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# Catalytic reduction of nitrogen oxides via nanoscopic oxide catalysts within activated carbons at room temperature

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**Abstract** Cabin air filters consisting of activated carbon infiltrated with nanoscopic metal oxide particles as catalysts have been investigated for the reduction of nitrogen oxides within motor-car cabins. In that concept, nitrogen dioxide is adsorbed on the activated carbon during operation conditions of the car and then reduced by the catalysts within the pores. The conversion has to take place at ambient temperature during the relatively long standstill periods of motor-cars. In this article we are going to discuss the manufacturing of the adsorbents by “liquid phase infiltration” and their characterization by techniques, such as nitrogen sorption analysis, X-ray diffraction, thermogravimetry, energy dispersive X-ray spectroscopy, and electron microscopy. The new adsorbents were evaluated in repeated breakthrough tests using $NO_2$ (4 $ppm_V$ as feed concentration) in humid air as the adsorptive. In the intermittent rest periods of varying duration the volume flow through the fixed bed of adsorbent was stopped. The measured breakthrough curves indicate a catalytic conversion of the nitrogen dioxide in the filter beds.

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**Keywords** Nitrogen dioxide · Nitrogen monoxide · Activated carbon · Nano catalysts · Metal oxide · Cabin air filters

## 1 Introduction

Adsorptive cabin air filters clean air coming into the passenger cabin of noxious gases by adsorption onto activated carbon. One important gaseous compound which has to be removed is nitrogen dioxide. The adsorption process in cabin air filtration is characterized by ambient conditions, thin activated carbon layers, and long non-operating times between driving cycles. Times between filter changes are in the range of 1 year or 15,000 km driving distance. In order to increase the activated carbon’s capacity for the adsorption of nitrogen dioxide, in the present survey catalysts were infiltrated into the adsorbent by incipient wetness impregnation. Metal oxides and mixed metal oxides have been used as catalysts with the size of the catalyst particles being in the range of a few nanometres. The basic concept was, in a first step, to adsorb nitrogen dioxide onto the activated carbon when the air flow passes the cabin air filter. Before in a second step, the adsorbed nitrogen dioxide is converted to physiological neutral substances by metal oxide catalysts, a very slow process at ambient temperature. The required time for that reaction should be provided by standstill periods of the car. Thus, a catalytic regeneration of the cabin air filter has been expected. In the present contribution, breakthrough experiments will be discussed as well as the preparation and characterization of the filter materials.

The study described here differs considerably from the multitude of investigations concerning catalytic reduction of $NO_x$ (e.g. Muniz et al. 1999, Park and Kim 2005) because its subject is the separation of $NO_2$ under ambient conditions and not from hot flue gases. In flue gas treatment temperatures range from 100 up to 600 °C, $NO_x$ concentrations are about several hundred $ppm_V$, the oxygen concentration and relative humidity depend on the respective process, and additives such as ammonia or hydrogen (Polychronopoulou and Efstathiou 2012) are used. Hu et al. (2001) report the reduction of NO at temperatures as low as 100 °C using CuO supported on $CeO_2$ as the active component. Using $H_2$ as reducing agent and Pt/MgO–$CeO_2$ catalysts, Costa and Efstathiou (2007) and Costa et al. (2007) achieved nearly complete NO conversion at temperatures between 100 and 200 °C. At ambient temperatures only the oxidation of NO to $NO_2$ by activated carbon materials has been subject of investigations (Mochida et al. 2000, Mochida et al. 1997), but again under substantially different reaction conditions. Here, we report on a survey on the use of a mainly microporous activated carbon that had been impregnated with mixed oxide catalyst as a catalytically active adsorbent for the reduction of $NO_2$. Preliminary studies showed that impregnation of activated carbon with a mixture of CuO and ZnO resulted in a more active adsorbent for the reduction of $NO_2$ from gas flows than activated carbons impregnated with only single oxide components. For that reason, activated carbon loaded with a mixture of both oxides has been subject of the present study.

## 2 Experimental procedure

### 2.1 Preparation of the adsorbents

Activated carbon beads, denoted as Kugelkohle R 1407, with a pronounced microporosity have been provided by Rütgers-CarboTech. The deposition of the nanoscopic metal oxide particles has been achieved by incipient wetness impregnation of the activated carbon and subsequent calcination (Schwickardi et al. 2002, 2005, 2006). The impregnation process is shown schematically in Fig. 1.

For a typical preparation, 1 mL aqueous 5.32 M $Cu(NO_3)_2$ solution was admixed to 1.31 mL aqueous 4.06 M $Zn(NO_3)_2$ solution. 1.35 mL of the resulting solution was diluted with 5.0 mL of de-ionized water to achieve in the impregnation solution (Cu : Zn = 1). The thus obtained solution then was immersed in 9.5 g activated carbon (Kugelkohle R 1407) by stirring with a magnetic stirrer bar for 10 min. The volume of the impregnation solution was adjusted to the pore volume of the activated carbon. Therefore, the solution was absorbed completely by the activated carbon, i.e., a dry powder was obtained. The impregnated carbon was exposed for 16 h to 90 °C and then heated up to 250 °C at a heating rate of 4 °C $min^{-1}$ and kept at that temperature for 30 min. During the heat treatment, water was released from the pores of the activated carbon, resulting in copper and zinc nitrates which decompose to result in the respective oxides at temperature around 200 °C. The sizes of the particles are restricted by the pore walls of the activated carbon.

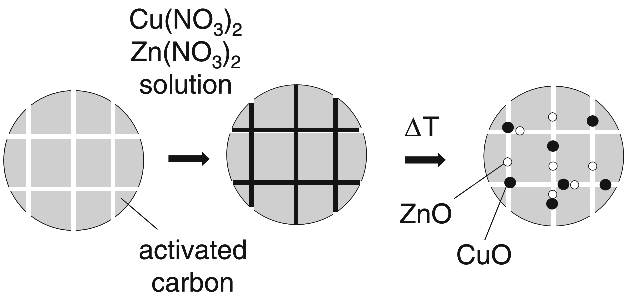

**Fig. 1** Schematic representation of the impregnation of the activated carbon via the incipient wetness method

### 2.2 Characterization of the infiltrated adsorbents

X-ray powder diffraction patterns have been recorded on a Stoe STADI P theta/theta diffractometer (Bragg–Brentano geometry) equipped with a secondary graphite monochromator using Cu $K_\alpha$ radiation. In addition scanning electron microscopy (SEM) investigations have been performed on a Hitachi S-5500 instrument that allowed EDX investigations of the samples. Element distribution maps across the carbon beads have been obtained by embedding the carbons beads in a resin. After polymerization of the resin, microtome cutting of the resin resulted in segmental cuts through embedded carbon particles. EDX investigations on these cuts allowed the monitoring of the element distributions. Nitrogen adsorption experiments at 77 K have been made on a Micromeritics ASAP 2010 sorption instrument. Data processing was performed with the Quantachrome Autosorb software package. The commonly used BET method for calculating specific surface areas cannot be applied on microporous materials since the boundary conditions for that method are not fulfilled for microporous materials. Since the activated carbon used here, was mainly microporous, specific surface areas have been calculated with the NLDFT method which has also been used for the calculation of the pore size distributions. Thermogravimetric experiments coupled with differential thermal analysis and mass spectrometric gas analysis have been performed on a Netzsch STA 449 C thermobalance attached to a Balzers ThermoStar (QMS 200) mass spectrometer.

### 2.3 Testing of the $NO_2$ reduction by the infiltrated activated carbon

For testing the infiltrated activated carbons as adsorbents in cabin air filters, repeated breakthrough experiments with nitrogen dioxide as adsorptive with concentrations in the low ppm range and humid air as carrier gas have been conducted. Between the loading procedures, the adsorbent was submitted to rest periods of varying duration.

The modified activated carbon as well as the base material has been tested in a fixed-bed flow reactor as illustrated in Fig. 2 by loading them six times with $NO_2$. During each loading procedure an air stream with a temperature of 23 °C and 50 % relative humidity passed through the fixed-bed consisting of 2 g of adsorbent with a flow velocity of 0.2 m/s. The volumetric inlet concentration of $NO_2$ was 4 ppm. The $NO_2$ was dosed to the air stream directly from a reservoir using a mass flow controller. The $NO_2$ reservoir, the tubing, and the mass flow controller were heated to achieve the required vapor pressure and to avoid condensation. At the inlet and outlet of the fixed-bed reactor, the concentrations of $NO_2$ and NO were measured and recorded quasi continuously with two nitrogen oxide analyzers (type AC31 M from Ansyco, Karlsruhe) based on chemiluminescence measurements. The measuring range of the analyzers is up to 10 $ppm_V$, the lower detection limit is ca. 0.5 ppb and the precision of the measurement is ±1 % of the upper range value.

For testing the performance of the adsorbents, they have repeatedly been loaded six times with $NO_2$ for 90 min. In between these breakthrough experiments rest periods without dosing of $NO_2$ were applied for varying time. During the resting times the adsorbents were stored in small sample containers.

Figure 3 illustrates the test procedure by reporting the measured values of $NO_2$ and $NO_x$ ($NO_x$ as the sum parameter of $NO_2$ + NO) behind the adsorber bed. The outlet concentration $c_2$ of $NO_2$ is given in relation to the inlet concentration $c_1$ during the first three loadings. After a first loading for 90 min, the $NO_2$ supply and the air stream were stopped. The fixed bed was then allowed to rest for 3 h. Then a second loading was performed for another 90 min, followed by a rest period of 15 h. The latter was supposed to simulate an over-night parking of a car. Four more breakthrough experiments have been performed with varying interim breaks. The effect of regeneration times has been investigated with rest times of up to several months.

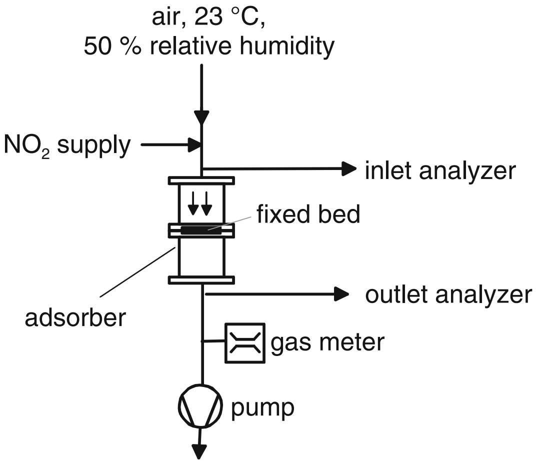

**Fig. 2** Sketch of the test device for breakthrough experiments

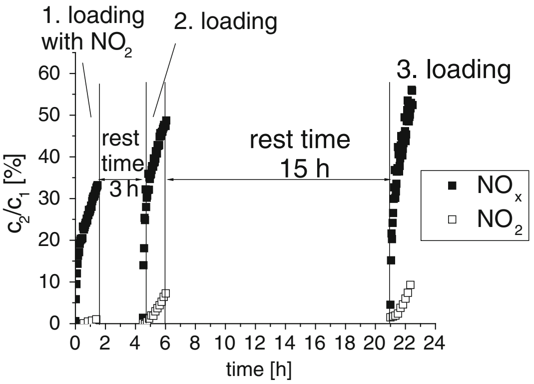

**Fig. 3** Breakthrough curves of $NO_2$ and $NO_x$ during the test procedure

Figure 3 shows that the breakthrough of $NO_2$ and $NO_x$ do not coincide. Although only $NO_2$ is added to the inlet air stream, substantial amounts of NO have been detected behind the adsorbent. The reduction of $NO_2$ to NO by activated carbon is commonly observed and is not due to the deposition of the metal oxides. Carbon is either oxidized to CO or oxo-functionalized groups are generated on the inner surface of the activated carbon. Further oxidation may even result in formation of $CO_2$ from the activated carbon (Heschel and Ahnert 1998, Unseld 1969).

## 3 Results and discussion

### 3.1 Characterization of the infiltrated adsorbents

The activated carbon beads (Kugelkohle R 1407) have very narrow pores as indicated by nitrogen adsorption isotherm shown in Fig. 4. Calculating the pore size distributions using the NLDFT method (model: nitrogen at 77 K on carbon with pores simulated as cylinders), the majority of pores is smaller than 3.5 nm whereby about 65 % of the pore volume is found in pores smaller than 2 nm (micropores). The specific pore volume of the parent carbon was 0.76 $cm^3g^{-1}$. Deposition of 5 wt% of the mixed

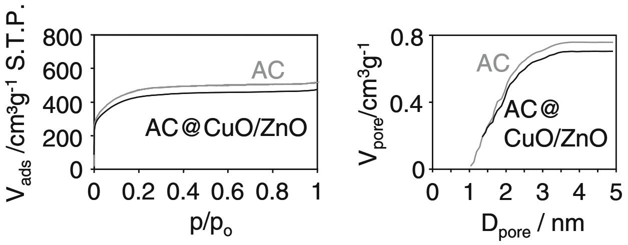

**Fig. 4** Nitrogen adsorption isotherms (*left*) and cumulative pore volumes (*right*) of the parent activated carbon (AC) and the activated carbon after deposition of CuO/ZnO (AC@CuO/ZnO)

oxide inside the pores of this carbon did not much affect the accessibility of the pores. The additional weight of the mixed oxide alone would reduce the specific pore volume of the parent material to 0.72 $cm^3g^{-1}$, a value which does not vary too much from the measured pore volume of 0.69 $cm^3g^{-1}$ of the loaded material. The majority of the pores was thus still accessible and the pore size distribution did not change significantly after the deposition of the oxides. The specific surface areas, as calculated using the NLDFT method, slightly reduced from 1,775 $m^2g^{-1}$ for the parent carbon to 1,720 $m^2g^{-1}$ for the impregnated one.

During the decomposition of the nitrates, the surrounding carbon is slightly oxidized to $CO_2$ resulting in slightly enlarged cages in which also somewhat larger oxide particles can be accommodated. The presence of nanoscopic CuO and ZnO particles is indicated by broad reflections in XRD patterns (Fig. 5).

The reflections of the oxides are visible in diffraction patterns of impregnated samples but they are not very strong due to the loading of only 5 wt%. In order to visualize the phase composition somewhat better, an XRD pattern has been measured also on a sample in which the carbon has been removed by calcination at 550 °C in air. To maintain the original particle sizes during the oxidation of the carbon matrix, this sample had been additionally doped with silica. (Cu:Zn:Si = 1:1:0.25). The silica prevents aggregation and sintering of the oxide nanoparticles during the calcination.

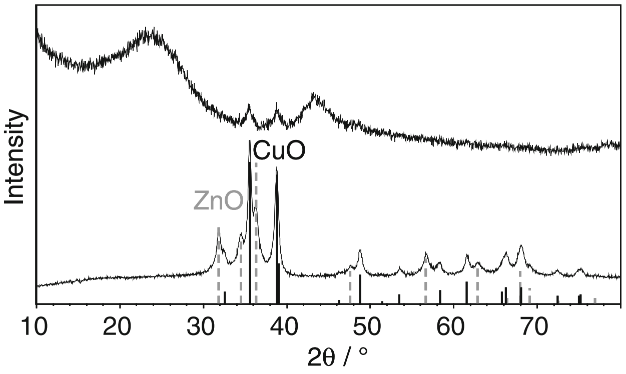

**Fig. 5** XRD patterns of CuO and ZnO within the carbon matrix (*top*) and of a sample after carbon combustion (*bottom*)/(*full lines* indicate positions of CuO reflections and *dashed lines* those of ZnO)

CuO and ZnO particles seem to be deposited homogeneously within the whole volume of the carbon beads as indicated by EDX investigations of the beads after carbon removal. The EDX maps in Fig. 6 clearly show a uniform distribution of the elements copper, zinc and silicon.

It should be noted here, that the silica doping was used only to maintain the particles sizes and shapes. For the catalytic tests, as discussed below, oxide-impregnated carbon samples were used that had been synthesized without silica doping.

### 3.2 Testing of the $NO_2$ reduction by the infiltrated activated carbon

Activated carbon (R 1407) loaded with 5 wt% of CuO/ZnO (Cu:Zn = 1) has been used as adsorbent in the formerly described long term tests with varying rest periods. Breakthrough curves of $NO_x$ and $NO_2$ have been measured at the beginning and after the respective rests. Figures 7 and 8 show the breakthrough curves for $NO_x$ and $NO_2$ after the first adsorption cycle, followed by a 3 h rest, the second adsorption cycle followed by a 15 h rest, and so on. Concentrations $c_2$ of $NO_x$ and $NO_2$, as measured downstream of the fixed bed, in relation to the inlet concentrations $c_1$ are shown in dependence of time of loading.

Figure 7 shows that during the first loading the breakthrough of $NO_x$ increases with time and reaches about 30 % after 90 min. After the first rest period of 3 h, the concentration at the outlet increased slightly. In the next two recovery and loading cycles (No. 3 and 4) with recovery periods of 15 h and 3 months, the concentration at the outlet after 90 min of loading remained more or less identical to the ones from the previous runs. After an additional rest of 24 h, the $c_2/c_1$ ratio increased slightly. After a second long term rest for 3 months, the $c_2/c_1$ ratio after 90 min of loading levelled out at the same value as in the second, third, and fourth runs. The $c_2/c_1$ ratios at the beginning of the breakthrough tests (initial breakthrough) remained lower than 6 % for all runs.

The breakthrough of $NO_2$, as shown in Fig. 8, shows that the exit concentration from the catalytic filter was very low and remained on a low level ($c_2/c_1 < 6$ %) for all runs. Considering the uncertainty in measurement and the fact that all uptake measurements have been performed as individual experiments, the uptake curves were rather similar.

In order to evaluate the performance of the AC@CuO/ZnO adsorbent, its breakthrough curves have been compared to those of the pure activated carbon. In Fig. 9 the breakthrough of $NO_x$ as well as of $NO_2$ are shown for both

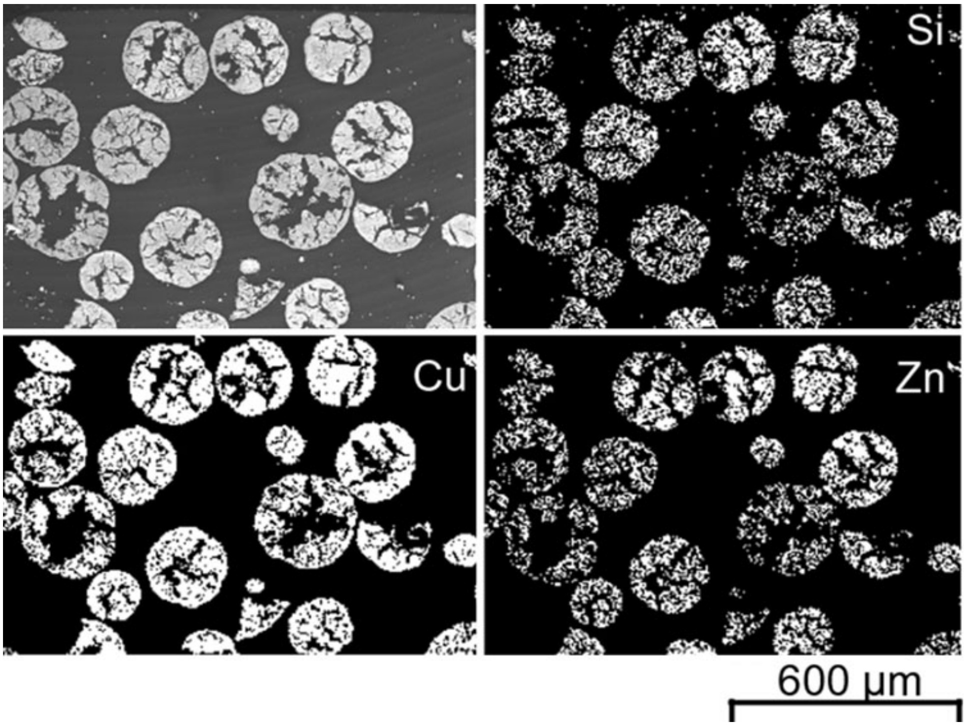

**Fig. 6** SEM image and element distributions of the silica-doped AC@CuO/ZnO particles embedded in a polymerized resin after carbon combustion

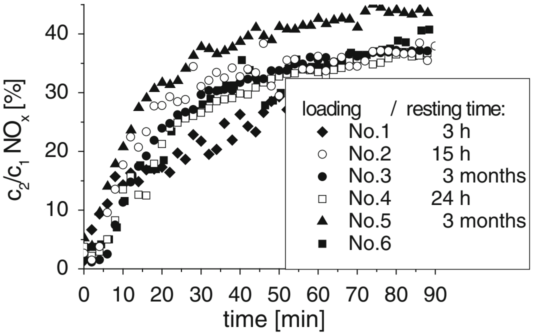

**Fig. 7** Breakthrough of $NO_x$ through AC@CuO/ZnO during six loading cycles (23 °C, 50 % r. H., $c_1$ $NO_2 = 4$ $ppm_V$, $v = 0.2$ m/s) after various rest periods

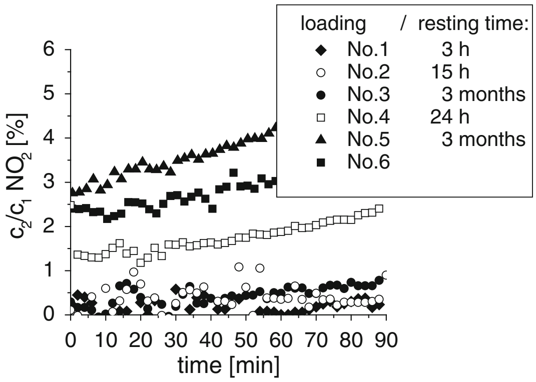

**Fig. 8** Breakthrough of $NO_2$ through AC@CuO/ZnO during the six loading cycles (23 °C, 50 % r. H., $c_1$ $NO_2 = 4$ $ppm_V$, $v = 0.2$ m/s) after various rest periods

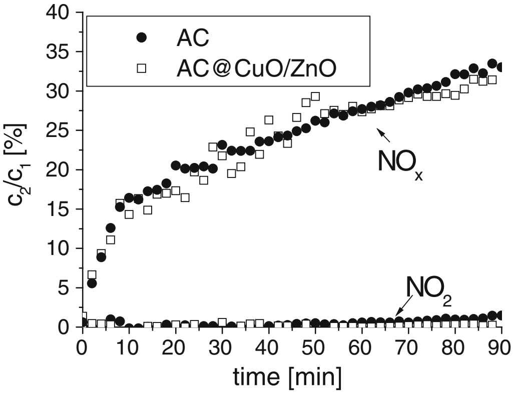

**Fig. 9** Breakthrough curves of $NO_x$ and $NO_2$ through AC@CuO/ZnO and AC during the first loading (23 °C, 50 % r. H., $c_1$ $NO_2 = 4$ $ppm_V$, $v = 0.2$ m/s)

adsorbents during a first loading cycle. Both adsorbents exhibited more or less identical separation characteristics. This is not too surprising since the specific surface areas of both materials are rather similar. The initial adsorption of $NO_2$ and its reduction to NO should be rather similar on both carbon materials. However a clear advantage of the AC@CuO/ZnO system for $NO_x$ reduction is observed with successive loading and rest cycles. While the breakthrough of both $NO_2$ and $NO_x$ remained more or less constant for the AC@CuO/ZnO adsorbent with successive runs, the reduction of the nitrogen oxides by the activated carbon (AC) deteriorates continuously, as shown for the breakthrough of $NO_x$ and $NO_2$ during the sixth loading cycle in

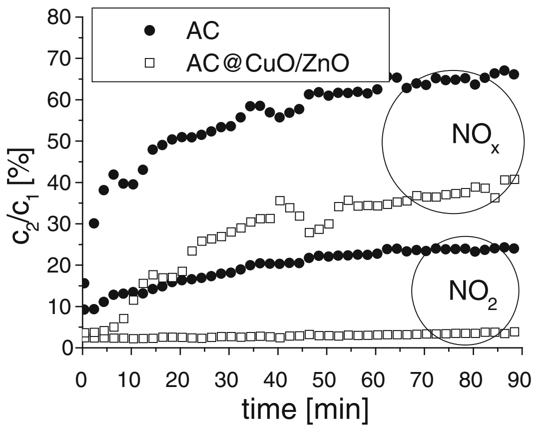

**Fig. 10** Breakthrough curves of NO$_x$ and NO$_2$ through AC@CuO/ZnO and AC during the 6th loading (23 °C, 50 % r. H., $c_1$ NO$_2$ = 4 ppm$_V$, v = 0.2 m/s)

Fig. 10. The breakthrough of NO$_x$ and NO$_2$ for AC@CuO/ZnO is considerably lower than for AC. This is particularly valid for the initial breakthrough. This indicates a better long-term stability of the modified activated carbon suggesting a regeneration of the carbon surface during the rest periods by the infiltrated catalysts.

The reactions taking place within the activated carbon could be tentatively summarized as follows.

$$NO_2 + AC \rightarrow AC - NO_2^{ads} \quad (1)$$

$$AC - NO_2^{ads} + C \rightarrow AC - NO^{ads} + CO \quad (2)$$

$$AC - NO^{ads} \rightarrow AC + NO \quad (3)$$

$$2CuO + CO \rightarrow Cu_2O + CO_2 \quad (4)$$

$$2NO + 2Cu_2O \rightarrow N_2 + 2CuO \quad (5)$$

In a first step, NO$_2$ gets adsorbed on the carbon walls within the pores of the activated carbon (1). Reduction of a certain fraction of NO$_2$ by the carbon then results in the formation of NO (2), which is then desorbed at least partially to the gas phase (3). Alternatively to reaction (2) disproportionation of NO$_2$ into HNO$_2$ and HNO$_3$ may take place due to coadsorption of water within the pores of the AC. This reaction would result in the formation of metal nitrites and nitrates. Inspection of the spent adsorbents by XRD showed no indication for such phases. This does not exclude the presence of nitrite or nitrate species on the surface of the metal oxides or as amorphous phases but shows that no crystalline nitrite or nitrate is formed to a larger extent. In a recent work it has been shown that copper oxide is able to oxidize carbon monoxide at room temperature (Pillai and Deevi 2006). If a similar reaction takes place in AC@CuO/ZnO, the formation of Cu$_2$O as an intermediate could be assumed (4). Finally, regeneration of CuO could proceed along with the formation of N$_2$ from NO over Cu$_2$O as the active species (5). The latter reaction has been shown to take place in CuO supported on activated carbon fibers at a temperature of 500 °C (Park and Kim 2005) but NO reduction over CuO-containing catalysts has also been reported to take place at a temperature as low as 100 °C with reasonable reaction rates (Hu et al. 2001). Thus, slow reduction of NO formed by reaction of NO$_2$ with the carbon is assumed to take place at room temperature during the prolonged rest periods within the AC@CuO/ZnO adsorbent.

## 4 Summary and conclusion

The aim of the present study was to develop an adsorbent for the application in cabin air filters that allows an efficient reduction of nitrogen dioxide. For this purpose, activated carbon beads have been successfully infiltrated with metal oxide catalysts by incipient wetness impregnation. XRD characterization confirmed the presence of CuO and ZnO catalysts particles in the range of 7–12 nm within the activated carbon and EXD mapping proved a uniform distribution of the metal oxides over the activated carbon particle. The specific surface area of the activated carbon decreased only slightly with the deposition of the oxides, mainly due to the additional weight of the oxides. The pore system remained basically open for adsorption processes. While the parent carbon and the modified material exhibited the same NO$_2$ removal efficiency in a first loading, the advantage of the new material developed in successive loading cycles. The breakthrough of NO$_x$ as well as of NO$_2$ remained more or less unchanged for the oxide-loaded carbon in successive runs, whereas the retention of these gases decreased significantly for the parent carbon. NO$_2$ is considered to primarily adsorb on the inner surface of the microporous activated carbon and then to react to NO with the carbon surface. Reduction of CuO by CO then could form Cu$_2$O that is active in the low temperature reduction of the formed NO. As the result of the reaction, NO$_2$ is catalytically transformed to CO$_2$ and N$_2$ on the activated carbon surface doped with CuO/ZnO. Thus, regeneration of the adsorbent was achieved. In summary, an active adsorbent for NO$_2$ reduction has been developed that was capable of regenerating itself during rest periods at room temperature. In order to reduce NO formation during breakthrough, infiltration of a second catalytically active phase into the activated carbon could be subject for further research.

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