i przetestowano ich aktywność podczas spalania w powietrzu mieszaniny zawierającej toluen, *n*-heptan i etanol. Aktywność tych katalizatorów porównano z aktywnością katalizatora platynowego zawierającego 0.05 % wag. platyny. Na bazie Cu–Cr–Mn wykonano przemysłową partię katalizatora C–T na nośniku $\gamma\text{-Al}_2\text{O}_3$ w formie pierścieni Raschiga. Przetestowano go podczas spalania mieszaniny symulującej pary rozpuszczalnika emitowanego z suszarki podwozi oraz w przewoźnej instalacji – zarówno podczas spalania par rozpuszczalnika, jak i oczyszczania rzeczywistych gazów odlotowych emitowanych z suszarki. Wyniki badań posłużyły do zaprojektowania instalacji w cyklach przemianowych dla Zakładów URSUS z zastosowaniem katalizatora tlenkowego.

КАТАЛИЗАТОРЫ ИЗ ОКИСЛОВ МЕТАЛЛОВ
В ОКИСЛЕНИИ ПАРОВ РАСТВОРИТЕЛЕЙ

Органическими газовыми загрязнениями воздуха являются прежде всего пары органических растворителей, в состав которых входят ароматические углеводороды (главным образом ксилон и толуол), спирты, эфиры, кетоны и др. Целью настоящей работы была разработка окисного катализатора более дешевого, чем традиционные, платиновые, служащего для обезвреживания отходящих газов из сушилки шасси тракторов на заводе УРСУС. Выполнены три лабораторных окисных катализатора на базе смешиваемых окислов металлов (Cu–Cr–Co, Cu–Cr–V и Cu–Cr–Mn), нанесенных на $\gamma\text{-Al}_2\text{O}_3$ и протестирована их активность во время сжигания в воздухе смеси, содержащей толуол, *n*-гептан и этанол. Активность этих катализаторов сравнена с активностью платинового катализатора, содержащего 0.05 вес.% платины. На базе Cu–Cr–Mn выполнена промышленная партия катализатора C–T на носителе $\gamma\text{-Al}_2\text{O}_3$ в форме колец Рашига. Его протестировали во время сжигания смеси, имитирующей пары растворителя, эмитируемого из сушилки шасси, а также в транспортируемых установках – как во время сжигания паров растворителя, так и очистки реальных отходящих газов, эмитируемых из сушилки. Результаты исследований послужили для проектирования установок в переменных циклах для завода УРСУС с применением окисного катализатора.