

SELECTIVE CATALYTIC REDUCTION OF NO WITH AMMONIA AT LOW TEMPERATURE OVER CU-PROMOTED AND N-MODIFIED ACTIVATED CARBON

Marwa Saad*, Anna Białas, Przemysław Grzywacz, Cezary Czosnek,
Bogdan Samojeden, Monika Motak

AGH University of Science and Technology, Faculty of Energy and Fuels,
al. Mickiewicza 30, 30-059 Kraków, Poland

Catalytic properties of activated carbons oxidized, treated with N-compounds, and promoted with copper were studied in selective catalytic reduction NO_x by ammonia (NH₃-SCR). The modification of the catalysts consisted of a series of steps (pre-oxidation of activated carbon, impregnation with urea, impregnation with copper). The physicochemical properties of the obtained samples were determined using X-ray diffraction, FT-IR spectroscopy, and low-temperature N₂ sorption. The modification with copper improved the catalytic activity and stability of the catalysts. All the functionalized carbon doped with copper reached more than 90% of NO conversion and CO₂ did not exceed 240 ppm at 220 °C. The sample doped with 5 wt.% Cu had the maximum NO conversion of 98% at 300 °C. The maximum N₂O concentration detected for the same sample was only 55 ppm, which confirmed its selectivity.

Keywords: SCR, activated carbon, copper oxides, DeNO_x, urea

1. INTRODUCTION

Selective catalytic reduction of NO_x with NH₃ is one of the most effective ways to eliminate NO_x emissions from stationary sources (Directive 2010/75/EU; Motak et al., 2015). Some effective catalysts, such as V₂O₅–WO₃/TiO₂, have been developed and successfully commercialized due to their high catalytic activities. However, some problems arose involving commercialized catalysts. In coal-fired power plants, the SCR reactor is installed upstream of the electrostatic precipitator and flue-gas desulfurization scrubber, so the catalyst suffers from deactivation due to dust accumulation and chemical poisoning from e.g. sulfur. To solve these problems, the SCR reactor should be set downstream of the electrostatic precipitator and flue gas desulfurization scrubber. However, the temperature of flue gas must be between 200 and 275 °C. For commercial SCR catalysts, such as V₂O₅–WO₃/TiO₂ catalyst, the optimum operating temperature is usually approximately 350 to 400 °C (Kiełtyka et al., 2015). Therefore, there is a need to develop low-temperature SCR catalysts, so the catalyst bed can be located at the end of the installation, where the flue gas has already been cleaned of fly ash and most of sulfur dioxide.

In recent years, carbonaceous materials have been recognized for the multi-functional roles that they perform as adsorbents, catalysts and support of metal catalysts by Samojeden et al. (2008). Examples of

* Corresponding author, e-mail: marwa@agh.edu.pl

Reprinted with permission in an extended form from the EYEC Monograph accompanying 8th European Young Engineers Conference.

the superiority of carbon-based materials over other supports include high surface area and well-developed pore structures. An additional advantage is that activated carbons (ACs) are also relatively cheap materials. Hence, AC becomes a good candidate for use as a support for catalysts in the low-temperature NH_3 -SCR reaction.

Modification of carbonaceous material with N-compounds is beneficial for enhancing NO_x sorption and increasing SCR activity according to the findings by Grzybek et al. (2008), who demonstrated that carbon modified with urea showed much higher activity than the untreated one. Also, Matzner and Boehm compared CO_2 formation of N-modified activated carbons with untreated carbon and proved that N-modification was essential for stability (Matzner and Boehm, 1998).

Nowicki et al. studied the effect of ammoxidation and the introduction of nitrogen groups into activated carbons (Nowicki et al., 2011; Pietrzak et al., 2006). Nowicki et al. (2011) showed that the introduction of new nitrogen functional groups into the structure of the activated carbon improved their sorption capacity towards NO_2 .

Many types of active metals supported on AC were proposed as DeNO_x catalysts. The most frequently studied active materials were oxides/hydroxides of vanadium (Huang et al., 2008), manganese (Grzybek et al., 1998), iron (Samojeden and Grzybek, 2016) and copper catalysts (Chunang et al., 2010; Singoredjo et al., 1990). Cu-modified AC (Cu/AC) catalyst exhibited high activity compared to unpromoted carbon and titania supported catalyst at low-temperature range of 150–250 °C. That was proved previously by Singoredjo et al. (1990). Moreover, Cu/AC showed higher activity compared to Fe/AC, according to Teng et al. (2001). Although the results of numerous studies on NO reduction on carbon-based catalysts have been reported, relatively few studies have been concerned with the triple modification technique: oxidation, modification with N-groups and active metal doping. Triple modification was carried out only by Grzybek et al. (2008); Samojeden and Grzybek (2016); Ziemiański et al. (2017) who studied N-modified AC promoted with Mn (Mn/N-AC) and Fe (Fe/N-AC) as SCR catalysts. Their results showed improvement in the activity and selectivity of the studied catalysts. Therefore, further investigations are needed to evaluate the possibility of applying triple modification using other metals.

This work focuses on activity, selectivity, and stability of functionalized carbon. It studies the impact of Cu in the NH_3 -SCR process over activated carbon and discusses the effect of adding different percentage of copper as metal oxide on SCR activity and the specific types of surface species of copper which are responsible for the enhancement of catalytic activity and the stability of the catalyst.

2. CATALYST PREPARATION

Commercial activated carbon (Gryfskand, Hajnówka, Poland) was oxidized by concentrated 10 M HNO_3 at 90 °C for 2 hours, followed by filtration, washing with distilled water (to neutral pH) and drying at 110 °C for 24 hours. The introduction of N groups was carried out by the incipient wetness impregnation with the urea solution (5 wt.%). The aim of urea treatment is not only physical deposition of urea but of the majority of nitrogen and oxygen species. These species are introduced into the surface layer of the carbon grain and cause a well-developed surface to enhance reactivity of the modified precursor for SCR reaction (Grzybek et al., 2008).

Then samples were dried at 110 °C for 24 hours. Subsequently, thermal treatment was conducted in the flow of O_2/He (2.25%), at a rate of 100 cm^3/min , at 350 °C, for 2 h. The obtained samples were ground and sieved to obtain 0.25–1 mm fraction and were ready at the end of this step for the active phase deposition. Copper was deposited by wet incipient impregnation with a solution of $\text{Cu}(\text{NO}_3)_2$, using

various concentrations of the Cu²⁺ to obtain 1 wt.%, 5 wt.% or 10 wt.% Cu loading. Finally, Cu doped AC was dried and calcined in He stream for 1 hour at 250 °C.

Table 1 summarizes the procedures of triple modification to obtain a series of copper promoted activated carbon catalysts which were followed by characterization and catalytic test.

Table 1. List of the obtained catalysts and preparation procedures of the samples

Preparation procedures				
Sample	Oxidation	Modification	Impregnation	Calcination
AC	10M HNO ₃ , 90 °C, 2 h	–	–	–
AC/U		5 wt.% urea, calcination 350 °C, 2h, 100 cm ³ /min (O ₂ /He)	–	250 °C, 1h, 100 cm ³ /min (O ₂ /He)
AC/U/1Cu			1 wt.% Cu	
AC/U/5Cu			5 wt.% Cu	
AC/U/10Cu			10 wt.% Cu	

3. CATALYST CHARACTERIZATION

Low-temperature sorption of nitrogen (–196 °C) was used to determine the textural parameters of the prepared catalyst by a Gemini V2.00 model 2380 apparatus (Micromeritics). Before measurements, samples were degassed at 150 °C for 2 hours.

X-ray powder diffraction measurements (XRD) were carried out by the PANalytical-Empryan diffractometer. The measurement range was $2\theta = 5\text{--}90^\circ$ with a step of $0.02^\circ/\text{min}$. The XRD patterns were obtained at room temperature. The phase identification of each diffraction pattern was performed using PANalytical HighScore Plus v.4.0–4.7a software.

Fourier-transform infrared spectroscopy (FTIR) analysis was performed with Perkin Elmer Frontier FT-IR spectrometer. Sixty scans were taken for each spectrum for wavenumbers from 4000 to 400 cm^{–1}, registered with a resolution of 4 cm^{–1}.

4. CATALYTIC PERFORMANCE

The NO reduction with NH₃ was performed at atmospheric pressure in a fixed-bed flow reactor. The bed consisted of 0.2 g of catalyst particles. Reactant gases (800 ppm NO, 800 ppm NH₃, and 3.5 vol.% O₂ and He to balance) were fed to the reactor through mass flow controllers and helium was added to make up a total flow rate of 100 cm³/min. Prior to entering the catalyst bed, the gas mixture passed a zone filled with glass beads for preheating and thorough mixing. NO reduction experiments were conducted at temperatures ranging from 140 to 300 °C. NO conversion was calculated according to the equation:

$$x(\text{NO}) = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \cdot 100\% \quad (1)$$

5. RESULTS AND DISCUSSION

5.1. Low-temperature sorption of nitrogen

In Fig. 1 N₂ sorption isotherms for the prepared catalysts are presented. The curves sharply increase at low relative pressure showing a high adsorptive capacity of nitrogen and then plateau at higher relative pressure. According to the IUPAC classification, the presented isotherm could be classified as Type I. The shape of the hysteresis loop may be classified as an H4 type, which corresponds to the presence of macropores (narrow slit-like pores) (Sing et al., 1985).

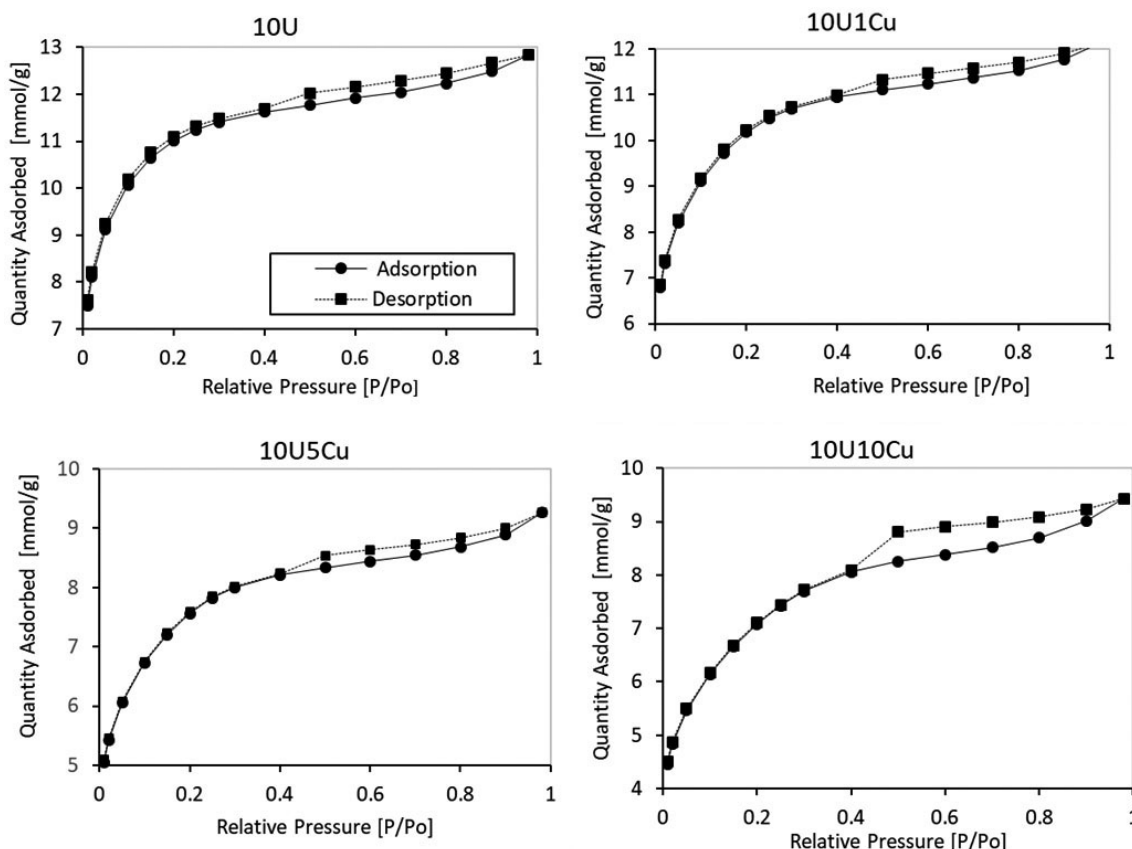


Fig. 1. Nitrogen sorption isotherm for the obtained catalysts

Table 2 presented the textural parameters for the studied samples; specific surface area, micropore volume, pore width, total pore volume, and micropore contribution. The raw carbon exhibited specific surface area S_{BET} over 700 m²/g; pore volume was 0.36 cm³/g. The specific surface area and the micropore volume increased after oxidation with 10M of nitric acid for the sample (denoted AC) due to the formation of new oxygen functional groups on the surface of activated carbon (Allwar et al., 2017). Also, nitric acid could react with the inorganic mineral impurities and the organic components in the coal and it produced new pores, which increased the total pore volume of the coal samples (Huang et al., 2019).

Most probably, the reduction of surface area from 829 to 670 m²/g follows from the fact that nitrogen groups introduced upon modification blocked the smallest pores in the porous structure of the carbon samples (Nowicki et al., 2015).

Introducing 1% of Cu led to the higher surface area, but the agglomeration of the more impregnating copper could clog the carbon pore and led to a decrease in the micropore volume. On the other hand, the activated carbons doped with more copper have more developed surface leading to higher catalytic efficiency.

Table 2. Textural parameters of the carbon-supported catalyst

Sample	Specific surface area [m ² /g]	Micropore volume [cm ³ /g]	Pore width [nm]	Total pore volume [cm ³ /g]	Micropore contribution [%]
Support	722	0.36	2.00	0.46	72.3
AC	829	0.41	1.96	0.53	77.4
AC/U	670	0.32	1.96	0.56	57.2
AC/U/1Cu	754	0.37	1.96	0.49	75.6
AC/U/5Cu	563	0.27	1.96	0.37	73.0
AC/U/10Cu	540	0.26	1.97	0.36	73.0

5.2. X-ray diffraction

XRD patterns for the obtained catalysts are presented in Fig. 2. Three diffraction reflections are seen for the sample AC/U at ca $2\theta = 25$ and 43 and 77° , respectively. Accordingly, they can be correlated to (002), (101) and (110) planes of the graphite phase of carbon [01-075-1621].

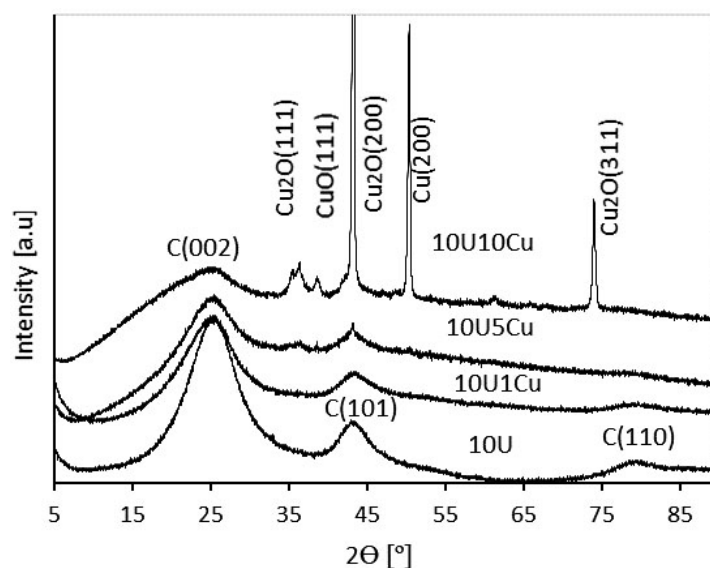


Fig. 2. XRD patterns of functionalized activated carbon doped with Cu

For the sample with 1 wt.% of copper, the graphite phase was also found at ca $2\theta = 25$ and 43 and 77° , respectively. The diffraction pattern of AC/U/1Cu is similar to that of AC/U. Thus, it may be concluded that copper in AC/U/1Cu is most probably either very well dispersed over the surface or is present in the amorphous form (Amanpour et al., 2013). The 5 wt.% addition of copper resulted in the appearance of the reflections at 2θ ca 42.2° . It can be ascribed to the (200) plane of Cu₂O [01-078-2076]. The reduced copper oxide was the most abundant crystalline phase in the AC/U/5Cu sample. Further, increase in copper content to 10 wt.% resulted in more crystalline copper-containing phases (Amanpour et al., 2013). The reflections at 2θ ca 36.5 , 42.2 , and 73.5° can be ascribed to the (111), (200) and (311) planes of Cu₂O, respectively; whereas, the reflections at 2θ ca 38.5 arise from the (111) plane of CuO [00-045-0937]. Pure copper also was found in the AC/U/10Cu sample with the reflections at 2θ ca 50.4° corresponding to the (200) plane of the face center cubic crystal structure of copper Cu [01-070-3039].

5.3. FT-IR spectroscopy

The presence of functional groups in obtained carbon materials was examined with FTIR spectroscopy and is illustrated in Fig. 3. The peak at 1120 cm^{-1} represents C–N (aliphatic) or N–H groups. The peak at 1560 cm^{-1} is ascribed to the stretching mode of carboxylic anions and the band at 1715 cm^{-1} is typical to the carbonyl stretching of the carboxylic group; the peak at 2900 cm^{-1} is ascribed to the C–H bond in CH_2 and CH_3 groups (Amanpour et al., 2013) whereas the peak at 3430 cm^{-1} can be attributed to absorbed water (Al-Qodah and Bansal, 2009; Bansal and Goyal, 2005).

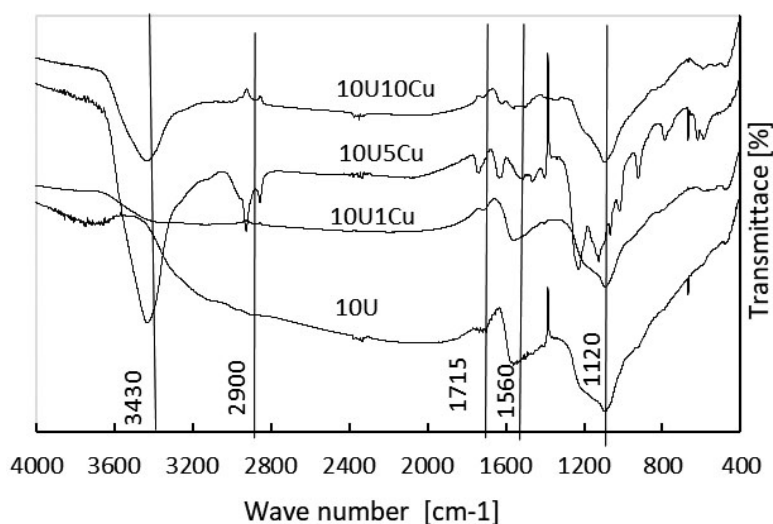


Fig. 3. FT-IR spectra of functionalized activated carbons doped with Cu

5.4. SCR for Cu doped functionalized activated carbon

In Fig. 4a), NO conversions of the studied catalysts at low-temperature window $140\text{--}300\text{ }^{\circ}\text{C}$ were compared. All copper promoted samples (AC/U/1Cu, AC/U/5Cu, AC/U/10Cu) reached about 95% of NO conversion at $220\text{ }^{\circ}\text{C}$, while AC/U reached 35% of NO conversion at the same temperature. At $300\text{ }^{\circ}\text{C}$, AC/U reached 50% of NO conversion, and AC/U/5Cu reached 98%. The conversion of AC/U/10Cu decreased with the increase of temperature over $220\text{ }^{\circ}\text{C}$. One of the reasons can be copper oxide accelerating the combustion of the support (Larionov et al., 2017) and taking into account the possibility of using the AC/U/10Cu catalyst in the flue gas installation at temperature $220\text{ }^{\circ}\text{C}$.

NO conversion reached 98%, N_2O was only 120 ppm, and CO_2 did not exceed 250 ppm at $220\text{ }^{\circ}\text{C}$. NO conversion formed a sequence: AC/U/5Cu > AC/U/1Cu > AC/U/10Cu > AC/U at $220\text{ }^{\circ}\text{C}$. It can be concluded that the impregnated quantity affected NO conversion. The efficiency of SCR reached the highest value when AC was impregnated with 5 wt.% Cu. This result indicates that the surface area and the pore volume are not the determining factors to improve catalytic activity in SCR, but surface chemistry played a significant role. The concentration of N_2O was relatively high but below 200 ppm for all the prepared samples, as presented in Fig. 4(b). AC/U/5Cu presented 55 ppm at $300\text{ }^{\circ}\text{C}$, and AC/U presented 65 ppm at $220\text{ }^{\circ}\text{C}$, while AC/U/10Cu presented 140 ppm N_2O .

There is another positive effect of smaller amounts of active metals. The selectivity of AC/U/5Cu was higher than AC/U/10Cu. The smaller amount of active material can lead to the formation of smaller aggregates and thus decrease the formation of undesired N_2O . A similar effect was observed by Grzybek et al. (2008). Since carbonaceous material can be oxidized under oxygen-containing atmosphere, the stability of the functionalized carbon samples, the CO_2 formation was also examined as presented

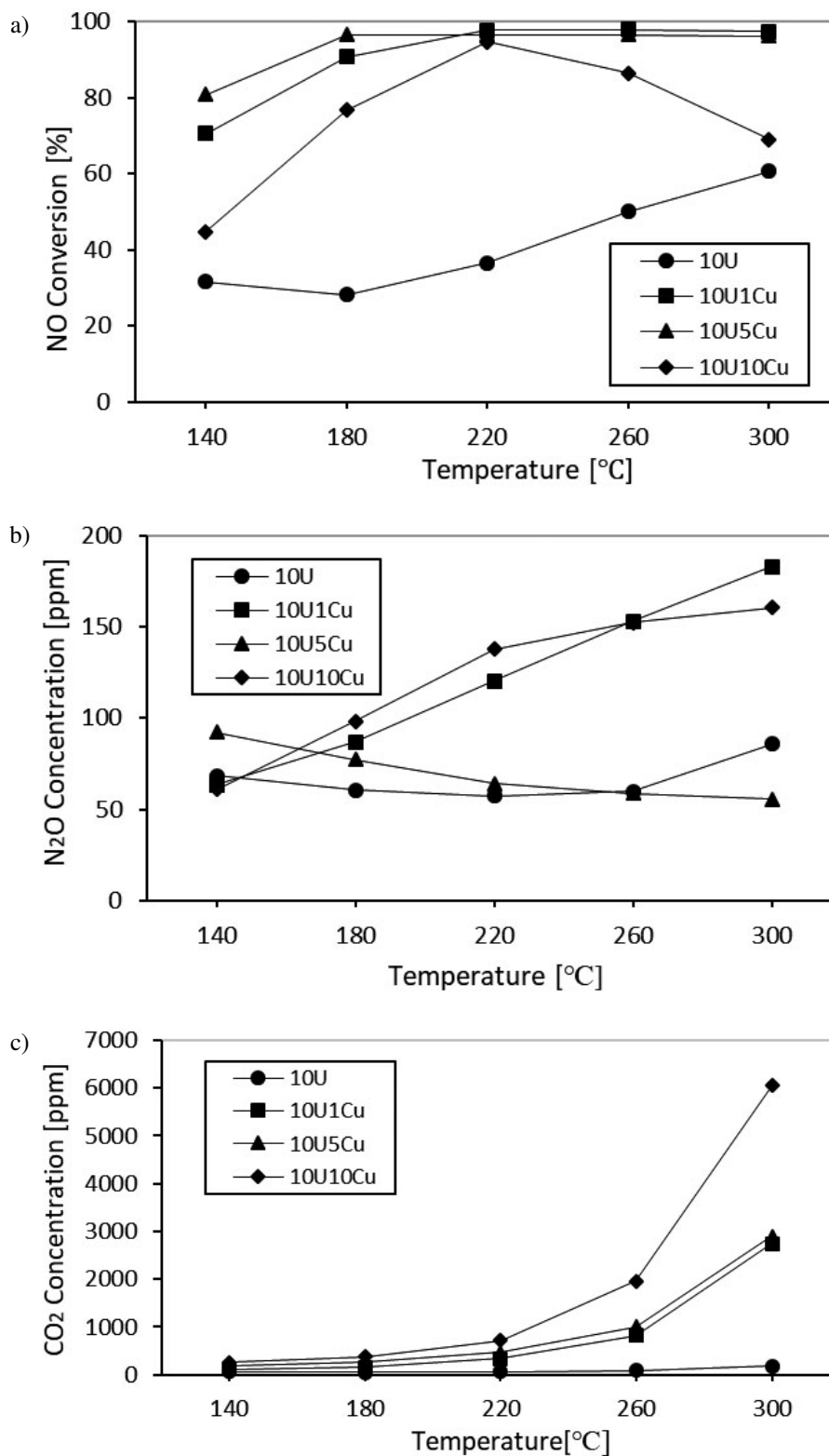


Fig. 4. a) NO conversion; b) N₂O formation; c) CO₂ concentration of functionalized activated carbon treated with HNO₃ and urea doped with Cu

in Fig. 4(c). For the catalysts with higher copper concentration, fast combustion of functionalized AC was observed. CO₂ concentration increased by increasing copper loading percentage in the sequence: AC/U < AC/U/1Cu < AC/U/5Cu < AC/U/10Cu along with SCR temperature range. The most exciting temperature region for AC-based catalysts is 220 °C, where the stability of all samples was high and CO₂ concentration did not exceed 240 ppm.

6. CONCLUSIONS

A series of carbon-supported catalysts were prepared by oxidation with 10M of nitric acid and modified with 5 wt.% of urea. Three different percentages of copper were loaded onto the activated carbon supports.

X-ray diffraction showed that 1 wt.% Cu was highly dispersed on the support surface, but with more Cu loading, the formation of copper oxide phases in the catalyst structure was registered. XRD proved that cupric nitrate was successfully loaded onto activated carbon with the resulting formation of copper, copper oxide, and cuprous oxide.

The modification with Cu improved the catalytic performance of the activated carbon catalysts. The sample without copper (AC/U) reached maximum NO conversion of 35% at 220 °C, while the sample modified with 10 wt.% Cu AC/U/10Cu reached 95% at the same temperature. The best results were observed for the catalysts modified with 5 wt.% of Cu (AC/U/5Cu). The catalytic activity for AC/U/5Cu increased along with the SCR temperature range (140–300 °C) from 82% to 98%.

This work was supported by Research Grant No. 16.16.210.476.

SYMBOLS

NO_{in} the inlet NO concentration, ppm
NO_{out} the outlet NO concentration, ppm

REFERENCES

- Al-Qodah Z., Shawabkah R., 2009. Production and characterization of granular activated carbon from activated sludge. *Braz. J. Chem. Eng.*, 127–136. DOI: 10.1590/S0104-66322009000100012.
- Allwar A., Hartati R., Fatimah I., 2017. Effect of nitric acid treatment on activated carbon derived from oil palm shell. In *AIP Conference Proceedings*, 1823, 020129. DOI: 10.1063/1.4978202.
- Amanpour J., Salari D., Niaei A., Mousavi S., Panahi P., 2013. Optimization of Cu/activated carbon catalyst in low temperature selective catalytic reduction of NO process using response surface methodology. *J. Environ. Sci. Health., Part A*, 48, 879–886. DOI: 10.1080/10934529.2013.761490.
- Bansal R.C., Goyal M., 2005. *Activated Carbon Adsorption*. Taylor & Francis Group Publishers. DOI: 10.1201/9781420028812.
- Chuang K., Shuliu Z., Yenwey M., 2010. Catalytic activity of copper-supported catalyst for NO reduction in the presence of oxygen. *Mater. Sci. Eng., B*, 175, 100–107. DOI: 10.1016/j.mseb.2010.07.011.
- Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control). *Official Journal of the European Union, OJ*, L 334, 17.12.2010, 17–119.
- Grzybek T., Klinik J., Helmut P., 1998. Manganese supported catalysts for selective catalytic reduction of nitrogen oxides with ammonia. *J. Chem. Soc., Faraday Trans.*, 24, 3527–3780. DOI: 10.1039/A803210F.
- Grzybek T., Klinik J., Samojeden B., Suprun V., Papp H., 2008. Nitrogen-promoted active carbons as DeNOx catalysts 1. The influence of modification parameters on the structure and catalytic properties. *Catalysis Today*, 137, 228–234. DOI: 10.1016/j.cattod.2007.11.009.
- Grzybek T., Motak M., Klinik J., Papp H., 2008. The influence of Mn promotion on the structure and catalytic properties in SCR. *Catal. Today*, 137, 235–241. DOI: 10.1016/j.cattod.2007.11.006.

- Huang B., Liu G., Wang P., Zhao X., Xu H., 2019. Effect of nitric acid modification on characteristics and adsorption properties of lignite. *Processes*, 7, 4–16. DOI: 10.3390/PR7030167.
- Huang H., Ye D., Huang B., Wei Z., 2008. Vanadium supported on viscose-based activated carbon fibers modified by oxygen plasma for the SCR of NO. *Catal. Today*, 139, 100–108. DOI: 10.1016/j.cattod.2008.08.028.
- Kiełtyka M., Soares Dias A.P., Kubiczek H., Sarapata B., Grzybek T., 2015. The influence of poisoning on the deactivation of DeNO_x catalysts. *Comptes Rendus Chimie*, 18, 1036–1048. DOI: 10.1016/j.crci.2015.05.004.
- Larionov K., Mishakov I., Slyusarskiy K., Bolgova D., Lavrinenko S., 2017. Influence of Cu(NO₃)₂ initiation additive in two-stage mode conditions of coal pyrolytic decomposition. In *MATEC Web Conf., Smart Grids 2017*, 141, 01026. DOI: 10.1051/mateconf/201714101026.
- Matzner S., Boehm H.P., 1998. Influence of nitrogen doping on the adsorption and reduction of nitric oxide by activated carbons. *Carbon*, 36, 1697–1703. DOI: 10.1016/S0008-6223(98)90047-1.
- Motak M., Kuterasiński Ł., Da Costa P., Samojeden B., 2015. Catalytic activity of layered aluminosilicates for VOC oxidation in the presence of NO_x. *Comptes Rendus Chimie*, 18, 1106–1113. DOI: 10.1016/j.crci.2015.05.005.
- Nowicki P., Pietrzak R., 2011. Effect of ammoxidation of activated carbons obtained from sub-bituminous coal on their NO₂ sorption capacity under dry conditions. *Chem. Eng. J.*, 166, 1039–1043. DOI: 10.1016/j.cej.2010.11.101.
- Nowicki P., Kazmierczak J., Sawicka K., Pietrzak R., 2015. Nitrogen-enriched activated carbons prepared by the activation of coniferous tree sawdust and their application in the removal of Nitrogen dioxide. *Int. J. Environ. Sci. Technol.*, 12, 2233–2244. DOI: 10.1007/s13762-014-0611-2.
- Pietrzak R., Wachowska H., Nowicki P., 2006. Preparation of nitrogen-enriched activated carbons from brown coal. *Energy Fuels*, 20, 1275–1280. DOI: 10.1021/ef0504164.
- Samojeden B., Klinik J., Grzybek T., Papp H., 2008. Charakterystyka modyfikowanych węgla aktywnych jako katalizatorów w reakcji DeNO_x – The characterization of modified active carbons for DeNO_x reaction. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management*, 24 (3/3), 295–303.
- Samojeden B., Grzybek T., 2016. The influence of the promotion of N-modified activated carbon with iron on NO removal by NH₃-SCR. *Energy*, 116, 1484–1491. DOI: 10.1016/j.energy.2016.04.059.
- Sing K., Everett D., Haul R.A.W., Moscou L., Pierotti R.A., Rouquerol J., Siemienińska T., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.*, 57, 603–619. DOI: 10.1351/pac198557040603.
- Singoredjo L., Slagt M., van Wees S., Kapteijn F., Moulijn J.A., 1990. Selective catalytic reduction of NO with NH₃ over carbon-supported copper catalysts. *Catal. Today*, 7, 157–165. DOI: 10.1016/0920-5861(90)85014-F.
- Teng H., Hsu L.-Y., Lai Y.-C., 2001. Catalytic reduction of NO with NH₃ over carbons impregnated with Cu and Fe. *Environ. Sci. Technol.*, 35, 2369–2374. DOI: 10.1021/es001674c.
- Ziemiański P., Kałahurska K., Samojeden B., 2017. Selective catalytic reduction of NO with NH₃ on mixed alumina–iron (III) oxide pillared montmorillonite “Cheto” Arizona, modified with hexamine cobalt (III) chloride. *Adsorpt. Sci. Technol.*, 35, 825–833. DOI: 10.1177/0263617417710141.

Received 10 July 2019

Received in revised form 05 March 2020

Accepted 09 March 2020