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CATALYTIC OXIDATION OF NAPHTHALENE IN TWO-COMPONENT MIXTURES

Polycyclic aromatic hydrocarbons (PAHs) are known as the compounds particularly hazardous to living organisms. The major portion of airborne PAHs in urban areas comes from motor exhaust gases. The aim of the paper presented was to test the catalytic combustion of the simplest PAH compound, i.e. naphthalene, in two-component reaction mixtures with ethanol or benzene over three noble metal catalysts. Two of them, M-6 and M-9, were prepared on the monolithic metallic support, while the third – KOR-4 – was prepared on the ceramic cordierite support. All catalysts under study showed very high activity in the process of naphthalene oxidation in the mixtures; at the temperature of 200 °C, oxidation of naphthalene was complete, irrespective of the catalyst used. Variations in the catalyst activities manifested themselves in the oxidation of either ethanol in the mixture, or naphthalene when it was combusted alone. The highest activity showed KOR-4, and among the monolithic catalysts – M-9.

1. INTRODUCTION

Because of their cancerogenic and mutagenic properties, polycyclic aromatic hydrocarbons (PAHs) are known as the compounds particularly hazardous to living organisms. But this adverse effect differs from one species to another. PAHs with a smaller number of rings – from naphthalene to pyrene – are classified as less dangerous [1]. According to SOLARSKI [2], even these PAHs are concancerogenic when occur with benzo(a)pyrene which is regarded as the most active among them. Combustion of different organic materials, including fossil fuels, is the most important source of PAHs emission. The volume of their emission depends strongly on the conditions in the post-combustion zone.

However, a major portion of airborne PAHs in urban areas comes from motor exhaust gases [3]–[6]. Their concentration in exhaust gases is considerably affected by the content of aromatic hydrocarbons in the fuel, and is particularly high when

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leadfree gasoline is used in automobiles without catalytic convertors [7]. PAHs are also found to cumulate in lubricant oil, thus increasing the air pollution following combustion by oil extra consumption. Diesel engines emit also considerable amounts of soot particles which consist mostly of elementary carbon and adsorbed organic compounds, including PAHs. Summary mass of organic carbon amounts to 50% of the total particulate mass emissions in automobile exhaust.

Another important source of PAHs emission is wood combustion or pyrolysis. Because of the chemical structure of wood (consisting predominantly of polysaccharides and lignins), the main product of wood burning or pyrolysis includes oxyderivative compounds. Wood smoke contains nearly 220 different organic compounds in the form of vapours or aerosol particles and is traditionally used in the process of meat or fish smoking. The organic composition of particulate matter can influence PAHs decay. The substituted phenols (metoxyphenols) abundant in wood smoke react rapidly with PAHs. In contrast, carbon black in particulates from engine exhaust appears to have a stabilizing effect [8]. PAHs associated with soot particle decay when exposed to sunlight. This process is responsible for significant decay of PAHs, particularly under some atmospheric conditions (solar radiation intensity, temperature, atmospheric concentration of water, ozone and NO_x). In opposite, PAHs are generally stable at night [1].

Our research team has been working on the preparation and manufacture of catalysts and their application to the combustion of organic air pollutants from industrial flue gases and car emissions for many years now. It was interesting for us to test the catalytic combustion of typical PAHs over our catalysts. For this study we have selected naphthalene, the simplest compound belonging to this group, with a boiling temperature of 218 °C. In industrial waste gases, car emissions or smoke-house flue gases, PAHs are emitted in the mixtures with a variety of volatile organic compounds (VOCs)– light aromatic and aliphatic hydrocarbons and their oxy- or nitrogen derivatives. Their concentration in exhaust gases is much higher than that of PAHs. It has routinely been assumed that catalytic oxidation of organic pollutants in the mixtures runs at a different reaction rate than when they are oxidized separately. It is difficult to predict this “mixture effect” because of the varying composition of the mixture and the varying type of the catalyst (chemical composition and quantity of active ingredients) [9], [10]. Therefore it seemed interesting to test the catalytic activity not only when naphthalene was oxidized separately, but also when it was combusted in two-component mixtures – with ethanol or benzene.

2. MATERIALS AND METHODS

For the purpose of the study, three noble-metal catalysts were prepared. Similar catalysts were made use of for the control of motor exhaust gases. Two of them, M-6 and M-9, had monolithic metal support made of heat-resisting steel with additives.

The other one, KOR-4, rested on a cordierite support in the form of the Raschig rings crushed to a diameter of about 2.5 mm. The same cordierite material is used for the formation of monolithic elements. Both the supports had a very small specific surface. To make it possible to incorporate sufficient mass of active ingredients, the support surface was provided with a layer of alumina of high specific surface as a washcoat, firmly attached to the substrate. The γ -Al₂O₃ layer accounted for 1.5% of the support mass. As active ingredients the catalyst KOR-4 contained platinum, palladium and rhodium amounting to 0.07 wt.%, 0.04 wt.% and 0.01 wt.%, respectively. The catalyst was used in the experiments in 10 cm³ portions. The parameters of the monolithic catalysts, M-6 and M-9, are listed in the table.

Table

Description of monolithic catalysts

Parameter	M-6	M-9
Cell geometry	triangle	triangle
Cell density, 1/cm ²	270	430
Cell size, mm	0.9	0.7
Wall thickness, mm	0.05	0.05
Open front area, %	82	78
Active ingredient, wt%	Pt, 0.015; Rh, 0.024	Pt, 0.04; Rh, 0.04
Monolith dimensions, mm	$\varnothing = 21; h = 70$	$\varnothing = 21; h = 70$

The experiments were run in a glass reactor of "tube-in-tube" type, heated electrically, at temperatures ranging from 150 to 370 °C. Gas inlet temperature and catalyst temperature were measured. When naphthalene was oxidized separately its vapours were generated directly in a heated batcher, by evaporation with air, and its concentration ranged from 0.1 to 0.3 g/m³. When naphthalene was combusted in the mixtures, it was dissolved in ethanol or benzene and evaporated from the mixture. In this test, naphthalene vapour concentration was kept between 0.02 to 0.08 g/m³, whereas that of the second component approached 15 g/m³. Although the investigations involved two space velocities, 10000 and 20000 h⁻¹, mixture combustion tests were run at 10000 h⁻¹ only. At the space velocity of 20000 h⁻¹, the oxidation of ethanol or benzene, which occurred at very high concentrations of these compounds, brought about a rapid increase in catalyst temperature, up to 450 °C and more.

The concentrations of the oxidized compounds were determined by gas chromatography, using a Hewlett-Packard 5980 Series II GC with a HP-1 capillary column, FID and computer-aided data processing unit. The conditions of analysis were programmed so as to detect products of incomplete oxidation, primarily aldehydes and light hydrocarbons (C₁-C₄).

3. RESULTS AND DISCUSSION

The results are plotted in figures 1–3. They show conversion efficiencies of naphthalene and ethanol oxidation in mixture versus temperature (with the contribution of aldehydes and products of incomplete oxidation of ethanol) at the space velocity of $10\,000\text{ h}^{-1}$. Conversion of naphthalene in the mixture is compared with its conversion when combusted separately at two space velocities $10\,000$ and $20\,000\text{ h}^{-1}$.

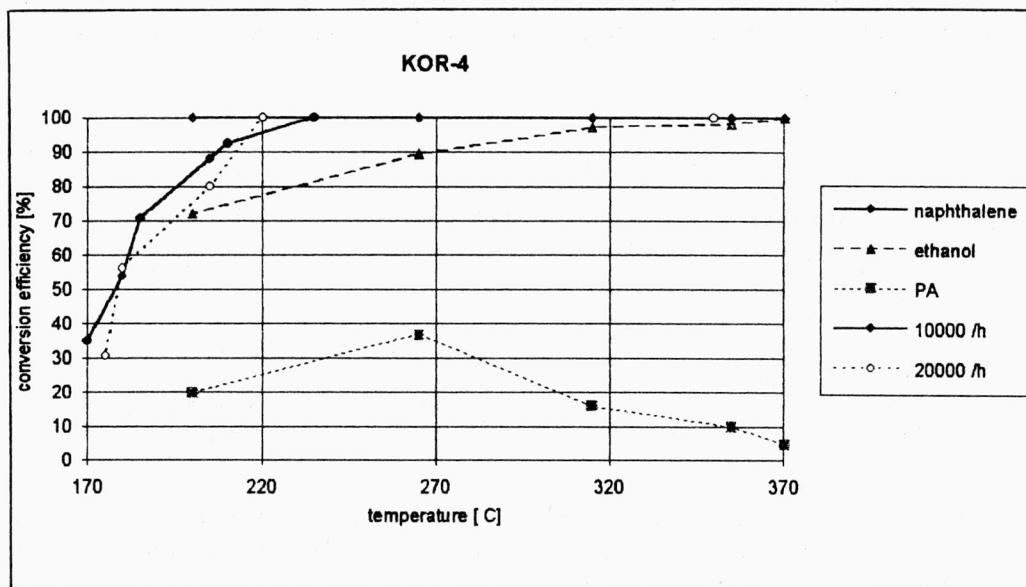


Fig. 1. Conversion of ethanol, with contribution of propionaldehyde (PA), and naphthalene, when combusted in mixture (at space velocity of $10\,000\text{ h}^{-1}$), and alone (at space velocities of $10\,000$ and $20\,000\text{ h}^{-1}$) over KOR-4

In the mixture with ethanol, as soon as the temperature of the inlet gases reached 200 °C , naphthalene was completely combusted over all the catalysts tested. When naphthalene was combusted separately, KOR-4 (catalyst on a cordierite support) showed the highest activity. Over that catalyst, irrespective of the space velocity applied, 90% oxidation was achieved at about $210\text{--}220\text{ °C}$. At temperatures above 240 °C naphthalene was completely oxidized. Over the more active monolithic catalyst M-9, 90% oxidation of naphthalene was achieved at 220 °C and 230 °C , whereas complete oxidation was reached at 250 °C and 280 °C for space velocities of $10\,000$ and $20\,000\text{ h}^{-1}$, respectively. In the presence of M-6, irrespective of the space velocity applied, 90% and complete oxidation of naphthalene was achieved at temperatures of 270 °C and 320 °C , respectively. Over all the catalysts tested, oxidation of naphthalene ran to the end products, CO_2 and H_2O ; no products of incomplete oxidation (light hydrocarbons or aldehydes) were detected.

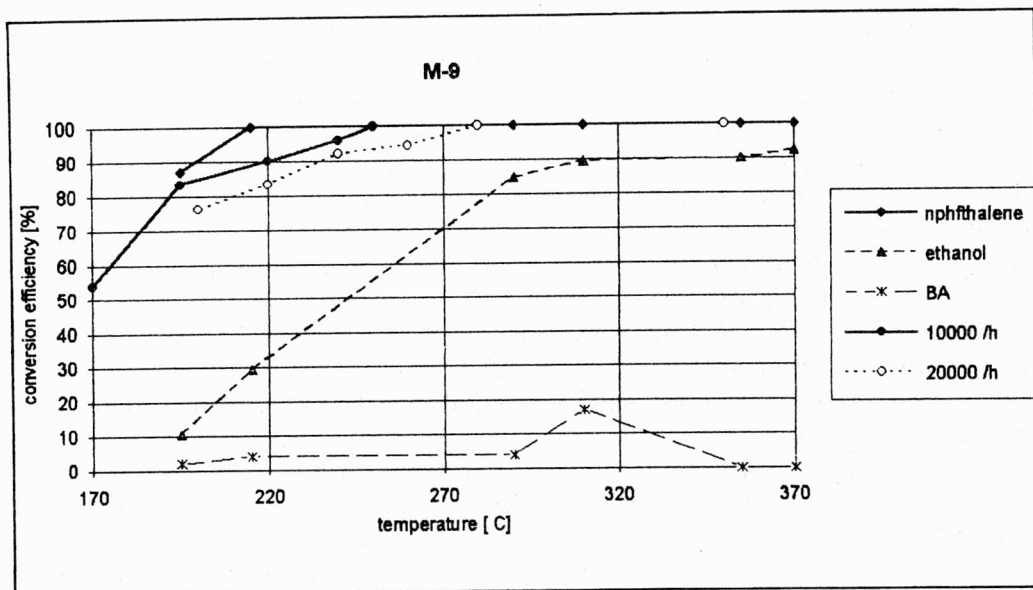


Fig. 2. Conversion of ethanol, with contribution of butyraldehyde (BA), and naphthalene, when combusted in mixture (at space velocity of 10000 h^{-1}) and alone (at space velocities of 10000 and 20000 h^{-1}) over M-9

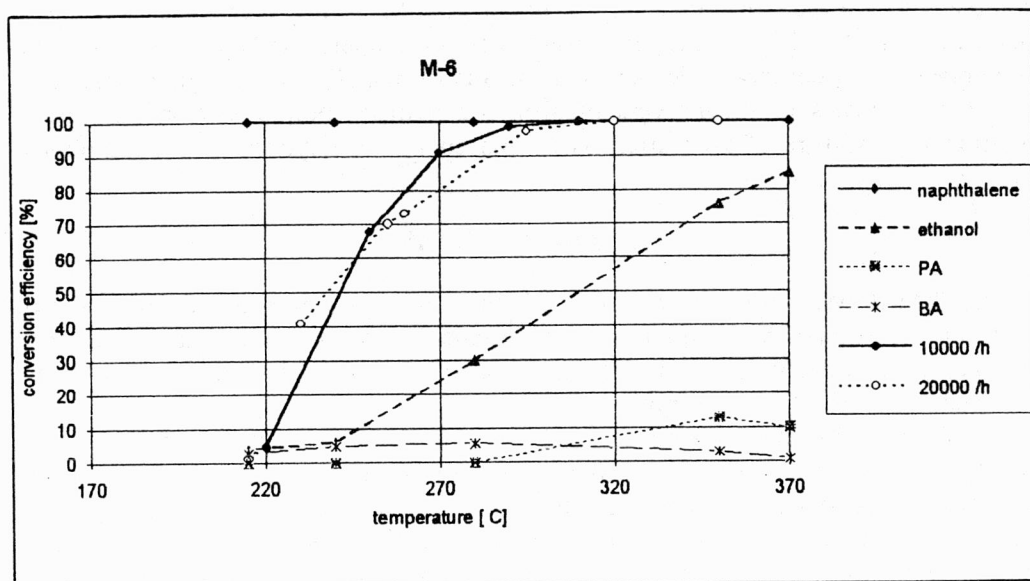


Fig. 3. Conversion of ethanol, with contribution of propionaldehyde (PA) and butyraldehyde (BA), and naphthalene, when combusted in mixture (at space velocity of 10000 h^{-1}) and alone (at space velocities of 10000 and 20000 h^{-1}) over M-6

The distinction between catalyst activities was also presented in the reaction of oxidation of ethanol in the mixture with naphthalene. In the presence of the most active catalyst, KOR-4, at the temperature of 265 °C the efficiency of ethanol conversion approached 80%, but nearly 38% of the inlet ethanol was converted to propionaldehyde, the product of incomplete oxidation. Even at 350 °C, when oxidation of ethanol reached 98%, propionaldehyde contribution to the flue gases was still as high as 12%, to drop below 1% only at 450 °C. Over M-9, 90% ethanol conversion was achieved at 300 °C. In this case, butyraldehyde was found in the flue gases as a product of incomplete oxidation. Its contribution accounted for about 4% at the temperature of 215 °C and reached a maximum of about 17.5% at 310 °C. At temperatures higher than 340 °C no aldehydes were detected in the flue gases. Catalyst M-6 showed the lowest activity also in the reaction of ethanol oxidation. At the highest temperature tested, e.g., at 370 °C, the reaction efficiency reached only 85%. Over that catalyst both aldehydes, i.e., propionaldehyde and butyraldehyde, were found as the products of incomplete ethanol oxidation. However, their contribution never exceeded 13% and 7%, respectively.

Regardless of the catalyst used, small amounts of light hydrocarbons and caproic aldehyde were measured in the flue gases, but their contribution to the inlet ethanol concentration never exceeded 0.5%.

When naphthalene was oxidized in mixture with benzene, the temperature of catalysts rose rapidly to about 350 °C. At this temperature, naphthalene was completely oxidized over all catalysts under investigations. This increase in temperature was set at 170 °C, e.g., the lowest inlet gas temperature, and observed in the presence of each contact under study. It results from well known higher activity of platinum catalysts in the process of aromatic hydrocarbon oxidation and lower ignition temperature of aromatics, as compared to the oxyderivative compounds.

4. CONCLUSIONS

1. The catalysts tested showed a very high activity in the process of oxidation of naphthalene in mixtures with ethanol or benzene. Practically, when the temperature of inlet gases approached 200 °C, the oxidation of naphthalene was complete, irrespective of the contact applied.

2. Variations in the activities of catalysts manifested themselves in the oxidation of ethanol in the mixture or naphthalene when combusted alone. The highest activity was that of KOR-4; complete oxidation of naphthalene was achieved at about 220 °C, regardless of the space velocity applied. In the presence of the more active monolithic catalyst M-9 and at the higher space velocity ($20\,000\text{ h}^{-1}$), 90% oxidation and complete oxidation of naphthalene were reached at 230 °C and 280 °C, respectively. In the process of ethanol oxidation, the activities of the catalysts decreased in the same sequence (from KOR-4 to M-6).

3. Ethanol oxidation ran with the formation of intermediate products. In the presence of KOR-4 and M-9, propionaldehyde and butyraldehyde were formed, respectively. Over M-6, both aldehydes were produced, but their concentrations were found to be lower. Irrespective of the catalyst applied, light hydrocarbons (C_1-C_4) and caproic aldehyde were detected in the flue gases, but their contribution never exceeded 0.5%.

4. Oxidation of naphthalene ran only to the end products, CO_2 and H_2O ; regardless of the catalyst tested, neither light hydrocarbons nor aldehydes were detected in the flue gases.

5. In the presence of benzene in the mixture with naphthalene, the reaction temperature rose very rapidly up to about 350 °C; at this temperature naphthalene was completely combusted over all catalysts tested.

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KATALITYCZNE UTLENIANIE NAFTALENU W MIESZANINACH DWUSKŁADNIKOWYCH

Wielopierścieniowe węglowodory aromatyczne (WWA) stanowią poważne zagrożenie dla organizmów żywych. Głównym źródłem ich emisji w atmosferze miast jest motoryzacja. Celem przedstawionej pracy było przebadanie aktywności trzech katalizatorów na bazie metali szlachetnych w spalaniu najprostszego z grupy WWA związku – naftalenu – w mieszaninach reakcyjnych z etanolem lub benzenem. Dwa z wykonanych do tych badań katalizatorów (M-6 i M-9) przygotowano na metalicznym nośniku monolitycznym, jeden – na nośniku ceramicznym, kordierytowym (KOR-4). Wszystkie przebadane katalizatory wykazały bardzo wysoką aktywność w tym procesie, praktycznie na wszystkich już

w temperaturze 200 °C naftalen w mieszaninach spalał się całkowicie. Różnice w aktywności katalizatorów ujawniły się natomiast w procesie spalania etanolu w mieszaninie oraz w spalaniu naftalenu, gdy spalany był sam. Najwyższą aktywność wykazał wówczas katalizator KOR-4, a spośród kontaktów monolitycznych – M-9.