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CATALYTIC COMBUSTION OF O-XYLENE AND M-CRESOL ON OXIDE TYPE CATALYSTS

The choice of catalysts for o-xylene and m-cresol combustion was based on the correlation of their activity with the oxygen bond energy in their surface layer. A number of contacts have been made, i.e. the pelleted ones (Co, Cu, Ni, Mn, Cr and Fe oxides) as well as those containing copper oxides deposited on γ -Al₂O₃ or on other kinds of carriers. The investigations were conducted on laboratory, pilot and industrial scales. The results obtained have confirmed the relationship between the activity of contacts and energy of oxygen binding in the oxide. The highest combustion efficiencies have been obtained on cobalt and copper catalysts which belong to the group of compounds characterized by the lowest heat of oxygen binding (below 35 kJ/mole).

1. INTRODUCTION

Some waste gases contain m-cresol and o-xylene in concentrations considerably exceeding these admissible ones [1]. An efficient method of elimination of these toxic compounds is their complete catalytic combustion. At present imported platinum and palladium catalysts are used for that purpose. Their high price and scarcity determine the growing interests in highly active and stable oxide type catalysts. The present paper contains results from laboratory, pilot-plant and industrial investigations carried out in this respect. The catalysts were chosen on the basis of the correlations [2], [3] between the activity of oxide type catalysts in complete oxidation and the oxygen bond energy in their surface layer.

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2. EXPERIMENTAL

The bulk oxide catalysts were prepared by thermal decomposition in air of the corresponding nitrates. They were additionally calcined in air in order to stabilize their specific surface areas. The latter were determined by the BET method using low-temperature adsorption of krypton and were found to be $0.53 \text{ m}^2/\text{g}$ for Co_3O_4 , $0.58 \text{ m}^2/\text{g}$ for CuO , $0.65 \text{ m}^2/\text{g}$ for Mn_2O_3 , $0.74 \text{ m}^2/\text{g}$ for Cr_2O_3 , $0.51 \text{ m}^2/\text{g}$ for Fe_2O_3 and $1.07 \text{ m}^2/\text{g}$ for NiO .

Several types of supported copper oxide catalysts were prepared by the method described in [4]. The carriers used were $\gamma\text{-Al}_2\text{O}_3$ (grain size 4–5 mm, catalysts MO-1), a mixture of $\gamma\text{-Al}_2\text{O}_3$ and caolin in a ratio of 1:9 (catalysts MO-2), a mixture of $\gamma\text{-Al}_2\text{O}_3$ and fireclay in a ratio of 1:9 (catalysts MO-3) and kieselguhr (catalysts MO-4).

Laboratory studies of the oxide catalyst activities were carried out in the flow apparatus [1] where a fraction of the corresponding catalysts (grain size 0.3–0.6 mm) was placed in the channels of a three-channel reactor (channel diameter 10 mm). The temperature of the catalysts layer was measured.

The m-cresol and o-xylene concentrations in the model reaction mixture were 0.5 vol %, i.e. higher than their amounts in waste gases. The air flow was saturated with these compounds in an evaporator at 500 K.

Large-scale experiments were carried out using a flow reactor OL-105/01 (made in Hungary). This apparatus made it possible to vary some process parameters (volume rate, temperature, composition of reaction mixture) over a wide range. The reaction mixture contained 0.20–0.30 vol % of o-xylene.

Industrial tests were made at 633–773 K, volume rates of $3\text{--}5 \times 10^4 \text{ h}^{-1}$ and a total amount of organic substances (cresol and xylene) corresponding to $10 \text{ mg}/\text{dm}^3$ of carbon.

The amount of CO_2 (the product of complete combustion) in the reaction mixture, after passing of latter through the catalysts layer, and the contents of cresol and xylene in the initial mixture were determined by the chromatographic methods, described in [5].

3. RESULTS AND DISCUSSION

The laboratory studies have shown that at temperatures below 593 K in the case of cresol and below 613 K in the case of xylene and a volume rate of $1\text{--}2.5 \times 10^4 \text{ h}^{-1}$, the degree of oxidation is relatively low and that at higher temperatures it sharply increases and that for the examined oxides almost complete catalytic combustion of m-cresol and o-xylene to CO_2 can be achieved (fig. 1).

It has been established that m-cresol oxidation proceeds at volume rates

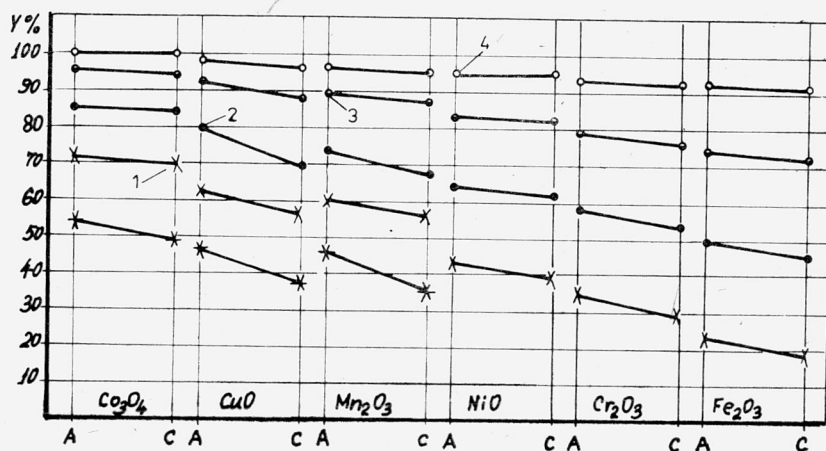


Fig. 1. Temperature dependence of the *m*-cresol-(A) and *o*-xylene (C) oxidation degrees
1 - 673 K, 2 - 773 K, 3 - 823 K, 4 - 873 K

Rys. 1. Zależność temperaturowa stopnia utlenienia *m*-krezolu (A) i *o*-ksylenu (C)
1 - 673 K, 2 - 773 K, 3 - 823 K, 4 - 873 K

ranging from 1×10^4 to $1.5 \times 10^4 \text{h}^{-1}$ and at a catalyst layer temperature of 773–823 K. Unlike in the case of *m*-cresol, the temperature range corresponding to a high (90–95 %) combustion degree of *o*-xylene over the same oxide catalysts is noticeably shifted to higher temperatures. At volume rates of 1×10^4 – $2 \times 10^4 \text{h}^{-1}$ this temperature ranges between 823–873 K.

As far as the catalysts activity of the oxides is concerned, it has been shown [7] that at a complete oxidation the oxide activity should correlate with the oxygen bond energy in the oxide surface layer.

In all reactions of this type the activities of simple and complex oxide catalysts vary in an analogous manner. In view of the above it can be assumed that these reactions have the same rate-determining step. This can be the interaction of the substances being oxidized with oxygen from the surface layer of the oxides resulting in the formation of oxidation products. This step associated with breaking of the catalyst–oxygen bond should depend on the bond energy of surface oxygen. This parameter should be included in the activation energy of the oxidation process, i.e.

$$E_a = E_0 + \beta q_s$$

where E_a is the activation energy of complete oxidation, q_s is the oxygen bond energy in the catalyst surface layer, and β is the proportionality coefficient.

As is evident from fig. 1, our data are in a good agreement with this assumption. All oxide catalysts show a high activity with respect to complete oxidation of *m*-cresol and *o*-xylene, the higher activity being observed with Co_3O_4 and

CuO. Although a more accurate evaluation requires proceeding in the kinetic region, our data show that very efficient catalysts can be obtained using Co_3O_4 and **CuO**.

Supported catalysts are of special interest, since with the increasing strength of catalysts and their thermal stability the content of active phase decreases, whereas the specific surface area increases. Moreover, the hydraulic resistance of the catalyst layer decreases. Because of the lower price of copper as compared to that of cobalt, supported copper oxide catalysts were studied in detail. The complete oxidation of *o*-xylene was assumed as a model reaction, since previous investigations have shown that this substance is relatively resistant to oxidation.

It has been found that almost complete combustion (90–98%) of *o*-xylene can be achieved over catalyst $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ (MO-1) at temperature of 713–773 K (fig. 2) and that MO-2 activity is completely satisfactory for purification of some industrial waste gases. The temperature range corresponding to 85–90% conversion was within 723–773 K. The X-ray analysis showed that in both catalysts the copper was in form of **CuO**.

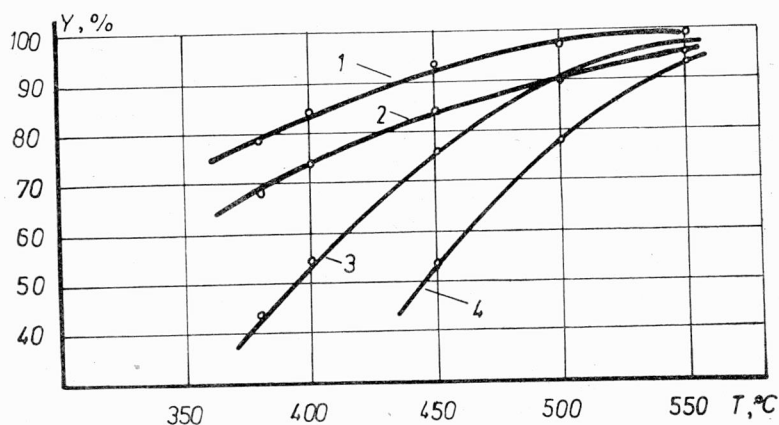


Fig. 2. Temperature dependence of the degree of *o*-xylene oxidation

1 – MO-1, 2 – MO-2, 3 – MO-3, 4 – MO-4

Rys. 2. Zależność temperaturowa utlenienia *o*-ksylenu

1 – MO-1, 2 – MO-2, 3 – MO-3, 4 – MO-4

Complete combustion of the same substance with the catalyst MO-4 (**CuO**-kieselguhr) was relatively lower when compared with these results. At temperature of 823 K a 72–73% conversion was attained. The X-ray fluorescence analysis made evident that the copper amount (calculated as copper oxide) was the lowest (6%). Moreover, the specific surface area of MO-4 catalyst was the smallest one. It should be mentioned that after the post-test, X-ray analysis of the catalyst confirmed the presence of **CuO**, **Cu₂O** and **Cu**.

Both catalysts MO-1 and MO-2 showed a constant activity for 100 h.

Table
Combustion degree of the toxic components (o-xylene and m-cresol) of the industrial waste gases

Stopień spalania toksycznych składników (o-ksylen i m-krezol) gazów przemysłowych

| Type of catalyst and its layer thickness | Temperature of gas entering catalyst layer K | Temperature of gas passing through catalyst layer K | Linear rate of gas m/s | Catalytic combustion degree % |
|--|---|--|---------------------------|----------------------------------|
| CuO/ γ -Al ₂ O ₃ 65 mm | 703 | 883 | 1.05 | 88-90 |
| CuO/ γ -Al ₂ O ₃ 30 mm | 683 | 833 | 1.05 | 84-88 |
| | 703 | 873 | | |
| CuO/ γ -Al ₂ O ₃ 25 mm | 613 | 793 | 1.28 | 88 |
| | 613 | 763 | 1.28 | 87 |
| | 633 | 763 | 1.00 | 79-80 |

A more rapid stabilization of the process by changing some of the parameters was observed with the kaolin — supported MO-2 catalyst. The hydraulic resistance of this catalyst was twice as low as the resistance of the layer of MO-1. On the other hand, MO-2 had a lower mechanical strength.

On the basis of these results, supported copper oxide catalyst MO-1 was used under industrial conditions. Tests carried out during 5-12 months confirmed the results of the laboratory studies. The table contains the data on combustion degree of the toxic components in the waste gas. It should be noted that under the same conditions the supported palladium catalyst ensure 70-75% combustion.

It should also be mentioned that the regeneration of MO-1 catalyst after a year's operation almost entirely restores its efficiency.

The results of the present investigation show that Co₃O₄ and CuO have high and stable activities towards complete oxidation of m-cresol and o-xylene. The obtained supported copper oxide catalysts showed high catalytic activity that can ensure almost complete combustion of the toxic compounds in some industrial waste gases.

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KATALITYCZNE SPALANIE O-KSYLENU I M-KREZOLU NA KATALIZATORACH TLENKOWYCH

Doboru katalizatorów do spalania o-ksylenu i m-krezolu dokonano na podstawie korelacji ich aktywności z energią wiązania tlenu na powierzchni tlenków metali. Wykonano szereg kontaktów tabletkowanych (tlenki Co, Cu, Ni, Mn, Cr i Fe) oraz kontaktów zawierających tlenki miedzi naniesione na γ -Al₂O₃ i inne typy nośników. Badania prowadzono w trzech skalach: laboratoryjnej, wielkolaboratoryjnej i przemysłowej. Wyniki potwierdziły zależność między aktywnością kontaktów a energią wiązania tlenu w tlenku. Największe skuteczności uzyskano na katalizatorach kobaltowych i miedziowych, które mieszczą się w grupie związków o najniższej wartości ciepła wiązania tlenu (poniżej 35 kJ/mol).

DIE KATALYTISCHE VERBRENNUNG VON O-XYLLOL UND M-KRESOL AUF OXYDARTIGEN KATALYSATOREN

Die Auswahl von Katalysatoren zur Verbrennung von o-Xylol und m-Kresol stützte sich auf der Korrelation deren Aktivität und der Bindungsenergie des Sauerstoffs auf der Oberfläche von Metalloxyden. Angefertigt wurden einige Kontakte (Oxyde von Co, Cu, Ni, Mn, Cr und Fe) in Tablettenform sowie weitere Kontakte die Cu-Oxyde beinhalteten und auf γ -Al₂O₃ und auf andere Träger aufgetragen wurden. Die Untersuchungen wurden in drei Maßstäben (Labor- und Großlabormaßstab, technische Skala) durchgeführt. Die Ergebnisse bestätigten die Beziehung zwischen der Kontaktaktivität und der Bindungsenergie des Sauerstoffs mit dem Oxyd. Maximale Ausbeuten sind auf Kobalt- und Kupferkatalysatoren erreicht worden. Diese gehören in die Gruppe mit der niedrigsten Sauerstoff-Abbindewärme (weniger als 35 kJ/Mol).

KATALITICHESKOЕ СЖИГАНИЕ О-КСИЛОЛА И М-КРЕЗОЛА НА ОКИСНЫХ КАТАЛИЗАТОРАХ

Подбор катализаторов для сжигания о-ксилола и м-крезола основан на корреляции их активности с энергией связи кислорода на поверхности окислов металлов. Произведён ряд таблеточных контактов (окиси Co, Cu, Ni, Mn, Cr и Fe), а также контактов, содержащих окиси меди, нанесённые на γ -Al₂O₃ и другие типы носителей. Исследования проводились в трёх масштабах: лабораторном, крупнолабораторном и промышленном. Результаты подтвердили зависимость между активностью контактов и энергией связи кислорода в окисле. Наивысшие эффективности были получены на кобальтовых и медных катализаторах, которые содержатся в группе соединений с наименьшим значением теплоты связи кислорода (ниже 35 кДж/моль).