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Thermo-photocatalytic oxidation of benzene under visible light over nitrogen-doped titania grafted with Cu and Pt

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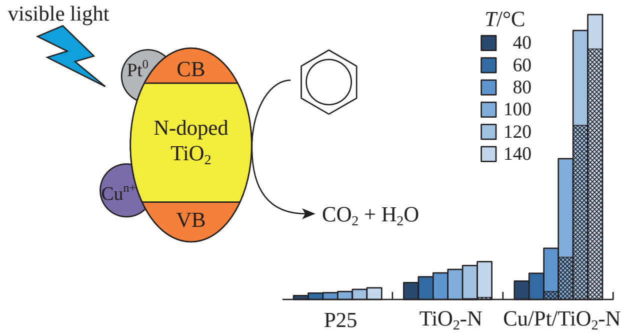
Nitrogen-doped titania (TiO_2-N) was synthesized and tested, both in unmodified form and with grafted Cu and Pt particles, in the reaction of photocatalytic oxidation of benzene under visible light irradiation at temperatures of 40, 100 and 140 °C. The results obtained indicate additional thermal activation of the reaction over Pt-containing samples with the maximum difference between the total and thermal activities at 100–120 °C. As modifiers, both platinum and copper separately improve the photoactivity of TiO_2-N, but when used together, their effects do not add up, and the photocatalyst behaves like a Pt-modified sample.



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Due to the active growth of resource consumption, emissions and waste are increasing every year and the environmental situation on the planet worsens. This forces researchers around the world to pay attention to the search for both alternative energy sources and ways to reduce emissions into the environment. These challenges are helping to change the development of the chemical industry and move it towards the use of efficient and environmentally friendly technologies. In this regard, a promising direction is photocatalysis, which makes it possible to carry out useful chemical transformations using the energy of light, and in the future, sunlight. Technologies based on photocatalytic transformations are also a promising direction in the development of methods for cleaning the environment. In particular, photocatalytic oxidation of vapors of volatile organic compounds is already used as a method of air purification from trace impurities.[1–6]

Nitrogen-doped titania (TiO_2-N) is a visible light-active photocatalyst effective for the oxidation of organic micropollutants.[7–9] Modification is also an effective way to expand the action spectrum of titanium dioxide and increase its activity in the visible range of spectrum.[10–13] In particular, when titanium dioxide is modified with copper, light absorption increases and photoactivity appears in the oxidation of vapors of organic compounds upon irradiation up to 530 nm.[14,15] It is known that the performance of titanium-based photocatalysts can be improved by modifying their surface by grafting platinum nanoparticles.[16–18] Moreover, a slight increase in the temperature of the photooxidation process can bring some advantages in the case of platinum due to the synergistic effect between photonic and thermal excitation of the titania structure.[16,19] Therefore, the question arises of the possibility of combining such modifications for a complete oxidation process.

Oxidation is often studied with model compounds that are relatively easy to oxidize. However, real pollutants differs from model ones, which are sufficient. Benzene is one of the most widespread pollutants. The main factors of its danger to health are the low threshold limit value and the carcinogenic effect on a living organism. It is benzene that is a typical air pollutant, which is targeted during testing of various air purification systems from molecular micro-impurities. Model mixtures of benzene, toluene, ethylbenzene and xylene were named BTEX after the initial letters of the compounds included in these mixtures.[18,20–22]

All photocatalytic experiments in this study were carried out in a continuous-flow set-up at a volume flow rate of 0.10 ± 0.02 dm^3 min^{-1}, 20% relative humidity of pre-cleaned inlet air at 25 °C and an inlet benzene concentration of about 10 μmol dm^{-3}. Other details of the experiment can be found elsewhere.[14,19,23] Figure 1 shows the obtained action spectra of the test TiO_2-N, synthesized according to a previously published method,[8,9,24] in the reactions of photocatalytic oxidation of acetone and benzene at temperatures of 40, 100 and 140 °C. The data allows us to state that the use of an aromatic oxidizable substrate under the considered conditions does not lead to additional photosensitization, as can be the case with a liquid-phase oxidation process.[25] The temperature points were chosen based on the literature data on the effect of temperature on the activity of the pristine titania under UV irradiation.[16] Namely, 40 °C is the baseline level of photoactivity in the low-temperature region. 100 °C is the point of maximum photoactivity of pristine titania. The value of 140 °C in the high-temperature region was chosen as relatively safe for a photoreactor, at which a noticeable decrease in activity is observed due to fundamental limitations associated with the adsorption of reagents.

X-ray photoelectron spectra (XPS) were measured[26] (see Online Supplementary Materials), and the obtained XPS data (Figure 2) illustrate that in a series of synthesized samples, the deposited platinum is in the metallic Pt^0 state.[26] In accordance

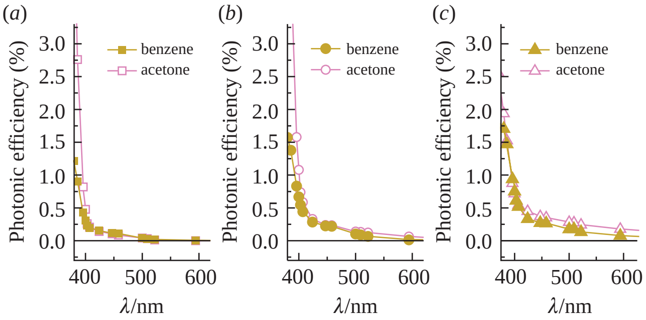

Figure 1 Action spectra of TiO_2-N during photocatalytic oxidation of acetone and benzene vapors at temperatures of (*a*) 40, (*b*) 100 and (*c*) 140 °C.

with the calculated Auger parameters, the Cu-grafted samples show that copper is in a Cu^{1+} state.[27]

Modification of TiO_2-N (with a measured specific surface area of about 94 $m^2 g^{-1}$) to obtain samples of Cu/TiO_2-N (94 $m^2 g^{-1}$), Pt/TiO_2-N (107 $m^2 g^{-1}$) and Cu/Pt/TiO_2-N (105 $m^2 g^{-1}$) was carried out in accordance with techniques known for commercial samples of titanium dioxide.[14–17,28,29] The only exception was the Cu/Pt/TiO_2-N sample, in which, according to the XPS data, the amount of copper deposited was 0.39% instead of 0.72% for both Cu/Pt/TiO_2-N and Cu/TiO_2-N samples with a calculated value of 1%. This indicates that copper deposition on a sample with platinum already deposited is limited by the surface's ability to accept copper ions. Meanwhile, in both cases, copper is in the Cu^+ state.

Since visible irradiation, in particular blue light (440 nm, 270 μE min^{-1}), does not directly excite the structure of titanium dioxide and is not absorbed in a thin near-surface layer of the sample, the entire volume of the photocatalyst is involved in the photooxidation process. As a result, the observed benzene vapor oxidation rates may exceed the activity of these samples under UV irradiation with the same photon flux.

The results obtained allow us to speak about the ability of the synthesized TiO_2-N to work both under visible radiation conditions and to efficiently oxidize not only volatile hydrocarbons, but also aromatic compounds, for example, benzene, too. The observed activity values always exceed those of commercial photoactive P25 titania. It is noteworthy that at a low process temperature (40 °C), the most active sample is Cu/TiO_2-N, whose activity under blue light is 7 times higher than that of P25, the most well-known standard for comparing photoactivity in various catalytic processes with visible light irradiation (Figure 3).

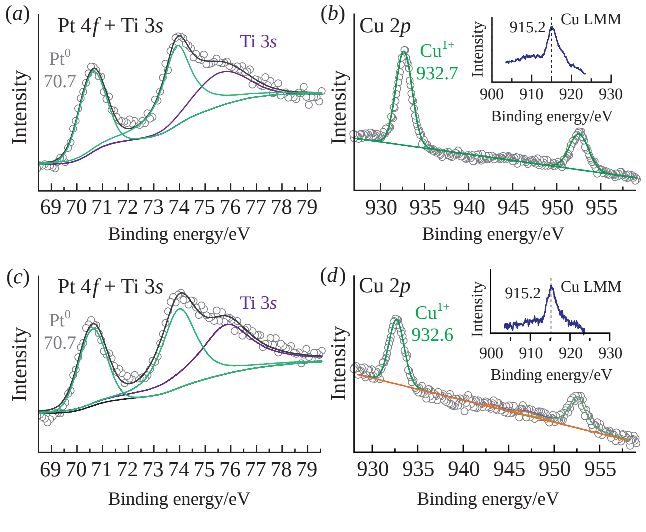

Figure 2 XPS spectra of (*a*) Pt/TiO_2-N, (*b*) Cu/TiO_2-N and (*c*),(*d*) Cu/Pt/TiO_2-N samples in the regions of (*a*),(*c*) Pt and (*b*),(*d*) Cu detection.

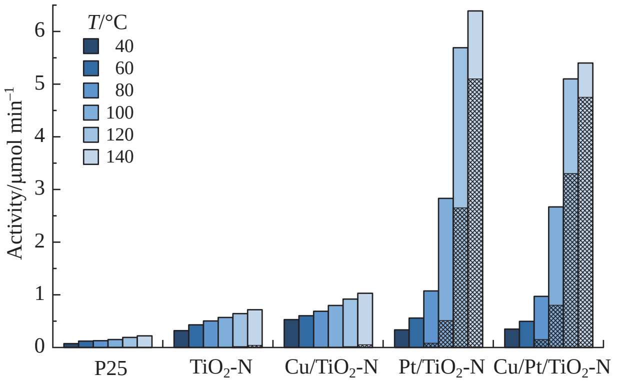

Figure 3 Thermo-photoactivity of TiO_2-based samples in the test reaction of benzene vapor oxidation under LED irradiation with maximum irradiance at 440 nm (270 μE min^{-1}). The shaded area corresponds to activity without exposure to light.

The most impressive results were obtained in the oxidation of benzene vapor over platinum-modified TiO_2-N under blue light irradiation. When comparing the activity of Cu/Pt/TiO_2-N and Pt/TiO_2-N samples with Cu/TiO_2-N and initial TiO_2-N, the ability of platinum nanoparticles to prevent deactivation of the photocatalyst by the intermediate products of benzene oxidation clearly manifests itself. Moreover, with an increase in temperature, it is the platinum nanoparticles that become responsible for the increase in the rate of the process: at a temperature of 140 °C, in both platinized samples, the activity under the influence of light practically does not exceed that without exposure to light at the same temperature.

The performance of Pt-modified titania photocatalysts against gaseous benzene is often attributed to effective charge separation, which slows down their recombination.[16,30] Since benzene ring opening is considered a key step in the aromatic VOC destruction reaction,[31] such charge separation and electron accumulation on platinum particles can facilitate the multielectron benzene ring opening step and accelerate the overall photocatalytic cycle. In short, in the case of the Cu modification, the enhancement of activity may be due to the creation of a charge transfer channel between titanium dioxide and copper compounds on its surface. The researchers propose a charge-transfer mechanism between titania and the Cu_xO cluster.[32] This leads to the reduction of Cu^{2+} to Cu^+, which is re-oxidized due to multielectron interaction with oxygen molecules, and holes in the valence band of titanium dioxide, in turn, oxidize the organic substrate. Thus, the reversibility of forms of copper provides a faster oxidation cycle.[33]

Separately, it should be noted that during the oxidation of benzene vapor, we did not observe the temperature dependence of activity with a local maximum at a temperature of 80–100 °C. This largely contradicts the classical concepts,[34,35] according to which the adsorption process is the limiting step when the temperature rises. During the oxidation of benzene vapor, the adsorption of the initial oxidized substance is very small and occurs on photoexcited titanium dioxide. Therefore, an increase in the temperature of the photocatalyst has virtually no effect on limiting the process (in contrast to the process of deactivation by surface intermediates) and, thus, the temperature rise increases the rate of all observed processes, and the overall rate of the complete oxidation process follows a general increasing trend.

In conclusion, we found that the use of benzene vapor instead of acetone vapor does not affect the edge of the action spectrum of titania-based photocatalysts in the photocatalytic oxidation process at any temperature in the range of 40–140 °C. The photoactivity of photocatalysts based on TiO_2-N in the test reaction of benzene oxidation enhances with increasing temperature, in contrast to the well-known activity–temperature dependence with a local maximum at 80 °C. This difference is associated with a different type of excitation of the photocatalyst and the use of benzene, whose adsorption does not become the rate-limiting step at any temperature. Thermal activation of the photocatalytic oxidation process over titania-based catalysts can affect the actual activity and increases the activity of Pt-modified samples due to the ability of Pt nanoparticles to exhibit synergy between thermal and photonic excitation. However, this effect diminishes as the temperature rises above 120 °C, and in general, the thermo-photoactivity is about the same as for a purely thermal oxidation process. Thus, we can conclude that the temperature range of 100–120 °C is the most suitable for achieving the highest rates of photoprocesses using doped and modified titania photocatalysts.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.06.018.

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