# Carbon Supported Cu and TiO$_2$ Catalysts Applied for Ozone Decomposition

Katya Milenova, Penko Nikolov, Irina Stambolova, Plamen Nikolov, Vladimir Blaskov

***Abstract***—In this article a comparison was made between Cu and TiO$_2$ supported catalysts on activated carbon for ozone decomposition reaction. The activated carbon support in the case of TiO$_2$/AC sample was prepared by physicochemical pyrolysis and for Cu/AC samples the supports are chemically modified carbons. The prepared catalysts were synthesized by impregnation method. The samples were annealed in two different regimes- in air and under vacuum. To examine adsorption efficiency of the samples BET method was used. All investigated catalysts supported on chemically modified carbons have higher specific surface area compared to the specific surface area of TiO$_2$ supported catalysts, varying in the range 590÷620 m$^2$/g. The method of synthesis of the precursors had influenced catalytic activity.

***Keywords***—Activated carbon, adsorption, copper, ozone decomposition, TiO$_2$.

## I. INTRODUCTION

OZONE is gas with blue color in high concentrations and with a characteristic strong odor. In the office it is generated by photocopiers, laser printers, and other office equipment using corona discharge processes [1]. In addition, residual gases from processing units such as for sterilization and deodorization or for wastewater treatment often contain ozone of high concentrations [2]. Ozone entering in aircraft cabins is a main contaminant and can be harmful to passengers' health [3]. Residual ozone near the surface of the Earth can cause ecological problems, because of its extreme toxicity [4]. Ozone in water is also toxic to aquatic life at concentrations greater than 0.05 mg/L [5], the harmful concentrations to humans is greater than 0.1 mg/L [6]. Because of all that it is important to downgrade the concentration of ozone. It has a high oxidizing ability and a tendency to decompose to molecular oxygen even at ambient temperatures [7]. The gas phase ozone can be decomposed catalytically. Catalytic ozone decomposition at room temperature is advantageous as compared to the thermal decomposition because of significant energy saving [8]. The ozone decomposition efficiencies of Al$_2$O$_3$, SiO$_2$, TiO$_2$, Fe$_2$O$_3$ and ZnO [9] and bone charcoal (composed of CaO, P$_2$O$_5$, MgO, SiO$_2$, Na$_2$O, K$_2$O and MnO) have been studied [10]. Carbons also have been shown to be active catalysts in the ozone decomposition and ozonation of organic pollutants [11]-[15]. Catalytic ozonation of organic compounds has been carried out on different transitional metals (Ni, Cu, Mn, Co, Fe) supported on activated carbon [15]-[17]. Photocatalytic degradation of gaseous ozone using activated carbon supported titanium dioxide was investigated in [18].

Activated carbon acted by destructing ozone by adsorptive decomposition, yielding oxygen [11]. Advantage of activated carbon is its low cost [19]. Suitable textural properties, including a large surface area and proper pore size distribution, are also required for activated carbons to show high efficiency in a particular application [20], [21]. It is important to found appropriate method for preparation of efficient carbon based catalysts.

Activated carbon can be obtained from different lignocellulosic raw materials like wood, coconut, turf, mineral coal, bone, wool, cotton, synthetic polymers and other [22]-[24]. Activation of carbon passes in two stage process: carbonization and activation, and can be achieved physically or chemically [25]. In the case of chemical activation method, the dehydrating effect of used active agents inhibits the formation of tar helping to enhance the yield of porous carbon and decreasing the activation temperature and activation time compared to the physical activation method [26], [27].

Activated carbons were prepared from precursor marigold straw [28] and reedy grass leaves [29] using H$_3$PO$_4$ as an activator in air to create an abundant pore structure. Activated carbon also has been obtained, by physical activation with steam, from a Moroccan agricultural by-product (Argan shells) [30].

The aim of this work is to compare properties of Cu/AC and TiO$_2$/AC powders as catalysts for ozone decomposition reaction at ambient conditions. Two different series of chemically modified carbon supported copper catalysts were synthesized and were annealed in different conditions: air or vacuum. TiO$_2$/activated carbon materials were prepared by physicochemical pyrolysis method. The porosity and their surface area were examined.

## II. EXPERIMENTAL

### A. Preparation of Catalyst Containing TiO$_2$

The activated carbon was obtained by physicochemical pyrolysis and activation by continuous blowing with exhausted gas 5.5x10$^{-5}$ m$^3$/s and addition of water vapour up to 680$^o$C. Gas-stream activation was carried out in a rotating tube reactor located in a tubular cylinder oven [31]. Beech

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sawdust was chosen as initial material for the synthesis. The sawdust possessed iodine adsorption capacity 423 mg/g and specific surface area S $_{BET}$ =275 m$^2$/g. The gas stream was composed by nitrogen, carbon oxide and carbon dioxide. The heating rate was in the range 10÷40$^o$C/min to provide a uniform heating of the specimen.

The desired final temperature was maintained for 30 min in order to homogenize the temperature field and to accomplish the chemical processes.

The obtained activated carbon was impregnated with 0,4 M ethanol solution of TiCl$_4$. The sample was dried at 100$^o$C for 2 h and then heated at 830$^o$C.

### B. Preparation of Catalyst Containing Copper

The investigated samples were prepared by impregnation of active carbon with various solutions and later were thermally treated. Two series of samples were prepared: Cu/AC synthesized in vacuum (Cu/AC vacuum) and Cu/AC synthesized in air (Cu/AC air), which are carbon promoted by a supported active copper phase and AC vacuum and AC air consisting of modified carbon without active phase. Samples Cu/AC vacuum and Cu/AC air were impregnated with aqueous ammonia solution of malachite buffered with ammonium carbonate. The concentration of copper ions in the impregnating solution was 0.22 mol/l for both Cu/AC vacuum and Cu/AC air. Samples AC vacuum and AC air were referent samples impregnated with aqueous solution of ammonium carbonate containing no copper ions. After impregnation the samples were calcined at 150$^o$C in two different regimes: in air (AC air and Cu/AC air) and under vacuum of 10$^{-3}$ Torr (AC vacuum and Cu/AC vacuum).

### C. Sample Characterization

XRD analysis was performed by means of Philips PW 1050 apparatus. Cu K$_\alpha$ radiation was applied. The step used for phase determination was 0,05$^o$.

The specific surface areas of the samples were determined by the BET method using low-temperature nitrogen adsorption. Pore size distribution for the mesopores was obtained from the adsorption curve of the isotherm, using the procedure developed by [32].

The copper content was determined by atomic absorption technique with Pye Unicam SP-90B.

### D. Catalytic test

The catalytic activity of the sample in the reaction of ozone decomposition was investigated in a plug flow reactor system permitting isothermal operation. The reactor was made of glass and had an inner diameter of 4.1 mm. The catalyst particle sizes were 0.25÷0.6 mm. The volume rate was 120 000 h$^{-1}$. Ozone was synthesized in a flow of oxygen (99.7%) and dried with silica gel using an ozone generator with silent discharge and coaxial electrodes. The inlet concentration of ozone varied from 13 to 15 g/m$^3$ (0.25÷0.3 mol/m$^3$). Ozone concentration was measured by an Ozomat GM (Anseros, Germany) ozone analyser with a resolution of ± 0.1 g/m$^3$. The conversion of ozone was evaluated using:

$$Conversion[\%] = \left[\frac{Co - C}{Co}\right] x100$$

where Co is initial concentration of ozone and C is every next concentration in the reaction pathway.

### III. RESULTS AND DISCUSSION

According to XRD analysis sample TiO$_2$/AC consist of three phases: mainly anatase, some Ti$_2$O$_3$ and traces of Ti$_4$O$_7$. XRD analysis of the copper-containing samples shows that they are amorphous which is due to the low copper content in them (not shown). Table I shows the specific surface areas as obtained by the BET method. The specific surface areas exhibit a relatively small change with both supported copper and modified samples. In comparison copper-containing samples shows sizably higher surface area to that with TiO$_2$.

TABLE I
BET SURFACE AREA ON THE CARBON SUPPORTED CU AND TiO$_2$ CATALYSTS

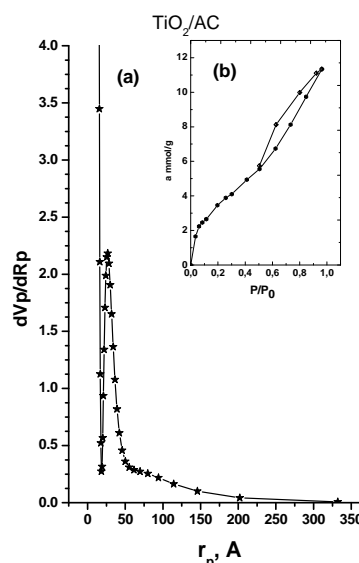| Sample | A$_{BET}$,m$^2$/g |
|---|---|
| TiO$_2$/AC | 480 |
| AC air | 614 |
| AC vacuum | 620 |
| Cu/AC vacuum | 567 |
| Cu/AC air | 590 |



Fig. 1 (a) Pore size distribution on TiO$_2$/activated carbon; (b) Nitrogen adsorption isotherm on TiO$_2$/AC

The active copper content established with AAS is less than 1wt %. The adsorption isotherms of all samples obtained by nitrogen adsorption at 77 K are shown in Figs. 1(b), 2 and 4. They are type IV according to the BDDT classification [32]. The hysteresis loop of the copper-containing samples is of H-3 type according to the IUPAC classification (type B according to de Boer), which is typical for active carbons due to the flat parallel pores in them. The mesopore size distribution as obtained from the adsorption branch of the isotherm by the Orr-Dalla Valle method [33]. The hysteresis loop - Fig. 1(b)

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for TiO$_2$/AC sample is H-3 type. Fig. 1 (a) shows the pore-size distributions of the sample. The sample obtained mesopores structure. The curve has a maximum at about 30 nm. The distribution of carbon supported Cu catalysts (Figs. 3 and 5) indicates that copper promotion leads to no change in mesopore size distribution. It was suggested that the catalytic decomposition of ozone was preceded by an adsorption step on the activated carbon surface [12]. The catalytic tests for the ozone decomposition of the as obtained samples were carried out. The degree of ozone decomposition is expressed as – ln (C/Co) (where Co is initial concentration of ozone and C is every next concentration in the reaction pathway) on Figs. 6-8.

The rate constant k is accepted as a measure of the catalytic activity. Degradation rate constants were calculated using the equation $-\ln(C/C_0) = kt$ on the basis of the slope of linear dependence and the values are presented in Table II. The activity of the investigated samples for ozone decomposition is as follows: Cu/AC air (4.9 x10$^{-2}$ min$^{-1}$) > Cu/AC vacuum (4.8 x10$^{-2}$ min$^{-1}$) > AC vacuum (3.9 x10$^{-2}$ min$^{-1}$) > AC air (3.2 x10$^{-2}$ min$^{-1}$) > TiO$_2$/AC (2.6 x10$^{-2}$ min$^{-1}$).

TABLE II
DEGRADATION RATE CONSTANT ON THE CARBON SUPPORTED CU AND TIO$_2$ CATALYSTS

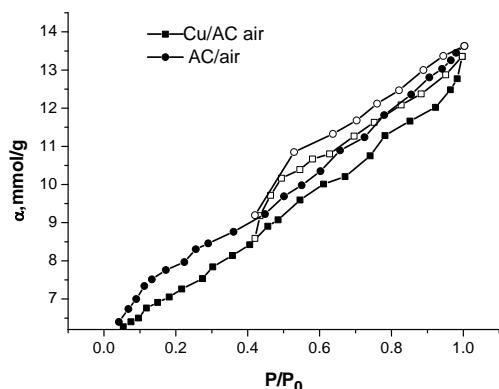| Sample | Rate constant, min$^{-1}$ |
|---|---|
| TiO$_2$/AC | 2.6x10$^{-2}$ |
| AC air | 3.2 x10$^{-2}$ |
| AC vacuum | 3.9x10$^{-2}$ |
| Cu/AC vacuum | 4.8x10$^{-2}$ |
| Cu/AC air | 4.9x10$^{-2}$ |



Fig. 2 Nitrogen adsorption isotherm on AC air and Cu/AC air samples

The TiO$_2$/AC shows (Fig. 9) very low catalytic activity probably due to the relatively high presence of rutile phase, the fact is in correlation with [34]. Although the fact that TiO$_2$ is widely used photocatalyst, it is not reliable for catalytic decomposition of ozone. Fig. 10 presents conversion of ozone for the samples, synthesized in air: AC air and Cu/AC air. There are small differences between their activities. Fig. 11 shows conversion of ozone for vacuum synthesized samples. Catalytic efficiency is better for Cu/AC vacuum sample in comparison to AC vacuum one. Deactivation was observed for all of the investigated samples, with two possible reasons

suspected – saturation of adsorption capacity of active carbon and temporary blockage of the active sites on the surface by O$_3^-$ ions.
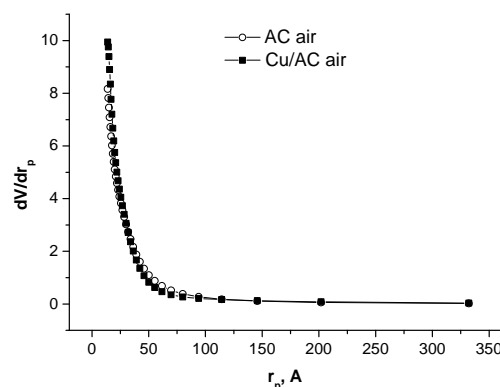


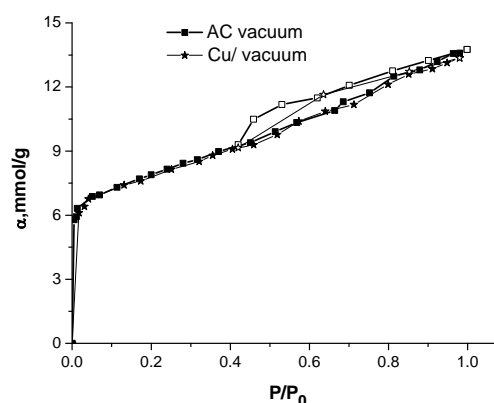Fig. 3 Pore size distribution on AC air and Cu/AC air samples



Fig 4 Nitrogen adsorption isotherm on AC vacuum and Cu/AC vacuum samples
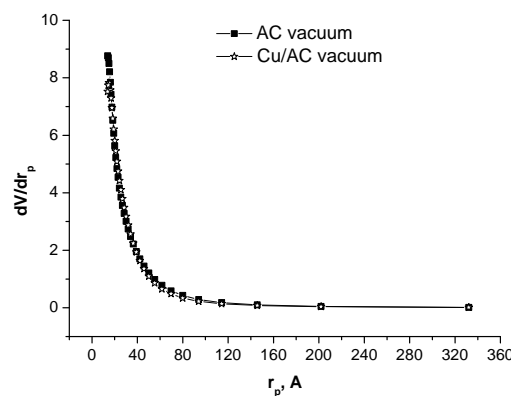


Fig. 5 Pore size distribution on AC vacuum and Cu/AC vacuum samples

Fig. 12 shows catalytic activity after 10 minutes work of the investigated catalysts. The catalytic activity of Cu/AC under vacuum is the highest – 74%, followed by Cu/AC air – 72%. Within 10 minutes the carriers exhibit a lower degree of conversion – 60% for AC air and 39% for AC vacuum. TiO$_2$/AC exhibits only 12% for 10 minutes work. Most likely, the method of preparation of the support contributes to a better

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catalytic performance. It is important to note that samples AC air and AC vacuum are chemically modified carbons. This probably leads to their higher activity in comparison with the TiO$_2$/AC with respect to the reaction of ozone decomposition. Activated carbon with identical textural properties but produced by different methods may show very different adsorption capacities because of differences in their surface chemistry [35]. As it is shown the activity of the Cu-containing catalyst is greater than the other tested catalyst. In [36], the addition of copper to the Ag/γ-Al$_2$O$_3$ catalyst greatly enhanced its catalytic activity, while the addition of cerium or lanthanum inhibited catalytic activity. The ozone removal ratio by the AC decreased fast, while supported MnO$x$ catalysts show better performance, due to the initial adsorption on the catalyst [15].

Carbon materials accelerate the decomposition of ozone and are consensual that both textural and surface chemical properties influence that decomposition, but still there are doubts on the mechanism of decomposition. Two possible pathways can explain the decomposition of O$_3$ in the presence of carbon materials. The first one assumes that activated carbon acts as an initiator of the decomposition of ozone, with possible intermediate formation of H$_2$O$_2$ [37]. Another possibility is formation of several intermediates, which cannot be mineralized by direct ozone oxidation [12].
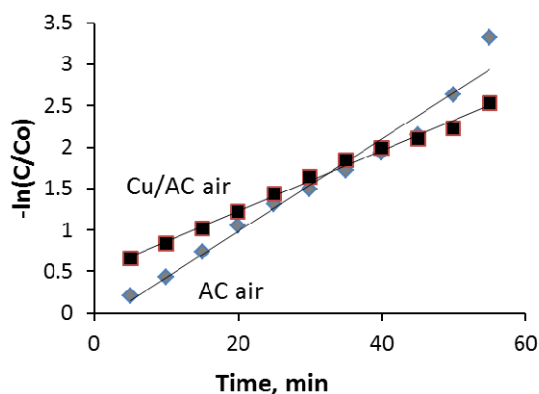


Fig. 6 Degree of conversion of the ozone into oxygen
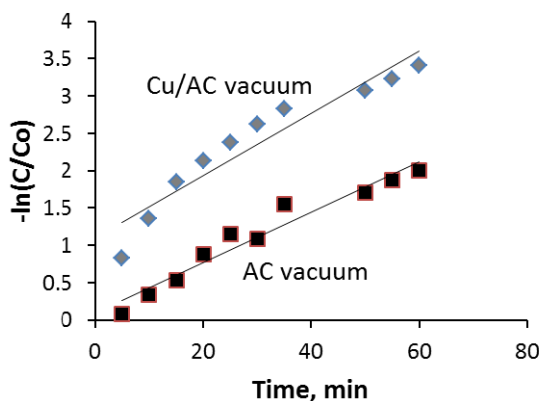– ln(C/Co) on AC air and Cu/AC air samples



Fig. 7 Degree of conversion of the ozone into oxygen
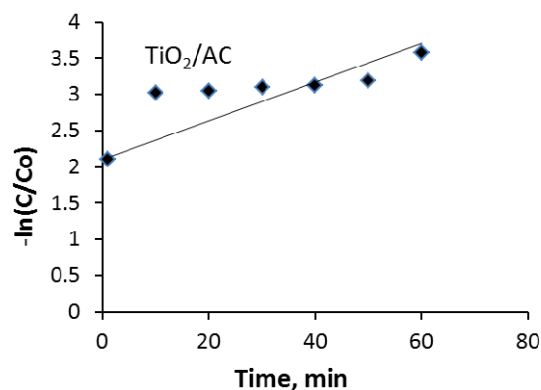– ln(C/Co) on AC vacuum and Cu/AC vacuum samples



Fig. 8 Degree of conversion of the ozone into oxygen
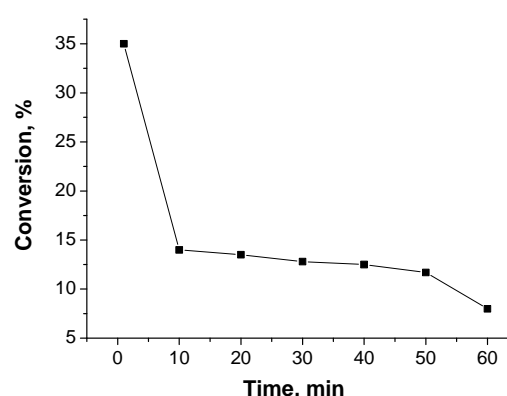– ln(C/Co) on TiO$_2$/AC sample



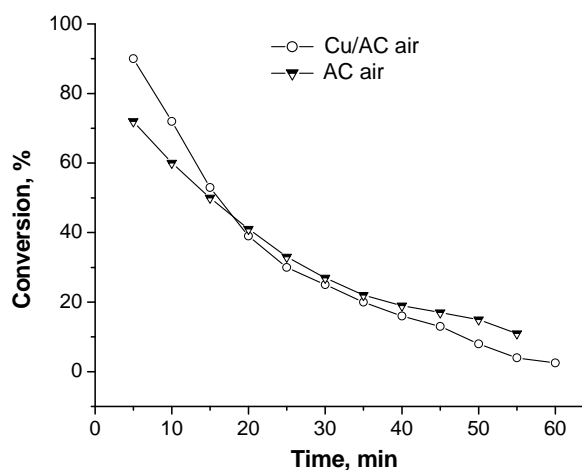Fig. 9 Conversion of ozone on TiO$_2$/AC at ambient condition



Fig. 10 Conversion of ozone on air, AC air and Cu/AC air samples

IV. CONCLUSION

The catalytic activity for the decomposition reaction of ozone was examined on copper and titanium dioxide catalysts prepared by impregnation of activated carbon of the metal salts of the corresponding precursors. TiO$_2$/AC was obtained by physicochemical method; Cu/AC samples calcined in air or vacuum were subject to chemical activation of the carbon support. The samples with chemically activated carbon exhibit higher catalytic activity, the impregnation of an active Cu

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phase increases further catalytic activity. The best performing sample is Cu/AC vacuum which reaches 96% conversion of ozone at the beginning of the process, its rate constant is 4.8 $\times 10^{-2}$ min$^{-1}$. The widely used as photocatalyst TiO$_2$/AC shows very low activity toward ozone decomposition and is not practically applicable for that purpose.
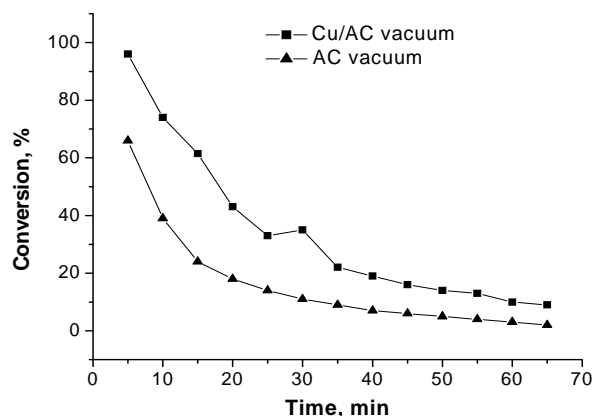


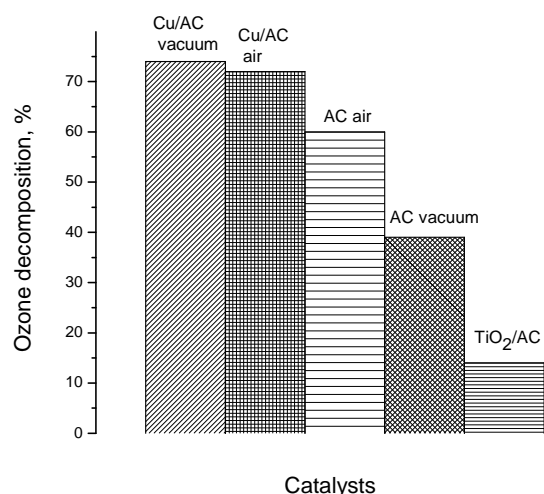Fig. 11 Conversion of ozone on AC vacuum, Cu/AC vacuum



Fig. 12 Comparison of ozone decomposition after 10 minutes work on all investigated catalysts

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