Original paper

Activated Carbon as a Support of Catalysts for the Removal of Nitrogen Oxides

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Abstract. Activated carbon was oxidised with concentrated nitric acid and impregnated with urea to form nitrogen-containing groups. Such a support was impregnated with cobalt, copper or silver nitrates to obtain catalysts for the selective catalytic reduction of nitrogen oxides with ammonia. Infrared spectra confirmed the formation of carboxylic and other organic oxygen-containing groups during oxidation. Nitrogen-containing species resulted from urea thermal decomposition. The metal-containing samples were hydrophilic. Cobalt and copper were present in the samples as small Co_3O_4 and CuO crystallites, while silver occurred in the form of large metallic crystallites, as seen from the X-ray diffraction patterns. Low temperature N_2 sorption revealed that all samples were microporous solids, and the chemical and thermal treatment did not change their textural properties. The copper admixture caused the highest NO conversion, but worsened the selectivity and thermal stability of functionalised carbon support.

Key-words: : activated carbon, functionalisation, catalyst, metal oxides, nitrogen oxides

1. Introduction

Nitrogen oxides (NOx) are one of the main air pollutants, which have a detrimental effect on the environment and human health as a result. The selective catalytic reduction (SCR) of NO_x with ammonia is nowadays applied as a commercial technique for the purification of off-gases from the stationary sources of emission. It uses the oxide system containing vanadium as a catalyst. This system attains its maximum activity above 300°C. The low temperature catalysts – efficient at 200°C – are yet to be elaborated. Carbonaceous materials after their functionalising with groups containing oxygen and nitrogen or their

promotion with transition metals are among such promising and investigated catalysts, while activated carbon (AC) is the cheapest one (Grzybek et al. 2008b). AC as a catalytic support exhibits a well-developed specific surface area and is a chemically inert material that does not cause the formation of reaction by-products (Shan, Song 2015). Moreover, its hydrophobic surface protects a catalyst from water poisoning (Liu et al. 2016). The functionalisation of AC is carried out in two stages: in the first stage, oxygen-containing groups are introduced; in the second, the carbonaceous material is doped with the groups containing nitrogen.

Nitric acid is the best oxidation agent of the carbonaceous materials for SCR, because it causes the highest activity (Grzybek et al. 2008a), and its concentration plays a crucial role (Amanpour 2013). Acid treatment improves AC sorption properties that are important during its doping with transition metal cations, due to the formation of negative charges on the surface as well as carboxylic ions. They improve the dispersion of a metal on the support and cause its improved insertion into pores; as a result, smaller metal-containing crystallites encourage the formation of a lower amount of nitrous oxide (Samojeden et al. 2015). The amount of deposited active material also depends on the AC's textural properties (Lazaro 2015), and nitric acid treatment results in the formation of wider pores (Samojeden, Grzybek 2017).

Oxygen-containing species formed during AC oxidation enable the deposition of the species containing nitrogen. The introduction of N-groups from a solution of urea with first wetness impregnation turned out to be more efficient than their deposition from the gas phase containing ammonia. The thermal treatment of the sample with deposited urea causes its decomposition into CO_2, thus increasing the oxygen content in the material as well as the number of acid sites (Grzybek et al. 2008a). The acid groups formed during the oxidation of AC are the adsorption sites for ammonia during SCR. N-groups play the role of the adsorption sites for NO_x and improve the thermal stability of carbonaceous support as well (Samojeden et al. 2015; Samojeden, Grzybek 2017). The thermal instability at higher temperatures is the main disadvantage of carbonaceous materials and their gasification is accelerated by the presence of the transition metals with oxidation properties.

The aim of the presented work was the functionalisation of active carbon with the groups containing oxygen and nitrogen, as well as the selection of a transition metal, which ensures the optimum catalytic efficiency, selectivity and thermal stability in the reduction of NO_x with ammonia.

2. Samples and methods

AC type N/m (produced by Gryfskand, Hajnówka, Poland) (designated as C) was treated with concentrated nitric acid (65wt%) at 90^oC for 2 h (CA). Such a material was filtered and washed with distilled water to attain a pH close to 7. Then, it was dried at 110^oC for 24 h. Next, the sample was impregnated with a solution of urea by the first wetness method to obtain its 5wt% concentration, and again dried under the same conditions. The urea was thermally decomposed at 350^oC in the flow of oxygen (2.25%) in helium at a rate of 100 mL/min for 2 h (CAU). The samples were sieved to obtain the 0.25-1 mm fraction, which was impregnated with the nitrate solutions of cobalt, copper or silver

to contain 3wt% of a metal (MepCAU). Metal precursors were decomposed at 250°C for 1 h under the same gas flow conditions as the urea (MeCAU).

The presence of functional groups in the catalysts was investigated with infrared spectroscopy (IR) in the diffuse reflectance mode (DRIFT). 10 mg of a sample, dried overnight at 50°C, was ground with 100 mg of potassium bromide and the Fourier-transform spectrum was taken in the wavenumber range of 4000–400 cm^{-1}. The resolution was equal to 4 cm^{-1} and 64 scans were collected with a PerkinElmer Frontier^{TM} FT–IR spectrometer.

The crystallographic structure of samples was determined with powder X-ray diffraction (XRD). Patterns were registered by means of a PANalytical-Empyrean diffractometer in the 2θ range of 5–90° with the step equal to 0.02^{o}. A copper lamp with λ=1.5406 Å was used as a radiation source.

To examine the textural properties of the catalysts, the low temperature sorption of nitrogen was carried out using a Gemini V 2.00 2380 (Micromeritics) analyser. Before measurement, the samples were outgassed at 150°C for 2 h. Then, the sorption was conducted in the relative pressure range of 0-0.98. The specific surface area was calculated applying the BET method (SSA$_{BET}$). The micropore volume was estimated by the t-plot method and the total volume of pores with a diameter lower than 2.7 nm was determined with the single point method at a relative pressure equal to 0.3.

The obtained samples were subjected to the catalytic tests in the selective catalytic reduction of NO with ammonia. For this purpose, 0.2 g of a sample was placed on quartz wool in a quartz reactor. The mixture of 800 ppm NO, 800 ppm NH$_3$ and 3.5% O$_2$ in helium was passed through the sample at a rate of 100 mL/min. NO conversion was measured in the temperature range of 140-300°C, with a step of 40°C. The concentration of NO, NH$_3$ and CO$_2$ was registered with IR ABB series 2020 A0 analysers.

3. Results and discussion

The presence of functional groups on the carbon materials was verified by IR spectroscopy (Fig. 1). The initial sample contained oxygen, which is confirmed by the bands at 1590, 1490 and 1010 cm^{-1} in the spectrum of the C sample. These bands can be ascribed to the stretching vibration of chelated carbonyl, phenolic groups or C-O bond, respectively (Bansal, Goyal 2005). The CA sample treated with nitric acid exhibits the new absorption bands at 1740 cm^{-1}, and the band at 1010 cm^{-1} is shifted to 1100 cm^{-1}, developing the new shoulder at 1220 cm^{-1}. The former band origins from carboxylic groups and the last band with lower wavenumber could correspond to oxidised carbon species (Bandosz, Ania 2006). Their presence proves the oxidation of the AC sample, which also caused the increase in the amount of alcoholic and ether groups. After urea decomposition, the shoulder at 1490 cm^{-1} corresponding to carbon–nitrogen bonds emerged, as seen in the spectrum of the CAU sample (Bandosz, Ania 2006). The content of the carboxylic groups (at 1740 cm^{-1}) lowered significantly, where they decomposed or transformed in nitrogen-containing species. The band at 1590 cm^{-1} decreased after this thermal treatment, suggesting that carbonyl groups underwent decomposition as well. The deposition of metal nitrates and their decomposition only caused changes in the content of carbon–nitrogen species and remnants of the carboxylic groups. The metal-containing samples were slightly

more hydrophilic than their carbon activated supports, which may confirm the presence of the broad bands above 3300 cm^{-1} attributed to the molecules of adsorbed water (Bansal, Goyal 2005).
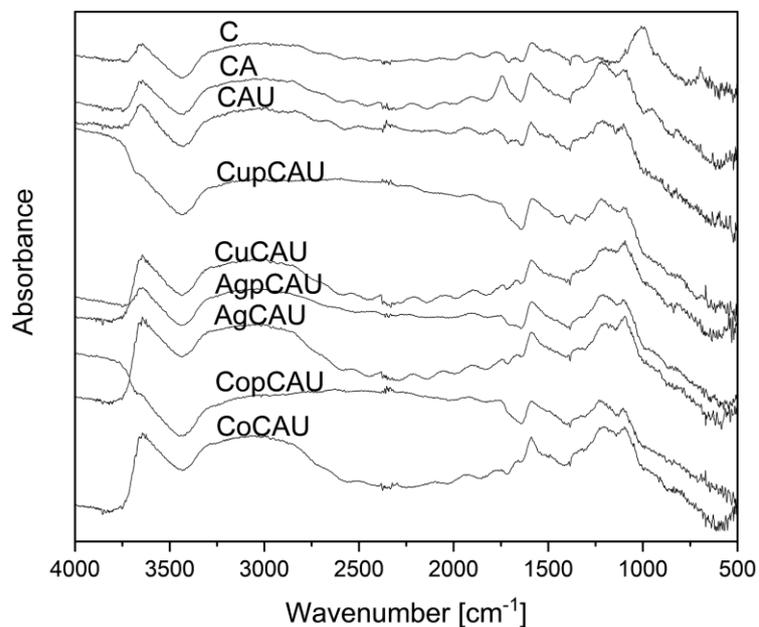
Fig. 1. IR spectra of carbonaceous materials.
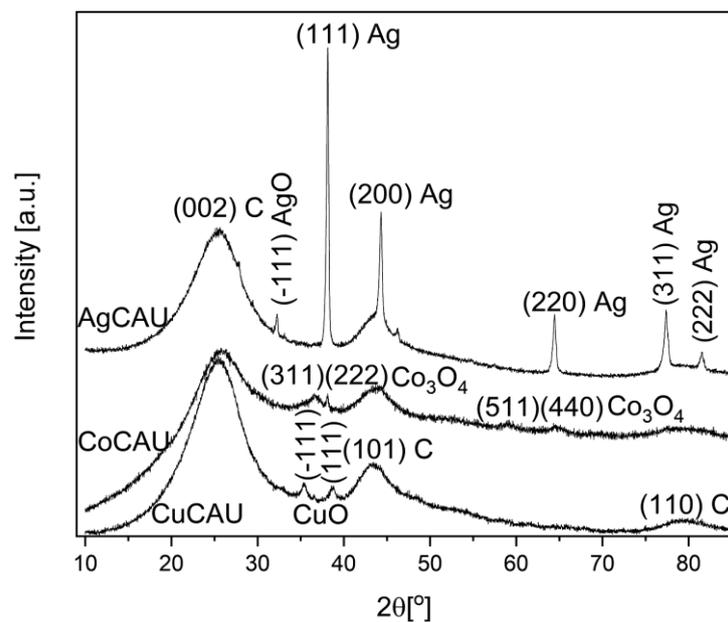
Fig. 2. XRD patterns of carbon-supported silver, cobalt and copper catalysts.

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To investigate the structure of carbon supported metal-containing catalysts, XRD patterns were recorded, as seen in Figure 2. In the spectra of all samples, broad bands at 2θ ca 25.5, 43.4 and 79.6° are present and can be ascribed to the (002), (101) and (110) planes, respectively, of poorly ordered graphite-like phase [01-075-1621]. For the CuCAU sample, one can observe maxima at 35.4 and 38.7°, which can be ascribed to the (-111) and (111) planes of CuO phase, respectively [01-089-2530]. The small maximum at 36.5° is seen as well and can originate from the (111) plane of Cu_2O [00-005-0667]. The cobalt CoCAU sample contained the Co_3O_4 phase, confirmed by the maxima at 36.7, 38.1, 59.1 and 64.6° corresponding to the (311), (222), (511) and (440) planes, respectively [01-080-1536]. The silver-containing sample was the most crystalline one with the narrow maxima at 38.1, 44.4, 64.4, 77.5 and 81.6° corresponding to the (111), (200), (220), (311) and (222) planes of Ag, respectively [01-087-0597]. The small maximum at 32.2° of 2theta can come from the (-111) plane of the AgO phase [01-084-1547]. The two shoulders at 27.8 and 46.3° are probably connected with the (110) and (211) planes of the Ag_2O phase, respectively [03-065-6811]. Carbon is a support with reducing properties, which is confirmed by the presence of metal oxides with a lower valence. In the case of silver oxides on carbon supports, Ag_2O is common but it is not stable under light radiation and forms metallic silver (Mohamed 2020).

Low temperature nitrogen sorption was enabled to determine the textural properties of the examined samples, as seen in Table 1. AC exhibited the specific surface area close to 780 m^2/g and was microporous/mesoporous material with an average pore width slightly below 2 nm and micropore volume equal to 0.24 cm^3/g. Carbon functionalisation and metal deposition did not cause any significant changes in its SSA$_{BET}$, which were below 10%. One can observe that acid treatment resulted in removing microporous material – a decrease of micropore volume and specific surface area. After the treatment with urea, the micropores decreased their volume but the total volume and micro- and narrow mesopores slightly increased, suggesting the formation of narrower mesopores, perhaps by the deposition of N-groups in wider mesopores. Silver deposition caused the smallest loss in the values of textural properties, its large crystallites (Fig. 2) probably formed on external sides of carbon particles, whereas cobalt and copper blocked micropores to a greater extent.

TABLE 1

Specific surface area, pore volume and width of carbonaceous materials.

Sample	SSA$_{BET}$ [m^2/g]	Micropore volume [cm^3/g]	Pore (d<2.7nm) volume [cm^3/g]	Pore width [nm]
C	782	0.24	0.38	1.97
CA	723	0.17	0.36	1.97
CAU	812	0.12	0.40	1.97
AgCAU	783	0.12	0.39	1.97
CoCAU	745	0.11	0.37	1.97
CuCAU	754	0.12	0.37	1.97
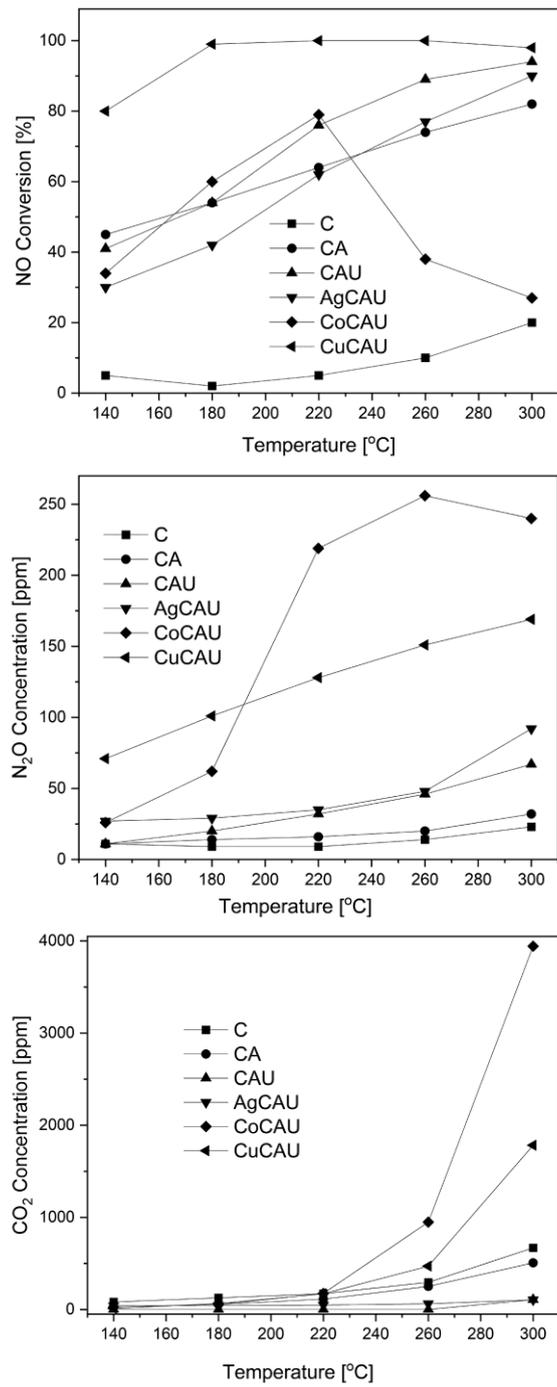
Fig. 3. NO conversion, N_2O and CO_2 formation over carbonaceous materials.

During catalytic tests NO conversion, undesired N_2O formation and carbon oxidation were investigated and the results are presented in Figure 3. As seen, the AC exhibited poor catalytic activity attaining ca 20% NO conversion at 300°C. Acid treatment of the C sample caused a significant increase in its efficiency – above 60% of NO was converted at 220°C and above 80% at 300°C. The introduction of N-containing groups improved the efficiency of the catalytic performance at these temperatures by above 10%. The deposition of silver decreased the sample activity at lower temperatures below the level of the CA sample. Above the temperature of 220°C this activity was lower than observed for the CAU catalyst. The addition of cobalt resulted in NO conversion slightly higher than this for the CAU sample at 180 and 220°C. With the temperature increase, the NO conversion drastically lowered over the CoCAU sample. The copper-containing sample exhibited the best catalytic activity with NO conversion equal to 80% at 140°C, while above 180°C NO was completely removed.

The amount of nitrous oxide – the undesired NO SCR by-product – was below the experimental error level (30 ppm) over the C and CA samples. This N_2O concentration level was exceeded for the CAU material at 220°C and attained ca 70 ppm at 300°C. Similar nitrous oxide concentration was observed for the silver-modified sample. For the CoCAU sample, the amount of N_2O was the highest, where above 220°C it exceeded 200 ppm. Over the copper catalyst the concentration of N_2O increased almost linearly with the temperature, from 70 ppm at 140°C to 170 ppm at 300°C.

The amount of forming CO_2 indicates the thermal stability of a carbonaceous material. Over AC, the concentration of carbon dioxide increased from 80 to 670 ppm with the temperature from 140 to 300°C. The oxidation of the C sample caused the suppression of CO_2 formation with the maximum concentration ca 500 ppm at the highest temperature. The presence of N-containing groups resulted in the complete protection of the material from burning to 260°C, and only 100 ppm of CO_2 was recorded at 300°C. Silver admixture did not influence the thermal stability of the functionalised carbon material. Cobalt doping caused rapid burning of the carbon support above 220°C, which could be the cause of a decrease in catalytic activity over this sample. The admixture of copper also caused the loss of thermal stability above this temperature, but less quickly.

4. Conclusions

AC was oxidised with nitric acid, which caused the formation of carboxylic and other oxygen-containing organic groups. After urea decomposition, the sample was enriched in nitrogen-containing species. The metal doped samples were hydrophilic. Metals were present in the catalysts mainly as small crystallites of CuO or Co_3O_4, and large crystallites of Ag. All samples occurred as micropore solids, and chemical and thermal treatments did not cause significant changes. Active carbon accelerated the reduction of NOx to a small degree (22% at 300°C). Its oxidation resulted in a large activity increase (80 %). The deposition of the functional groups containing nitrogen caused a further increase in NO removal to 92%. Silver doping lowered the catalyst activity to 60% at 220°C and did not change it at 300°C. The addition of cobalt did not influence the catalyst efficiency at the low temperature, while at the higher one an increase to the level for unmodified carbon was registered. The copper-containing catalyst was the most active, attaining the total NO

conversion at 180°C. At 220°C, only doping with copper and cobalt resulted in the formation of the harmful product: N$_2$O. At 300°C, nitrous oxide was observed, as well for the urea and silver samples, and for the Cu and Co samples the increase in its amount was registered. The deposition of nitrogen-containing groups brought about the improvement of material thermal stability. On the other hand, copper and particularly cobalt accelerated carbon oxidation above 260°C.

Copper deposition on carbonaceous materials ensures their highest activity, but the improvement of their selectivity and thermal stability is necessary.

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