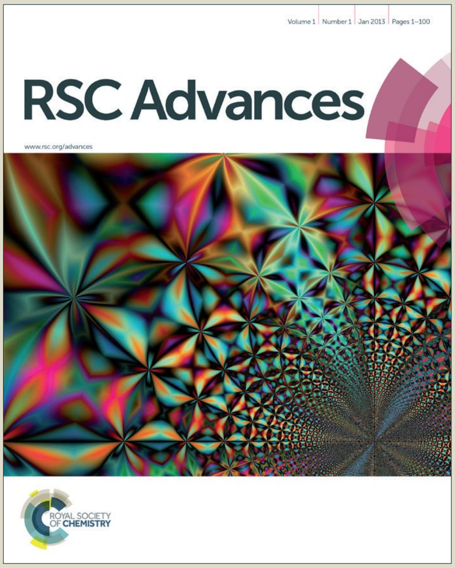
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Catalytic Oxidation of Nitric Oxide (NO) with Carbonaceous Materials

Yafei Shen [a] *, Xinlei Ge [a], Mindong Chen [a]

[a] *Jiangsu Engineering and Technology Research Center of Environmental Cleaning Materials (ECM), Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control (AEMPC), Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (AEET), School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China*

***Corresponding Author**

Email: yafeisjtu@gmail.com; 376754097@qq.com (Y. Shen);

Abstract

The catalytic oxidation of NO to NO_2 at ambient temperatures has been a promising route for controlling NO emissions, since NO_2 is subsequently removed as nitric acid in the presence of water. Because of their large surface area, high porosity, and relative chemical inertness, the carbon-based materials are very attractive in de-nitrification (De-NO_x) as catalysts or catalyst supports. This paper reviewed the catalytic oxidation of NO to NO_2 over the common-used carbon materials including activated carbons (ACs), activated carbon fibers (ACFs) and carbon xerogels (CXs). The NO conversion is often influenced by the surface characteristics of carbon materials (e.g., pore structure, surface areas, functional groups, and morphology), O_2 concentration, and reaction temperature. With the addition of metal actives, the catalytic performance could be significantly improved. Catalytic reaction and adsorption are two key points. Further, the strong dependence of NO conversion on the O_2 concentration concludes that O_2 is first adsorbed on the carbon surface, and then it reacts with NO to form adsorbed NO_2, which desorbs to the gas phase. Considering the economic efficiency, carbon precursor from biomasses could be fabricated into the desired carbonaceous materials by means of functionalization. In addition, the integrated strategy of desulfurization (De-SO_x) and De-NO_x could be developed by carbon materials with the proper modification methods.

Keywords: *NO oxidation; carbon catalysts; adsorption; nanofiber; activated char*

1. Introduction

Atmospheric contamination is one of the most significant environmental problems caused by the progressive industrialization of the planet [1]. Nitrogen oxides (NO_x) commonly derived from the combustion of fossil fuels or solid wastes are considered primary atmospheric pollutants, being responsible for a wide range of environmental problems such as photochemical smog, acid rain, tropospheric ozone and ozone layer depletion [2]. Furthermore, they cause serious health problems in humans [3]. Hence, many great efforts have been made to develop technologies for flue gas purification. As for NO_x removal, advanced flue gas treatment technologies are adopted, including dry and wet techniques. The dry techniques could be classified as selective catalytic reduction (SCR) by NH_3 at 300-500 ^oC [4], selective non-catalytic reduction (SNCR) [5], adsorption [6] and electron beam irradiation [7]. The wet techniques use scrubber columns in which NO_x is absorbed by absorbent.

The most popular NO_x abatement technology is SCR with ammonia (NH_3), but this process has several obvious drawbacks, such as high reaction temperatures (>300^oC) and un-reacted reducing agents [8]. Besides, typical NO_x emissions from combustion processes contain significantly more NO than NO_2, and the inclusion of NO oxidation step prior to the SCR process is useful for increasing SCR rates of reaction [9]. Thus, the catalytic oxidation of NO to NO_2 at ambient temperatures has been a promising route for controlling NO emissions, since NO_2 is subsequently removed as nitric acid in the presence of water [10-13]. The NO_2 absorption efficiencies can reach as high as 100% in water or basic solutions [14-17]. Consequently, oxidation of NO into NO_2 at lower temperatures (e.g., room temperature) has been a prospective high-efficiency step for the removal of NO. In particular, it is practicable to remove NO at ambient temperature in the presence of water vapor, thus much attention has been paid to the oxidation of NO into NO_2 [18-20].

NO oxidation is thermodynamically favorable below 200 ^oC, but kinetically limited

[21]. Oxidation strategies consist of homogeneous catalysis with oxidizing additives, and heterogeneous catalysis with unsupported metal oxides or supported catalysts [21-23]. Homogeneous gas-phase NO oxidation is unusual in that the reaction rate increases with the decrease of temperature from 273 to 600 K, resulting in a small but negative activation energy [24]. These techniques are generally effective, but the costs resulting from the use and potential release of hazardous chemicals, catalyst deactivation due to SO_2 poisoning, and thermodynamic limitations associated with necessarily high temperatures inhibit their application. Low temperature oxidation of NO coupled with absorption of NO_2 is an alternative NO_x abatement strategy. Such a strategy could avoid expenses associated with SCR (e.g., catalysts, gas reheating) and the threat of ammonia slip.

2. Carbon-catalyzed Oxidation

Carbon materials have been regarded as good catalysts for NO oxidation to NO_2 [25]. The surface chemistry of carbon materials often influences their adsorption, catalytic, acid-base and redox properties, as well as their hydrophilic or hydrophobic character. Hydrogen, oxygen, sulfur, nitrogen, and other elements could also be found on the activated carbon surface.

Catalytic oxidation of NO ($2NO + O_2 \rightarrow 2NO_2$) over microporous activated carbons combined with subsequent absorption process of NO_2 as a more soluble NO_x specie is an alternative to SCR. Compared with SCR, carbon catalyzed NO oxidation operates at low temperatures (<100 ^oC) and could potentially be used for simultaneous control of multiple pollutants [26]. While combination of NO oxidation with NO_2 absorption, a thorough understanding of the carbon-catalyzed NO oxidation is also important for improving NO reduction via fast SCR reactions [27, 28]. Since Mochida's initial studies introducing the carbon-catalyzed NO oxidation, extensive efforts have been taken on understanding the reaction mechanism. After twenty years, however, the mechanism continues to be debated [29-32]. The complexity of activated carbon (i.e., variability in the physical and chemical properties of activated carbon) and NO auto-oxidation

[33] make characterizing the NO oxidation mechanism challenging. The investigation of chemical functionalities on NO oxidation showed that oxygen functional groups can impact NO_2 adsorption capacity and transient oxidation kinetics [34-36].

The kinetics of heterogeneous catalysis mainly depends on: (1) reactant adsorption, (2) catalytic reaction at active sites, and (3) product desorption. The reaction rate, therefore, is influenced by the physical and chemical properties of the catalysts [37]. Proposed mechanisms for carbon-catalyzed NO oxidation are summarized as follows. Mochida [29-31] first investigated the influence of physical and chemical properties of carbon, as well as processing parameters (e.g., NO and O_2 concentrations, reaction temperature, and gas hourly space velocity), on steady-state NO oxidation kinetics. Mochida et al. [30] suggested that $[NO\text{-}O\text{-}NO_2]_{ad}$ is a crucial intermediate for NO_2 formation/desorption and that NO adsorption is the rate-determining step due to competition with desorbed NO_2 and intermediates. This mechanism, consistent with observed kinetic profiles, suggests that $(NO)_2$, NO_2, and $(NO_2)_2$ are not necessary as reaction intermediates [38]. Then, Adapa et al. [32] proposed Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) mechanisms for catalyzed NO oxidation. Herein, in the L-H mechanism, dissociated oxygen activated by carbon reacts with adsorbed NO. In the E-R mechanism, gaseous O_2 can directly react with NO adsorbed in micropores. Both mechanisms rely on the evolution of similar reactive intermediates, including C*-NO, C*-NO_2, C*-NO_3, and C*-NO-NO_3.

The mechanism of catalytic NO oxidation over carbonaceous materials is a complex process, since it involves multiple steps, including carbon gasification, oxidation of NO and the release of NO_2. Some reaction pathways have been proposed to explain the oxidation of NO into NO_2. Ahmed et al. [39] suggested that NO is oxidized by oxygen to NO_2 in the gas phase and then NO_2 is adsorbed on the carbon surface. However, the homogeneous oxidation of NO in the gas phase is too slow to account for the conversions observed with the activated carbon. Mochida et al. [40] proposed that NO is adsorbed, oxidized into adsorbed NO_2, which desorbs as NO_2. Since NO is a supercritical gas at ambient temperature, very little NO can be physically adsorbed. Zhang et al. [41] proposed that NO oxidation on the activated carbon is a micropore filling process with NO as the adsorbed species. Namely, the narrow micropores in activated carbon act as catalytic nanoreactors for NO oxidation. It is well known that narrow micropores are very important for gas adsorption [42-44]. Rathore et al. [45] defended that the gaseous NO and O_2 adsorb on the active sites of activated carbon fibers, followed by NO oxidation into adsorbed NO_2. The adsorbed NO_2 further reacts and forms various intermediates in the adsorbed phase, such as NO_3 and NO-NO_3. Finally, the NO-NO_3 adsorbed intermediate is desorbed into NO_2. It has also been proposed that NO reacts with the surface oxygen atoms present on activated carbons [46, 47]. However, this argument is difficult to reconcile with the literature, which refers that pre-adsorption of O_2 on carbon materials inhibits the removal of NO [39, 48, 49]. It is suggested that NO from the gas phase reacts with chemisorbed oxygen, forming the chemisorbed NO_2 [48]. The improvement of the catalytic performance of nitrogen-containing carbons in NO oxidation can be explained from the point of view of the electronic theory of catalysis. The extra π-electrons of nitrogen groups could facilitate the formation of NO_2 caused by molecular oxygen activation [50]. Activated carbons treated with nitric acid as well as with melamine are the most active for NO oxidation [51]. The catalyst bed is saturated with NO_2 resulting in a large increase in the NO outlet concentration. Meanwhile, breakthrough of NO_2 occurs, which results in vacant sites. Adsorption of O_2 on the new vacant sites may proceed only when NO_2 is desorbed to release these sites. Therefore, NO_2 desorption is the rate-limiting step [32].

In addition, Zhang [34, 52] proposed that NO_2 formed via the NO catalytic oxidation, decomposes and causes rapid oxidation of the carbon surface with subsequent NO_2 chemisorption. Furthermore, this proposed concept was extended by identifying and quantifying these generated oxygen groups, highlighting their contribution toward the acidity of carbon-based catalyst and describing their impact on transient NO oxidation kinetics [36]. In theory, all proposed NO oxidation mechanisms stress the significance of catalytic sites of carbon, the number of which should be proportional to accessible surface area of carbon. However, steady-state NO oxidation kinetics are independent of the accessible surface area of carbon [31]. Steady-state NO conversion efficiency increases with the increase of the NO concentration (i.e., [NO]). This Langmuir-type dependence on [NO] supports that the reaction is not limited by the availability of active sites. This is the opposite of SCR systems [53] and metal oxide catalyzed NO oxidation, where the steady-state NO conversion efficiency is inversely proportional to [NO] [54]. Further investigation into the carbon-catalyzed NO oxidation is necessary to address the role of the physical and chemical properties of carbon on transient and steady-state oxidation kinetics.

Recently, Zhang et al. [55] studied an updated mechanism of NO oxidation catalyzed by microporous activated carbon fiber cloth. The updated NO oxidation mechanism mainly consists of two consecutive steps: (1) NO_2 is rapidly formed through gas phase reactions between NO and O_2 in carbon micropores; formation and decomposition of $C^*–NO_x$ species [40], does not take place, and (2) newly formed NO_2 adsorbs to the carbon surface is associated with NO_2 reduction and development of $C^*–NO_x$ and $C^*–O$ functionalities. The physical properties of activated carbon control steady-state NO oxidation kinetics with chemical properties of carbon having no apparent impact. Additionally, carbon's adsorption and surface reaction tendencies impact transient conversions by allowing for destruction of the NO_2 product and regeneration of the NO reactant. The second mechanistic step diminishes as the carbon surface saturates with adsorbed NO_x species and oxygen functionalities. At steady-state, the carbon surface is saturated, preventing the further NO_2 reduction. In summary, the first step of the mechanism (NO oxidation in micropores) controls steady state NO oxidation kinetics, while the second step (NO/carbon surface reactions) controls transient NO oxidation kinetics.

3. Carbon-based Catalysts

Carbon-based materials including activated carbons, activated carbon fibers are very attractive in de-nitrification (De-NO_x) as catalysts or catalyst supports [56, 57]. Most researches involved in the De-NOx over carbon-based materials primarily focused on the removal or conversion of high concentration NO in flue gas [58, 59], and carbon materials were used as catalyst supports.

Porous materials of carbon molecular sieves are disordered forms of graphitic carbon produced from the pyrolysis and activation of organic materials at high temperatures [60]. These carbon materials have important applications in gas adsorption, catalysis, and phase separation [61]. Their porous structures typically contain combinations of micropores (<20 Å), mesopores (20-500 Å), and macropores (>500 Å) [60]. And these materials exhibit adsorption volumes and specific surface areas up to 0.5-0.8 cm^3/g and 700-1800 m^2/g, respectively [62]. Loiland et al. [63] studied the porous carbon molecular sieves for the NO oxidation based on the results of Artioli et al. [18], which suggested that many microporous solids could provide increased reactivity compared to the homogeneous phase reaction.

3.1. Activated Carbon (AC)

ACs have been widely used as adsorbents of gases and vapors, catalyst supports, and separation media [65, 66]. Their features for pollutant removal are large surface area, rich microporosity [67], and rapid adsorption velocity [68-71]. AC desulfurizer can be used for gas cleaning and H_2S removal by sorption enhanced catalytic oxidation at low temperatures [72]. Guo [25] studied the NO oxidation by the commercialized ACs, such as coconut-AC, pitch-ACF, polyacrylonitriale-ACF (i.e., PAN-ACF and PAN-ACF_{KOH}) using the dry gas of NO-O_2-N_2 at 30 ^oC. The steady-state conversion of NO to NO_2 mainly depends on the O_2 concentration, the temperature and the properties of AC.

NO conversion with various ACs versus the O_2 concentration is shown in Fig. 1. The oxidation of NO to NO_2 obviously increased with the increase of O_2 concentration with ACF. However, the dependence is not obvious with the coconut-AC. Even in the presence of 2% O_2, the NO conversion can reach 83% by AC. The pitch-ACF showed the higher activity than the PAN-ACF for the oxidative removal of NO. In the same gas space flow rate of 1500 h^{-1}, the order of activity is PAN-ACF < pitch-ACF < coconut-AC. Interestingly, the coconut-AC shows very high activity for the oxidation of NO to NO_2 even with the low concentration of O_2. This suggests that oxidative removal of NO by ACs could be a compatible process for industry. In addition, ACs have higher strength and lower cost than ACFs [25].

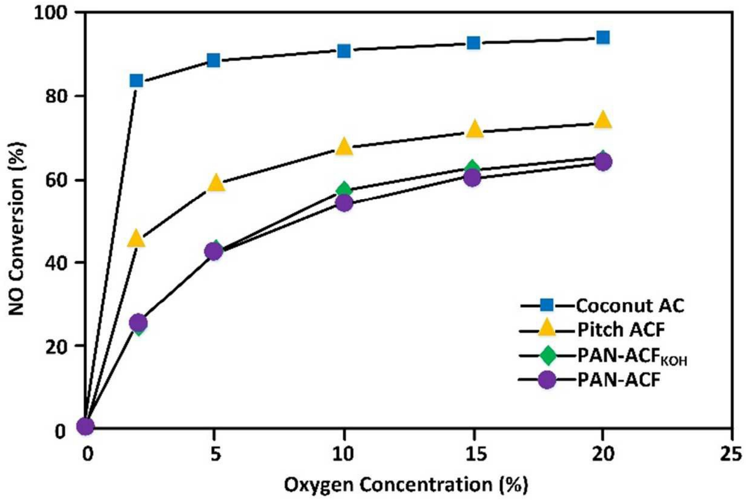


Figure 1. NO conversion in steady state versus O_2 concentration by different ACs at 30 °C for the dry gas with 400 ppm NO and space flow rate 1500 h^{-1}. (Reproduced from Ref. 25 with permission from Elsevier)

The overall oxidation reaction of NO to NO_2 in a dry gas is expressed as: $NO + 1/2O_2 = NO_2$. And the oxidation reaction rate of NO in a dry gas can be given by the following kinetic equation: $r = kP_{NO}^{\alpha}P_{O2}^{\beta}$.

where k is a reaction rate constant, α and β are the apparent reaction orders. By fitting the data in Fig.1, the reaction rates were determined to be 0.042, 0.16 and 0.31 with the order of the O_2 concentration for the coconut-AC, the pitch-ACF and the PAN-ACF, respectively. The conversion rate R (mmol/min · g) of NO to NO_2 in dry gas on AC at 30 °C can also be given by the following equation:

$$R = k_c P_{NO} P_{O2}^{\beta}(F/W)$$

where k_c is the apparent rate constant, being 0.94, which is calculated by the slope in Fig.2. P_{NO} and P_{O2} are the partial pressure (atm) of NO and O_2 in dry gas, respectively. The values of β are 0.042, 0.31 and 0.16 for the coconut-AC, the pitch-ACF and the PAN-ACF (including PAN-ACF_{KOH}), respectively. *F* is gas flow rate (ml/min) and *W* is the weight of AC (g).

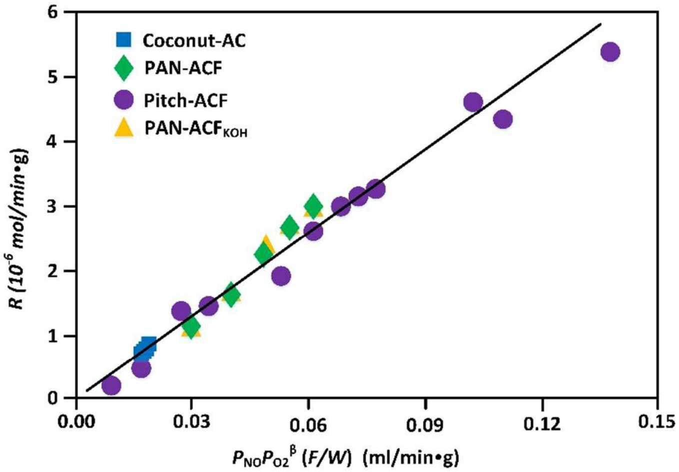


Figure 2. Apparent reaction rate versus $P_{NO}P^{\beta}_{O2}$ (F/W) of NO oxidation in dry gas on ACs at 30 °C. (Reproduced from Ref. 25 with permission from Elsevier)

Recently, there has been an increasing interest for N-doped carbon materials [73-78]. The presence of nitrogen atoms in the carbon matrice could enhance the catalytic activity of carbon materials in oxidation reactions and increase the ability to adsorb acidic gases [79, 80]. The effect of nitrogen doping of carbons on catalytic properties could be attributed to two overlapping effects, catalysis by basic surface sites and by electron donation [81]. Nitrogen containing functionalities confer basic properties to the surface of AC, which enhance the interaction with acid molecules [77]; moreover, the extra electrons can be transferred to adsorbed species [82].

The nature and concentration of functional groups present on the surface of AC mainly depend on the activation method in the synthesis, but they can be modified by thermochemical treatments [83]. Nitrogen groups can be often introduced to the structure of AC by treatments with urea in the liquid phase or with ammonia in the gas phase at high temperatures [84, 85]. Sousa et al. [18, 51] modified the AC with a high density of surface nitrogen Lewis basic sites for NO oxidation. The incorporation of nitrogen can significantly improve the catalytic activity of the modified AC. The NO conversion increased with the nitrogen content is associated with electron transfer from the carbon surface to the NO molecules. Stöhr et al. [84] found that ammonia treatment of the carbon surface can facilitate the chemisorption of molecular oxygen. According to them, when carbon atoms are substituted by nitrogen atoms within the graphene layers, the extra electrons can be easily transferred to the adsorbed species, forming reactive surface intermediates. The highest amount of NO oxidized at room temperature was achieved with the highest amount of nitrogen containing groups [86].

O_2 concentration can strongly influence the NO oxidation over carbon materials. O_2 is first chemisorbed on the surface (Eq. 1) and then NO reacts with surface O_2 to form NO_2 adsorbed on the carbon surface (Eq. 2). O_2 favours the formation of new active sites on the surface of carbon material for NO adsorption. Formation of a NO dimer $(NO)_2$ has been proposed as a possible mechanism to explain the reduction of NO to N_2 at low temperatures (Eq. 3). The formation of $(NO)_2$ occurs as the concentration of strongly adsorbed NO is high and there is a higher probability that two NO molecules could be located adjacently to form a $(NO)_2$ dimer.

$$2C_f + O_2 \rightarrow 2C\text{-}O \qquad (1)$$

$$C\text{-}O + NO \rightarrow C\text{-}NO_2 \qquad (2)$$

$$(NO)_2 + 2C_f \rightarrow N_2 + C_f\text{-}O \qquad (3)$$

The formation of N-N and C-O bonds, followed by splitting of N-O bonds to produce a N_2 molecule. These reactions are exothermal, which means that they are favored at lower temperatures. To assess the influence of the nitrogen groups, the amount of NO converted, normalized by the surface area, was plotted against the nitrogen content of the AC as shown in Fig. 3. It can be indicated that the presence of nitrogen groups enhances the oxidation of NO to NO_2. The extra electrons resulting from the substitution of C for N in the aromatic ring are delocalized and can be transferred to absorbing species to form reactive surface intermediates [87].

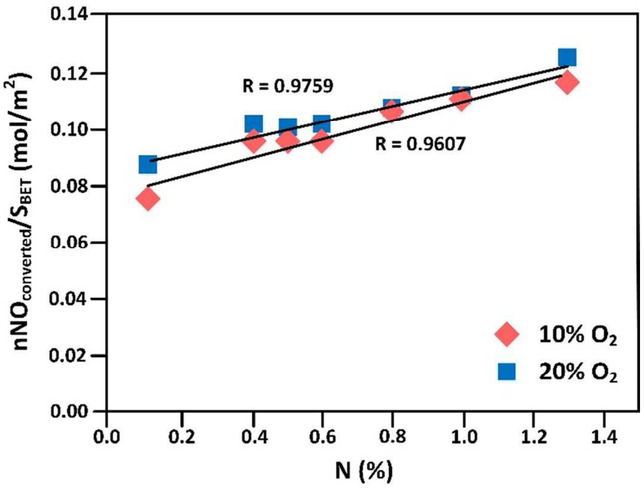


Figure 3. Amount of NO converted per unit surface area versus nitrogen content of the AC. (Reproduced from Ref. 18 with permission from Elsevier)

3.2. Activated Carbon Fiber (ACF)

ACFs have been widely used as adsorbents and catalysts supports due to their micro porous texture having large surface area, significant adsorption characteristics for a number of air pollutant species, and ability of regeneration with ease. Besides, ACFs have flexibility to be applied in reactors, where they can be wrapped or rolled easily [32]. Two possible states of O_2 can be considered, either dissociately adsorbed on the surface or molecular in the gaseous phase, in the mechanism for the oxidation of NO by ACF. Table 1 presents the two possible mechanisms of NO oxidation over carbon catalysts. As for the Langmuir-Hinshelwood model (mechanism 1), gaseous NO and O_2 are assumed to adsorb on the vacant active sites of ACF, followed by oxidation of NO into adsorbed NO_2. Subsequently, the adsorbed NO_2 reacts and forms various intermediates such as, NO_3 and NO-NO_3 in the adsorbed phase. Finally, the adsorbed intermediate NO-NO_3 is desorbed into NO_2 from the surface, thereby releasing the vacant sites for adsorption of successive molecules of adsorbates. In accordance with the Eley-Rideal model (mechanism 2), adsorbed NO could be assumed to react with the gaseous O_2 (instead of adsorbed O_2) and yield the adsorbed NO_2. The subsequent reactions of adsorbed NO_2 are proposed to proceed similar to those outlined for mechanism 1.

Table 1. Possible mechanisms of NO oxidation to NO_2 over carbon catalysts

Mechanism 1	**Mechanism 2**
$NO + C_f \leftrightarrow C\text{-}NO$ (a)	$NO + C_f \leftrightarrow C\text{-}NO$ (a)
$O_2 + 2C_f \leftrightarrow 2C\text{-}O$ (b)	$2C\text{-}NO + O_2 \leftrightarrow 2C\text{-}NO_2$ (b)
$C\text{-}NO + C\text{-}O \leftrightarrow C\text{-}NO_2 + C_f$ (c)	$C\text{-}NO_2 + C\text{-}NO_2 \leftrightarrow C\text{-}NO_3 + NO + C_f$ (c)
$C\text{-}NO_2 + C\text{-}NO_2 \leftrightarrow C\text{-}NO_3 + NO + C_f$ (d)	$C\text{-}NO_3 + C\text{-}NO \leftrightarrow C\text{-}NO\text{-}NO_3 + C_f$ (d)
$C\text{-}NO_3 + C\text{-}NO \leftrightarrow C\text{-}NO\text{-}NO_3 + C_f$ (e)	$C\text{-}NO\text{-}NO_3 \rightarrow 2NO_2 + C_f$ (e)
$C\text{-}NO\text{-}NO_3 \rightarrow 2NO_2 + C_f$ (f)	

Zhang et al. [36, 55] studied the mechanism and kinetic of NO oxidation by ACF cloth. To date, most carbon-catalyzed NO oxidation studies aim to maximize steady-state NO conversion rates. There has been limited emphasis on accelerating the path to achieving steady-state conversions, which involves at least co-adsorption of NO and O_2, catalytic reaction, and subsequent desorption of formed NO_2 [40]. To improve this facet of the carbon catalysts, studies describing the interfacial catalytic reactions between NO_x and carbon are required. The impact of surface functional groups (e.g., nitrogen, oxygen) on AC has been studied the interactions between NO_x and carbon [18, 48, 88]. Oxygen functionalities are retained on carbon due to the decomposition of formed NO_2 intermediates over the reducing carbon surface [79]. The formation of oxygen groups can impact NO/NO_2 adsorption/desorption kinetics, accelerating the release of NO_2 from the carbon surface. In Atkinson's work [36], the acidic oxygen functional groups on ACF cloth are developed for NO oxidation. Carbon catalysts with acidic oxygen functionalities has been considered as promising NO oxidation catalysts, as confirmed with NO_2 and nitric acid treatments. In general, chemical properties of carbon materials impact NO oxidation kinetics, while physical properties impact the steady-state NO oxidation rate.

Wang et al. [89] verified that NO can be catalytically oxidized into NO_2 over activated carbon nanofibers (ACNFs). After further graphitized at high temperature, graphitized porous carbon nanofibers (GPNF) is formed. The catalytic efficiency of NO oxidation could be enhanced remarkably at ambient temperature [90]. The morphology of the ACNFs is shown in Fig. 4. The average fiber diameter of ACNF without graphitization is in the range of 200-300 nm, and the surface is clean and smooth (Fig. 4A). After graphitization, the fiber diameter shrank visibly due to the burn-off and ordering of graphite layers at higher temperatures of 1900 ^{o}C and 2400 ^{o}C (Fig. 4, B and C). Moreover, the surface of GPNFs became rough with some wrinkle and small holes.

TEM analysis can provide more insights into the stacking of graphite layers, and the crystallographic changes in ACNFs can be directly acquired. As shown in Fig. 4, D-F, compared with the non-graphitized ACNF, great changes occurred in the inner layer where the graphite sheets became stiff and amorphous carbon layer in outer-layer became thinner. With the increase of graphitization temperature, the graphite sheets in inner layer were arranged in order and more continuous, and the orientation of disorganized hexagonal surface of crystallite became ordered. Interestingly, some new defects appeared in the surface and end of the graphite sheets. The defects in ACNFs are derived from the dangling bonds, which are saturated with oxygen functionalities. However, graphitization can remove those functionalities to form new defects at the surface of fibers. Due to the high degree of graphitization and defects, GPNFs can provide more active sites for the catalytic oxidation of NO transformation into NO_2. In particular, the NO oxidation ratio for ACNFs, GPNF-1900 and GPNF-2400 was 11%, 38%, 45%, respectively, revealing that the GPNFs could be used as promising catalysts in catalytic oxidation of NO at room temperature.

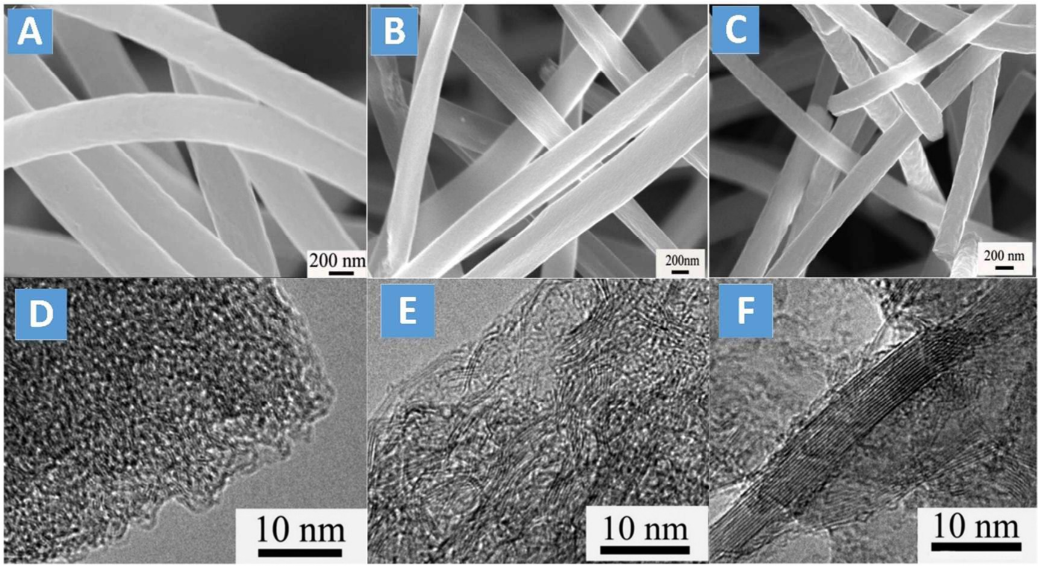


Figure 4. SEM images of ACNF (A), GPNF-1900 (B) and GPNF-2400 (C); TEM images of ACNF (D), GPNF-1900 (E) and GPNF-2400 (F). (Reproduced from Ref. 90 with permission from Elsevier)

The graphitic CNFs (pyrolytically stripped) were found to be the most active in the catalytic process followed by heat treatment from 1500 to 3000 ^{o}C [91]. For example, it was proved that activated polyacrylonitrile carbon nanofibers (PCNFs) to determine effect of high temperature treatment on their catalytic activity during the oxidation of NO to NO_2 [90]. The oxidation conversion could be significantly improved by using graphitized PCNFs, but this method always requires higher temperatures [92, 93] that is not economical due to energy consumption; therefore it is necessary to prepare CNFs with similar structure that can be formed at low temperatures.

Graphene is a commercially attractive material that possesses a large theoretical specific surface area [94-98], a high Young's modulus, good thermal conductivity and good electrical conductivity that could be used for a variety of potential applications including in transparent conductive electrodes [99, 100]. More recently, Guo et al. [101] prepared microdomain-graphitized polyacrylonitrile (PAN) nanofibers by adding the graphene oxide (GO) into the precursor via the electrospinning method. These electrospun nanofibers were stabilized in ambient atmosphere, carbonized in N_2 and treated in NH_3 atmosphere for NO oxidation with a low concentration (50 ppm) at room temperature. The GO nanosheets can be embedded in the electrospun fibers and converted to reduced graphene oxide (rGO) by heat treatment (namely PGCNFs as illustrated in Fig. 5J). A series of rGO content was embedded in the PCNFs forming a carbon-carbon hybrid material that showed a microdomain-graphitized and porous structure. SEM images of the PCNF and PGCNF samples are shown in Fig. 5, A-F. The samples experienced instantaneous cyclization, dehydrogenation and cross-linking reactions in the presence of O_2, thereby creating nanofibers that are infusible at higher temperatures [102, 103]. The PCNFs are homogeneous, and smooth with average diameters of approximately 200 nm. With the addition of GO, the surface of the PGCNFs becomes coarser. Furthermore, large amounts of tiny rGO fragments are embedded inside the PCNFs and are not externally visible. However, the large-scale GO sheets with lateral dimensions of 0.5-1.0 µm cannot be enclosed completely by the PCNFs resulting in the presence of some ‘‘rose-like’’ nodes on the surfaces of the materials. The rGO sheets provide catalytic active sites embedded inside the PCNFs. In addition, the nitrogen-containing functional groups can play important roles on the enhancement of the catalytic oxidation of NO to NO_2. As shown in Fig. 5, G-I, the samples with 5 wt.% GO exhibit the most catalytic oxidation of NO into NO_2.

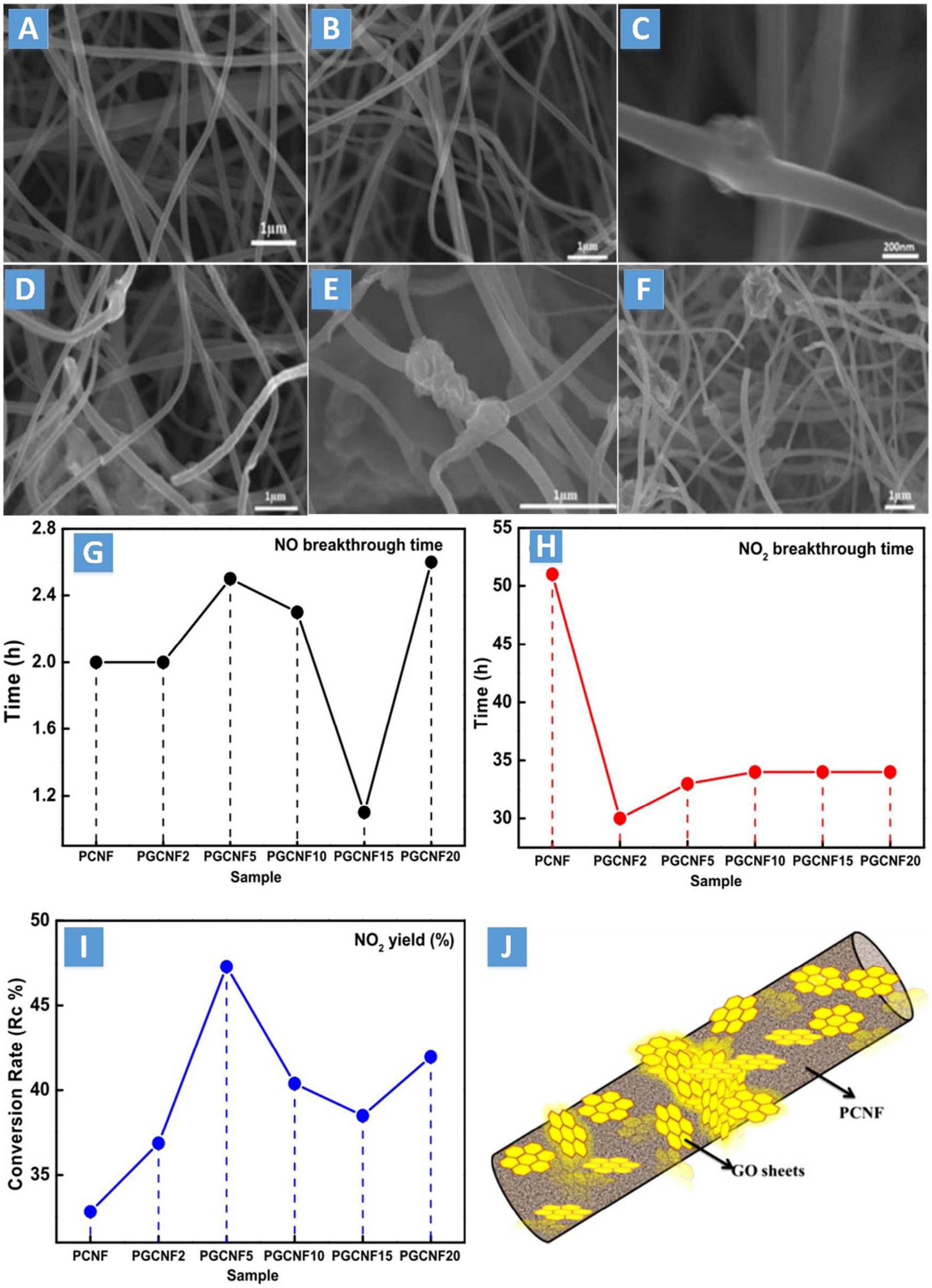


Figure 5. SEM images of PCNF and PGCNF samples: (A) PCNF, (B) PGCNF2, (C) PGCNF5, (D) PGCNF10, (E) PGCNF15, and (F) PGCNF20. Variations in (G) NO breakthrough time, (H) NO_2 breakthrough time and (I) NO to NO_2 conversion rate of the PCNF and PGCNF samples. The numerals following PGCNF reflect the wt.% of GO incorportation. (J) Schematic of a microdomain-graphitized PCNF. (Reproduced from Ref. 101 with permission from Elsevier)

The superiority of CNFs over ACFs in catalytic and adsorption applications lies in the higher stability of CNFs in acidic/basic media and chemical activity [104-107]. ACF- or CNF-supported metal catalysts can be also used in the abatement of NO emissions by oxidation or reduction [89, 90, 108]. Talukdar et al. [109] developed the CeO_2 and Cu nanoparticles dispersed in CNFs/ACFs for the removal of NO by catalytic oxidation at room temperature. The CNFs/ACFs were prepared by means of growing CNFs on an ACF substrate via catalytic chemical vapor deposition (CVD). Subsequently, CeO_2 and Cu nanoparticles could be in situ incorporated into the ACFs prior to CVD. The Cu nanoparticles can therefore play dual roles: (1) catalyzing the growth of CNFs and (2) catalyzing the oxidation of NO to NO_2. CeO_2 had a promotional effect on the catalytic activity of Cu through the release of nascent oxygen during the redox cycle and a synergistic interaction with the Cu nanoparticles.

Oxygen is dissociatively adsorbed on the vacant sites of ACFs. It reacts with the NO adsorbed on the adjacent sites to produce NO_2. Then, the adsorbed NO undergoes transformations to produce intermediate surface complex and NO_2, leaving behind the active sites for successive adsorption. The redox reaction involving the synergistic interaction between Ce^{3+} and Cu^{2+} produces lattice oxygen and restores the oxidation state (4+) of Ce in CeO_2. Fig. 6 schematically illustrates adsorption/desorption of the reacting species and the synergistic interaction between CeO_2 and Cu nanoparticles. The proposed mechanism for the reaction, $2NO + O_2 \rightarrow 2NO_2$ is as follows.

The catalytic oxidation of NO over CeO_2-Cu-CNFs/ACFs consists of two simultaneous steps. Step A involves the adsorption-desorption of NO and O_2 on the CNFs/ACFs and catalytic oxidation of NO to NO_2.

$$NO + X \rightleftharpoons NO\text{-}X \qquad (4)$$

$$O_2 + 2X \rightleftharpoons 2O\text{-}X \qquad (5)$$

$$NO\text{-}X + O\text{-}X \rightleftharpoons NO_2\text{-}X + X \qquad (6)$$

$$2NO_2\text{-}X \rightleftharpoons NO_3\text{-}X + NO + X \qquad (7)$$

$$NO_3\text{-}X + NO\text{-}X \rightleftharpoons NO_3\text{-}NO\text{-}X + X \qquad (8)$$

$$NO_3\text{-}NO\text{-}X \rightarrow 2NO_2 + X \qquad (9)$$

Step B involves the release of nascent oxygen and synergistic interaction between CeO_2 and Cu nanoparticles.

$$2CeO_2 \rightarrow Ce_2O_3 + O_{(lattice)} \qquad (10)$$

$$Ce^{3+} + Cu^{2+} \rightarrow Ce^{4+} + Cu^{+} \qquad (11)$$

$$Cu^{+} + 1/2O_2 \rightarrow Cu^{2+} + O^{-}_{(adsorbed)} \qquad (12)$$

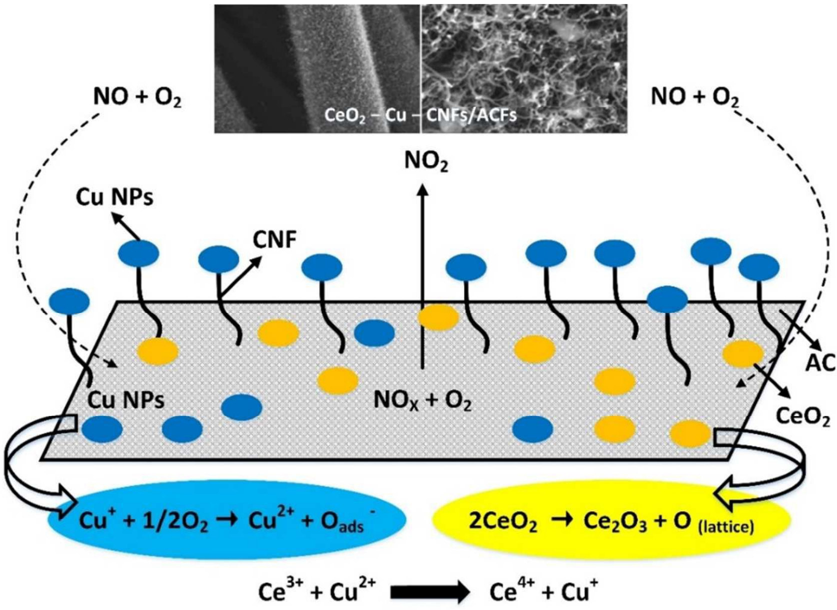


Figure 6. Schematic diagram of the adsorption − desorption reaction and synergistic interaction between CeO_2 and Cu. (Reproduced from Ref. 109 with permission from the American Chemistry Society)

Fig. 7 presents the comparative performances of the ACFs/CNFs based materials for the NO oxidation. The catalytic performances were found to be in the following order: CeO_2-Cu-CNFs/ACFs > Cu-CNFs/ACFs > Cu-ACFs > CeO_2-ACFs > ACFs. The synergistic interaction between the Cu nanoparticles and CeO_2 enhanced the oxidation rate. The maximum NO conversion using the CeO_2-Cu-CNFs/ACFs developed was 80% for a 500 ppm NO concentration at room temperature (30 °C). Generally, loading some specific metal actives could enhance the catalytic performance for NO conversion. However, the synergistic interaction is considerable for the preparation of metal loaded carbon catalysts.

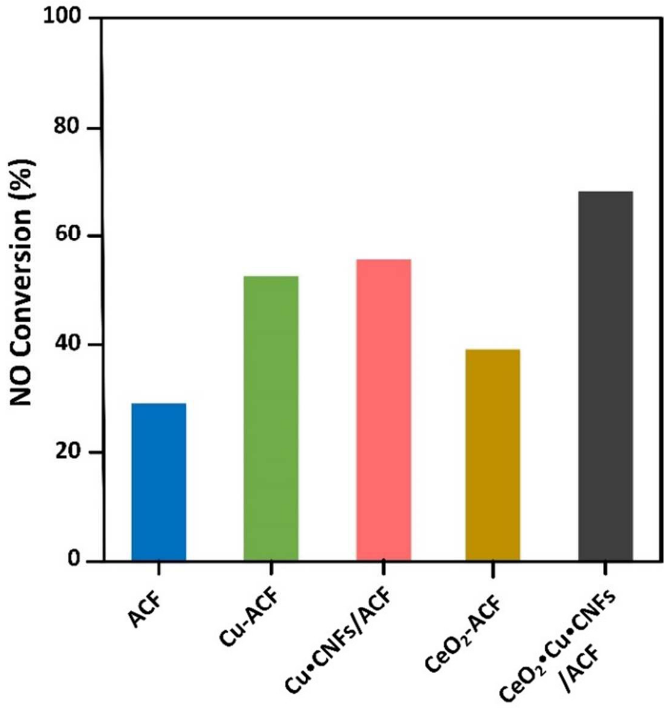


Figure 7. Comparative performance of the prepared materials in the oxidation of NO (T = 30 °C, P = 1 bar, W = 1 g, NO = 1000 ppm, Q = 37.5 sccm, O_2 = 20%). (Reproduced from Ref. 109 with permission from the American Chemistry Society)

3.3. Carbon Xerogel (CX)

CXs have been considered as novel porous carbon materials that can be obtained from carbonization of organic xerogels prepared by sol-gel polycondensation of some specific monomers, such as resorcinol and formaldehyde, following Pekala's method [110]. A polycondensation reaction can occur between resorcinol and formaldehyde, yielding a three-dimensional polymer matrix, the RF hydrogel. After solvent exchange and drying, followed by carbonization, CX is obtained. Subsequent activation can be used for modification of the surface properties of the material [111]. In addition, CXs can be prepared with other monomer combinations, such as melamine/formaldehyde/resorcinol, phenol/furfural, urea/formaldehyde/resorcinol or polyurethane [112]. If nitrogen containing precursors (i.e., melamine and urea) are used, CXs enriched with non-reactive nitrogen located in the graphene sheets can be obtained as well [113, 114].

Sousa et al. [48, 115] studied the CXs with or without nitrogen-doped treatment for the catalytic oxidation of NO. The strong dependence of NO conversion on the O_2 concentration results in the conclusion that O_2 is first adsorbed on the surface of CXs, and then it reacts with NO to form adsorbed NO_2. Finally, NO_2 can desorb to the gas phase (as illustrated in Fig. 8A). Fig. 8B shows the effect of O_2 concentration on NO conversion at 25 ^{o}C. In the presence of O_2, the carbon materials catalytically oxidize NO with rates larger than those of the homogeneous oxidation (36% for 20% O_2). The oxidation of NO to NO_2 increases with the increase of O_2 concentration from 2% to 10%. Further increase of O_2 concentration from 10% to 20% does not affect so much the conversion. Even in the presence of 2% O_2, the NO conversion can reach 86% with sample CX-5.3-900 ^{o}C. The maximum NO conversion can be obtained when 10% of O_2 was used. Above the optimum O_2 concentration, the NO conversion levels off ascribed to saturation of the adsorption sites with atomic oxygen. The highest NO conversion was obtained on CX-5.3-900 ^{o}C with 10% of O_2 (98%). The CXs showed a high stability for the NO oxidation. With 1000 ppm of NO and 10% of O_2 over the most efficient catalyst (namely CX-5.3-900 ^{o}C), a steady-state conversion is reached after 26 h of reaction (98%), and does not change thereafter (Fig. 8C) [115]. The removal of NO by the catalytic oxidation of NO to NO_2 on CXs is feasible at relatively low temperatures. Generally, NO conversion increases with the O_2 concentration in the gas phase. The highest NO conversions were obtained by the samples with the highest specific surface areas. In a steady state, the micropores are occupied with NO_2 adsorbed, so only the mesopore surface area is available for reaction.

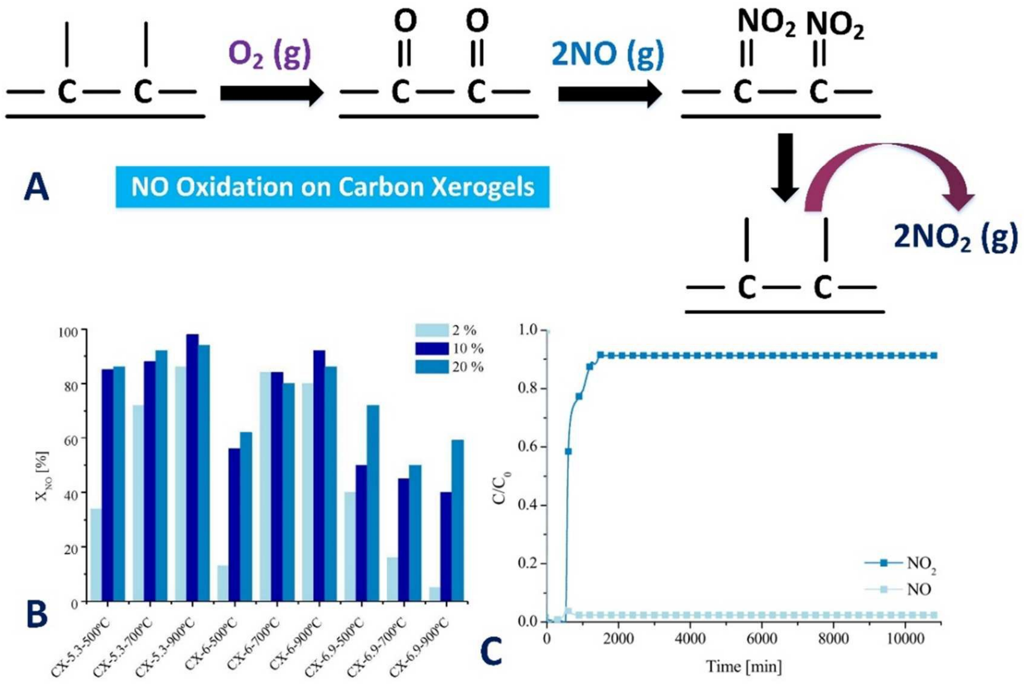


Figure 8. (A) Simplified scheme of NO oxidation on CXs; (B) Effect of O_2 concentration on NO conversion at 25 ^{o}C; (C) Evolution of profiles of NO and NO_2 during one week of reaction with sample CX-5.3-900 ^{o}C. (Reproduced from Ref. 115 with permission from the MDPI)

3.4. Other Carbon Materials

Carbon plays a dual role as a catalyst or a catalyst support due to its large specific surface area, high porosity, and relative chemical inertness. Advantageously, carbon materials can be prepared from biomass, an attractive property for decreasing the so-called “carbon-footprint” of a biomass transformation process. Carbon could be chemically functionalized and/or decorated with metallic nanoparticles and enzymes to impart or improve novel catalytic activity [116]. Furthermore, the development of multifunctional catalysts, possibly originated from more emerging carbon materials such as graphene, carbon nanotubes, and carbon monoliths is also required for deep theoretical study of NO oxidation. However, a relative economical carbon catalyst is urgently developed for industrialization. In addition, carbon precursors derived from residual biomasses could be fabricated into the desired carbonaceous materials by functionalization [117].

Biochar is a by-product from thermal processing of biomass, such as hydrothermal carbonization, pyrolysis, and gasification [118]. Additionally, biochar is considered as a sustainable carbon material, which could be employed as a sorbent or a catalyst for environment and energy applications, including gas cleaning [119]. To date, several works have been conducted for the NO_x reduction with char [120-124]. Most of them focused on the NO reduction over the char materials at higher temperatures. NO can react with carbon atoms in char to produce N_2 and CO. A few work has been done for the NO oxidation by char-based materials. As mentioned above, Guo et al. [25] used the commercialized AC prepared from coconut char (namely coconut-AC) for the NO oxidation. Moreover, the coconut-AC shows very high activity for the oxidation of NO to NO_2 even with the low concentration of O_2. In common, biochars possess many nitrogen or oxygen groups such as $–NH_2$/–OH, C–O, C=O, possibly contribute a lot on the adsorption performance and catalytic activity. Besides, inherent minerals in the char matrice show a certain specific catalytic effects [119]. However, the property of char is often unstable, mainly depending on biomass types, processing methods, etc.

Chemical activation is one of the most effective ways to modify the characteristics of char. Chen et al. [125] used KOH and $ZnCl_2$ as activation agents to produce activated char, which can be used for De-NO_x process. Sewage sludge were impregnated with the activation agent before the pyrolysis step. In this study, SO_2, NO, N_2O and HCl are main emissions from sewage sludge pyrolysis volatile combustion, in accordance with coals combustion. SO_2 emission can be avoided by impregnation of KOH and $ZnCl_2$. Activated char derived from the KOH-impregnated sewage sludge exhibited the best De-NO_x performance. In the previous studies, the pitch-based ACFs showed higher De-SO_x activity than other ACFs derived from different precursors. De-SO_x activity can be further modified by the heat-treatment, continuous and complete removal of SO_x. ACF is also effective for removing NO_x in the presence of NH_4 [58]. Furthermore, De-SO_x and De-NO_x could be achieved by using microwave irradiation over AC-based catalysts. It showed that adsorption capacities and removal efficiencies of Cu-based AC catalyst were higher than Mn-based or Zn-based AC catalyst [126]. Nanoporous molecular basket sorbent was developed for NO_2 and SO_2 capture and separation from gas streams at room temperature based on polyethylene glycol (PEG)-loaded mesoporous molecular sieve SBA-15 [127]. Consequently, the integrated strategy of De-SO_x and De-NO_x could be achieved by porous carbon materials including activated char with the proper modification.

4. Concluding Remarks

The catalytic oxidation of NO to NO_2 at ambient temperatures has been a promising route for controlling NO emissions, since NO_2 is subsequently removed as nitric acid in the presence of water. Because of their large specific surface area, high porosity, and relative chemical inertness, the carbon-based materials including ACs, ACFs are very attractive in De-NO_x as catalysts or catalyst supports. However, the catalytic oxidation of NO to NO_2 is still in its early stage of development and therefore there are many aspects that require additional research. The catalytic oxidation of NO to NO_2 over these carbonaceous materials is mainly determined by the influence parameters of surface characteristics of carbon materials (e.g., pore structure, specific surface area, functional groups, and morphology), O_2 concentration, and reaction temperature as described in Fig. 9. Additionally, in addition of specific metal actives, the catalytic performance could be significantly improved. Adsorption and catalytic reaction are two key points of NO oxidation over carbon-based materials. Furthermore, the strong dependence of NO conversion on the O_2 concentration concludes that O_2 is first adsorbed on the carbon surface, and then it reacts with NO to form the adsorbed NO_2, desorbing to the gas phase thereafter.

Consideration of the economic efficiency, carbon precursor derived from sustainable biomass can be fabricated into the desired carbon materials through functionalization. For example, biochar is considered as a sustainable carbon material that can be used as a sorbent or a catalyst support for gas cleaning. To date, only a few works have been conducted for the NO_x reduction by char. In the future, more research works should be done for NO oxidation over char-based materials with and/or without activation. In addition, the integrated strategy of De-SO_x and De-NO_x could be developed by carbon materials with the proper modification methods.

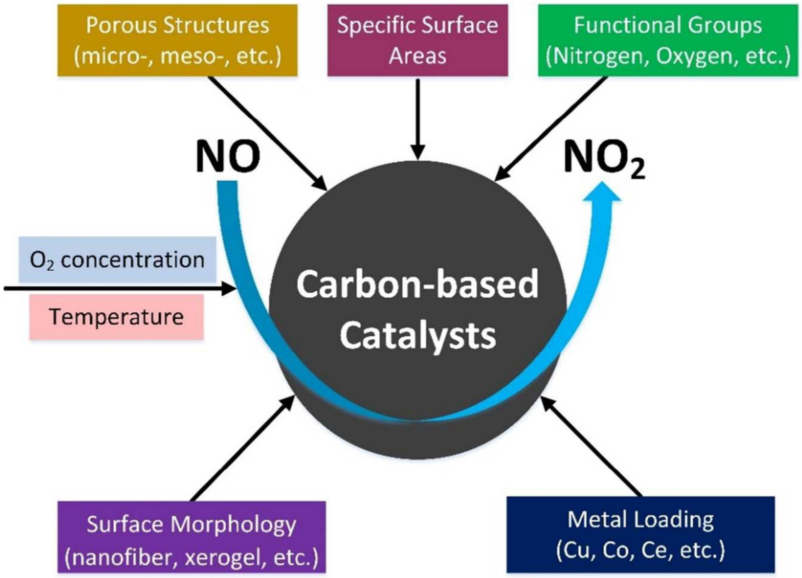


Figure 9 Influence parameters on oxidation of NO to NO_2 over carbon-based catalysts

Acknowledgements

This work is supported by the *Startup Fund for Talents* at NUIST under Grant No. 2243141501046. The authors are grateful to the financial supports by the National Science Foundation of China (21407079, 21577065, 91543115 and 91544220).

References

[1] J. Zawadzki, M. Wisniewski, K. Skowronska, Heterogeneous reactions of NO_2 and NO-O_2 on the surface of carbons. *Carbon* 2003, 41, 235-246.

[2] M. Wojciechowska, S. Lomnicki, Nitrogen oxides removal by catalytic methods, *Clean Products and Processes* 1999, 1, 237-242.

[3] A. Fritz, V. Pitchon, The current state of research on automotive lean NO_x catalysis. *Appl. Catal. B: Environ.* 1997, 13, 1-25.

[4] N.Y. Topsoe, H. Topsoe, J.A. Dumesic, Vanadia/Titania catalysts for selective catalytic reduction (SCR) of nitric-oxide by ammonia: I. Combined temperature-programmed in situ FTIR and on-line mass-spectroscopy studies. *J. Catal.* 1995, 151, 226-240.

[5] B. Leckner, M. Karisson, K. Dam-Johansen, C.E. Weinell, P. Kilpinen, M. Hupa, Influence of additives on selective noncatalytic reduction of NO with NH_3 in circulating fluidized bed boilers. *Ind. Eng. Chem. Res.* 1991, 30, 2396-2404.

[6] H.Y. Huang, R.T. Yang, Removal of NO by reversible adsorption on Fe-Mn based transition

metal oxides. *Langmuir* 2001, 17, 4997-5003.

[7] D. Ighigeanu, D. Martin, E. Zissulescu, R. Macarie, C. Oproiu, E. Cirstea, H. Iovu, I. Calinescu, N. Iacob, SO_2 and NO_X removal by electron beam and electrical discharge induced non-thermal plasmas. *Vaccum* 2005, 77, 493-500.

[8] J. Muñiz, G. Marbán, A.B. Fuertes, Low temperature seletive catalytic reduction of NO over modified activated carbon fibres. *Appl. Catal. B: Environ.*1999, 23, 25-35.

[9] M.F. Irfan, J.H. Goo, S.D. Kim, Co_3O_4 based catalysts for NO oxidation and NO_x reduction in fast SCR process. *Appl. Catal. B: Environ.* 2008, 78, 267.

[10] A.A. Verma, S.A. Bates, T. Anggara, C. Paolucci, A.A. Parekh, K. Kamasamudram, A. Yezerets, J.T. Miller, W.N. Delgass, W.F. Schneider, F.H. Ribeiro, NO oxidation: A probe reaction on Cu-SSZ-13. *J. Catal.* 2014, 312, 179-190.

[11] I. Ellmers, R.P. Velez, U. Bentrup, A. Brückner, W. Grünert, Oxidation and selective reduction of NO over Fe-ZSM-5 – How related are these reactions? *J. Catal.* 2014, 311, 199-211.

[12] Y. Kong, C.Y. Cha, Reduction of NO_x adsorbed on char with microwave energy. *Carbon* 1996, 34, 1027-1033.

[13] A. Claudino, J.L. Soares, R.F.P.M. Moreira, H.J. José, Adsorption equilibrium and breakthrough analysis for NO adsorption on activated carbons at low temperatures. *Carbon* 2004, 42, 1483-1490.

[14] J. Choi, K.S. Lee, D.Y. Choi, Y.J. Kim, S.S. Kim, Dry De-NO_x process via gas-phase photochemical oxidation using an ultraviolet and aerosolized H_2O/H_2O_2 hybrid system. *Energy Fuels* 2014, 28, 5270-5276.

[15] L. Chen, J. Lin, C. Yang, Absorption of NO_2 in a packed tower with Na_2SO_3 aqueous solution. *Environ Prog* 2002, 21, 225-230.

[16] G.A. Chappell, *Aqueous scrubbing of nitrogen oxides from stack gases.* In: Jimeson R et al., editors. Pollution Control and Energy Needs-Advances in Chemistry. Washington DC: American Chemical Society; 1974.

[17] G. Ruitang, X. Gao, *Simultaneous removal of SO_2 and NO_2 by wet scrubbing using aqueous limestone slurry.* Extended abstracts, 11th international conference on electrostatic precipitation. 2008; p. 602-605.

[18] J.P.S. Sousa, M.F.R. Pereira, J.L. Figueiredo, Catalytic oxidation of NO to NO_2 on N-doped activated carbons. *Catalysis Today* 2011, 176, 383-387.

[19] N. Tang, Y .Liu, H. Wang, Z. Wu, Mechanism study of NO catalytic oxidation over MnO_x/TiO_2 catalysts. *J. Phys. Chem. C* 2011, 115, 8214-8220.

[20] L. Li, Q. Shen, J. Cheng, Z. Hao, Catalytic oxidation of NO over TiO_2 supported platinum clusters I: Preparation, characterization and catalytic properties. *Appl. Catal. B: Environ.* 2010, 93, 259-266.

[21] J. Despres, M. Elsener, M. Koebel, O. Krocher, B. Schnyder, A. Wokaun, Catalytic oxidation of

nitrogen monoxide over Pt/SiO$_2$. *Appl Catal B: Environ* 2004, 50, 73-82.

[22] V.M. Zamansky, H. Loc, P.M. Maly, W.R. Seeker, Oxidation of NO to NO$_2$ by hydrogen peroxide and its mixtures with methanol in natural gas and coal combustion gases. *Combust Sci Technol* 1996, 120, 255-272.

[23] B. Weidenhof, M. Reiser, K. Stowe, W.F. Maier, M. Kim, J. Azurdia, et al. High-throughput screening of nanoparticle catalysts made by flame spray pyrolysis as hydrocarbon/NO oxidation catalysts. *J. Am. Chem. Soc.* 2009, 131, 9207-9219.

[24] H. Tsukahara, T. Ishida, M. Mayumi, Nitric Oxide- Biol. Ch. 1999, 3, 191.

[25] Z. Guo, Y. Xie, I. Hong, J. Kim, Catalytic oxidation of NO to NO$_2$ on activated carbon. *Energy Conversion and Management* 2001, 42, 2005-2018.

[26] J.H. Pavlish, E.A. Sondreal, M.D. Mann, E.S. Olson, K.C. Galbreath, D.L. Laudal, S.A. Benson, State review of mercury control options for coal-fired power plants. *Fuel Process. Technol.* 2003, 82, 89-165.

[27] X. Gao, S. Liu, Y. Zhang, X. Du, Z. Luo, K. Cen, Low temperature selective catalytic reduction of NO and NO$_2$ with NH$_3$ over activated carbon-supported vanadium oxide catalyst. *Catalysis Today* 2011, 175, 164-170.

[28] Z. Wang, Y. Wang, D. Long, I. Mochida, W. Qiao, L. Zhan, X. Liu, S.-H. Yoon, L. Ling, Kinetics and mechanism study of low-temperature selective catalytic reduction of NO with urea supported on pitch-based spherical activated carbon. *Ind. Eng. Chem. Res.* 2011, 50, 6017-6027.

[29] I. Mochida, Y. Kawabuchi, S. Kawano, Y. Matsumura, M. Yoshikawa, High catalytic activity of pitch-based activated carbon fibers of moderate surface area for oxidation of NO to NO$_2$ at room temperature. *Fuel* 1997, 76, 543-548.

[30] I. Mochida, N. Shirahama, S. Kawano, Y. Korai, A. Yasutake, M. Tanoura, S. Fujii, M. Yoshikawa, NO oxidation over activated carbon fiber (ACF). Part 1. Extended kinetics over a pitch based ACF of very large surface area. *Fuel* 2000, 79, 1713-1723.

[31] I. Mochida, S. Kisamori, M. Hironaka, S. Kawano, Y. Matsumura, M. Yoshikawa, *O*xidation of NO into NO$_2$ over active carbon fibers. *Energy Fuels* 1994, 8, 1341-1344.

[32] S. Adapa, V. Gaur, N. Verma, Catalytic oxidation of NO by activated carbon fiber (ACF). *Chem. Eng. J.* 2006, 116, 25-37.

[33] B. Galliker, R. Kissner, T. Nauser, W.H. Koppenol, Intermediates in the autoxidation of nitrogen monooxide. *Chemistry-A European Journal* 2009, 15, 6161-6168.

[34] W.J. Zhang, S. Rabiei, A. Bagreev, M.S. Zhuang, F. Rasouli, Study of NO adsorption on activated carbons. *Appl. Catal. B: Environ.* 2008, 83, 63-71.

[35] J.D. Atkinson, Z. Zhang, M.J. Rood, 105th Annual Meeting of the Air & Waste Management Association, San Antonio, 2012, Paper 2012-A-2058-AWMA.

[36] J.D. Atkinson, Z. Zhang, Z. Yan, M.J. Rood, Evolution and impact of acidic oxygen functional groups on activated carbon fiber cloth during NO oxidation. *Carbon* 2013, 54, 444-453.

[37] Z. Yan, *Introduction to Catalysis*, Press of Chemical Industry, Beijing, 2005.

[38] J.A. Loiland, R.F. Lobo, Oxidation of zeolite acid sites in NO/O_2 mixtures and the catalytic properties of the new site in NO oxidation. *J. Catal.* 2015, 325, 68-78.

[39] S.N. Ahmed, R. Baldwin, F. Derbyshire, B. McEnaney, J. Stencel, Catalytic reduction of nitric oxide over activated carbons. *Fuel* 1993, 72, 287-292.

[40] P. Nikolov, M. Khristova, D. Mehandjiev, Low-temperature NO removal over copper-containing activated carbon. *Colloids & Surfaces A Physicochemical & Engineering Aspects* 2007, 295, 239-245.

[41] A. Claudino, J.L. Soares, R.F.P.M. Moreira, H.J. Jose, Adsorption equilibrium and breakthrough analysis for NO adsorption on activated carbons at low temperatures. *Carbon* 2004, 42, 1483-1490.

[42] D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, D.F. Quinn, Influence of pore size distribution on methane storage at relatively low pressure: preparation of activated carbon with optimum pore size. *Carbon* 2000, 40, 989-1002.

[43] E. Raymundo-Piñero, D. Cazorla-Amorós, C. Salinas-Martínez de Lecea, A. Linares-Solano, Factors controling the SO_2 removal by porous carbons: relevance of the SO_2 oxidation step. *Carbon* 2000, 38, 335-344.

[44] M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Behaviour of activated carbons with different pore size distributions and surface oxygen groups for benzene and toluene adsorption at low concentrations. *Carbon* 2005, 43, 1758-1767.

[45] R.S. Rathore, D.K. Srivastava, A.K. Agarwal, N. Verma, Development of surface functionalized activated carbon fiber for control of NO and particulate matter. *J. Hazard. Mater.* 2010, 173, 211-222.

[46] A.M. Rubel, M.L. Stewart, J.M. Stencel, Activated carbon for control of nitrogen oxide emissions. *J. Mater. Res.* 1995, 10, 562-567.

[47] E. Richter, H.-J. Schmidt, H.-G. Schecker, Adsorption and catalytic reactions of NO and NH_3 on activated carbon. *Chem. Eng. Technol.* 1990, 13, 332-340.

[48] J.P.S. Sousa, M.F.R. Pereira, J.L. Figueiredo, NO oxidation over nitrogen doped carbon xerogels. *Appl. Catal. B: Environ.* 2012, 125, 398-408.

[49] H. Teng, Y.-F. Hsu, Y.-T. Tu, Reduction of NO with NH_3 over carbon catalysts — the influence of carbon surface structures and the global kinetics. *Appl. Catal. B: Environ.* 1999, 20, 145-154.

[50] X. Wan, H. Shi, X. Zou, G.E. Peng, D. Wang, Effect of nitrogen doping on the reduction of nitric oxide with activated carbon in the presence of oxygen. *Journal of Zhejiang University Science A* 2008, 9, 113-117.

[51] J.P.S. Sousa, M.F.R. Pereira, J.L. Figueiredo, Modified activated carbon as catalyst for NO oxidation. *Fuel Process. Technol*. 2013, 106, 727-733.

[52] W.-J. Zhang, A. Bagreev, F. Rasouli, Reaction of NO_2 with activated carbon at ambient

temperature. *Ind. Eng. Chem. Res.* 2008, 47, 4358-4362.

[53] S. Yang, J. Li, C. Wang, J. Chen, L. Ma, H. Chang, L. Chen, Y. Peng, N. Yan, Fe-Ti spinel for the selective catalytic reduction of NO with NH_3: Mechanism and structure-activity relationship. *Appl. Catal. B: Environ.* 2012, 117-118, 73-80.

[54] J. Després, M. Elsener, M. Koebel, O. Kröcher, B. Schnyder, A. Wokaun, Catalytic oxidation of nitrogen monooxide over Pt/SiO_2. *Appl. Catal. B: Environ.* 2004, 50, 73-82.

[55] Z. Zhang, J.D. Atkinson, B. Jiang, M.J. Rood, Z. Yan, Nitric oxide oxidation catalyzed by microporous activated carbon fiber cloth: An updated reaction mechanism. *Appl. Catal. B: Environ.* 2014, 148-149, 573-581.

[56] J. Miyawaki, T. Shimohara, N. Shirahama, A. Yasutake, M. Yoshikawa, I. Mochida, S.-H. Yoon, Removal of NO_x from air through cooperation of the TiO_2 photocatalyst and urea on activated carbon fiber at room temperature. *Appl. Catal. B: Environ.* 2011, 110, 273-278.

[57] W. Wang, G. McCool, N. Kapur, G. Yuan, B. Shan, M. Nguyen, U.M. Graham, B.H. Davis, G. Jacobs, K. Cho, X. Hao, Mixed-phase oxide catalyst based on Mn-mullite (Sm, Gd)Mn_2O_5 for NO oxidation in diesel exhaust. *Science* 2012, 337, 832-835.

[58] I. Mochida, Y. Korai, M. Shirahama, S. Kawano, T. Hada, Y. Seo, M. Yoshikawa, A. Yasutake, Removal of SO_x and NO_x over activated carbon fibers. *Carbon* 2000, 38, 227-239.

[59] J. Ding, Q. Zhong, S. Zhang, F. Song, Y. Bu, Simultaneous removal of NO_x and SO_2 from coal-fired flue gas by catalytic oxidation-removal process with H_2O_2. *Chem. Eng. J.* 2014, 243, 176-182.

[60] W. Shen, W. Fan, Nitrogen-containing porous carbons: synthesis and application. *J. Mater. Chem. A* 2013, 1, 999-1013.

[61] B. Cosane, C. Alba-Simionesco, F. Audonnet, G. Dosseh, K.E. Gubbins, Adsorption, structure and dynamics of benzene in ordered and disordered porous carbons. *Phys. Chem. Chem. Phys.* 2011, 13, 3748-3757.

[62] S.M. Manocha, Porous carbons. *Sadhana* 2003, 28, 335.

[63] J.A. Loiland, R.F. Lobo, Low temperature catalytic NO oxidation over microporous materials. *J. Catal.* 2014, 311, 412-423.

[64] N. Artioli, R.F. Lobo, E. Iglesia, Catalysis by confinement: Enthalpic stabilization of NO oxidation transition states by microporous and mesoporous siliceous materials. *J. Phys. Chem. C* 2013, 117, 20666-20674.

[65] R. Yan, T. Chin, Y.L. Ng, H.Q. Duan, D.T. Liang, J.H. Tay, Influence of surface properties on the mechanism of H_2S removal by alkaline activated carbons. *Environ. Sci. Technol.* 2004, 38, 316-323.

[66] T.J. Bandosz, On the adsorption/oxidation of hydrogen sulfide on activated carbons at ambient temperature. *J. Colloid Interface Sci.* 2002, 246, 1-20.

[67] T.J. Bandosz, Effect of pore structure and surface chemistry of virgin activated carbons on removal of hydrogen sulfide. *Carbon* 1999, 37, 483-491.

[68] S.V. Mikhalovsky, Y.P. Zaitsev, Catalytic properties of activated carbons I. Gas-phase oxidation of hydrogen sulphide. *Carbon* 1997, 35, 1367-1374.

[69] F. Adib, A. Bagreev, T.J. Bandosz, Effect of surface characteristics of wood-based activated carbons on adsorption of hydrogen sulfide. *J. Colloid Interface Sci.* 1999, 214, 407-415.

[70] F. Adib, A. Bagreev, T.J. Bandosz, Effect of pH and surface chemistry on the mechanism of H2S removal by activated carbons. *J. Colloid Interface Sci.* 1999, 216, 360-369.

[71] A. Bagreev, F. Adib, T.J. Bandosz, pH of activated carbon surface as an indication of its suitability for H2S removal from moist air streams. *Carbon* 2001, 39, 1897-1905.

[72] T. Sun, Y. Shen, J. Jia, Gas cleaning and hydrogen sulfide removal for COREX coal gas by sorption enhanced catalytic oxidation over recyclable activated carbon desulfurizer. E*nviron. Sci. Technol.* 2014, 48, 2263-2272.

[73] A. Bagreev, J.A. Menendez, I. Dukhno, Y. Tarasenko, T.J. Bandosz, Bituminous coal-based activated carbons modified with nitrogen as adsorbent of hydrogen sulfide. *Carbon* 2004, 42, 469-476.

[74] A.D. Budaeva, E.V. Zoltoev, Porous structure and sorption properties of nitrogen-containing activated carbon. *Fuel* 2010, 89, 2623-2627.

[75] H.F. Gorgulho, F. Gonçalves, M.F.R. Pereira, J.L. Figueiredo, Synthesis and characterization of nitrogen-doped carbon xerogels. *Carbon* 2009, 47, 2032-2039.

[76] K. Jurewicz, R. Pietrzak, P. Nowicki, H. Wachowska, Capacitance behaviour of brown coal based active carbon modified through chemical reaction with urea. *Electrochimica Acta* 2008, 53, 5469-5475.

[77] R. Pietrzak, XPS study and physico-chemical properties of nitrogen-enriched microporous activated carbon from high volatile bituminous coal. *Fuel* 2009, 88, 1871-1877.

[78] W. Shen, Z. Li, Y. Liu, Surface chemical functional groups modification of porous carbon. *Recent Patents on Chemical Engineering* 2008, 1, 27-40.

[79] J. Alcañiz-Monge, A. Bueno-López, M.A. Lillo-Rodenas, M.J. Illán-Gómez, NO adsorption on activated carbon fibers from iron-containing pitch. *Mircoporous and Mesoporous Materials* 2008, 108, 294-302.

[80] K. Li, L. Ling, C. Lu, W. Qiao, Z. Liu, L. Liu, I. Mochida, Catalytic removal of SO_2 over ammonia-activated carbon fibers. *Carbon* 2001, 39, 1803-1808.

[81] H.-P. Boehm, Catalytic properties of nitrogen-containing carbons, in: P. Serp, J.L. Figueiredo (Eds.), Carbon Materials for Catalysis, Wiley, Hoboken, New Jersey, 2009, pp. 219-265.

[82] S. Matzner, H.P. Boehm, Influence of nitrogen doping on the adsorption and reduction of nitric oxide by activated carbons. *Carbon* 1998, 36, 1697-1703.

[83] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Modification of the surface chemistry of activated carbons. *Carbon* 1999, 37, 1379-1389.

[84] B. Stöhr, H.P. Boehm, R. Schlögl, Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate. *Carbon* 1991, 29, 707-720.

[85] B.J. Ku, J.K. Lee, D. Park, H.-K. Rhee, Treatment of activated carbon to enhance catalytic activity for reduction of nitric oxide with ammonia. *Ind. Eng. Chem. Res.* 1994, 33, 2868-2874.

[86] R.S. Rathore, D.K. Srivastava, A.K. Agarwal, N. Verma, Development of surface functionalized activated carbon fiber for control of NO and particulate matter. *J. Hazard. Mater.* 2010, 173, 211-222.

[87] S. Matzner, H.P. Boehm, Influence of nitrogen doping on the adsorption and reduction of nitric oxide by activated carbons. *Carbon* 1998, 36, 1697-1709.

[88] X. Gao, S. Liu, Y. Zhang, Z. Luo, K. Cen, Physicochemical properties of metal-loaded activated carbons and relationship with their performance in the removal of SO_2 and NO. *J. Hazard. Mater.* 2011, 188, 58-66.

[89] M. Wang, Z. Huang, T. Shimohara, F. Kang, K. Liang, NO removal by electrospun porous carbon nanofibers at room temperature. *Chem. Eng. J.* 2011, 170, 505-511.

[90] M. Wang, Z. Huang, K. Shen, F. Kang, K. Liang, Catalytically oxidation of NO into NO_2 at room temperature by graphitized porous nanofibers. *Catal. Today* 2013, 201, 109-114.

[91] A. Ramos, I. Cameán, A.B. García, Graphitization thermal treatment of carbon nanofibers. *Carbon* 2013, 59, 2-32.

[92] M. Endo, Y.A. Kim, T. Hayashi, T. Yanagisawa, H. Muramatsu, M. Ezaka, et al. Microstructural changes induced in ‘‘stacked cup’’ carbon nanofibers by heat treatment. *Carbon* 2003, 41, 1941-1947.

[93] S. Lim, S.H. Yoon, I. Mochida, J.H. Chi, Surface modification of carbon nanofiber with high degree of graphitization. *J. Phys. Chem. B* 2004, 108, 1533-1536.

[94] X. Wang, X. Li, L. Zhang, Y. Yoon, P.K. Weber, H. Wang, et al. N-doping of graphene through electrothermal reactions with ammonia. *Science* 2009, 324, 768-771.

[95] N.O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang, et al. Graphene: an emerging electronic material. *Adv. Mater.* 2012, 24, 5782-5825.

[96] S.Y. Pan, I.A. Aksay, Factors controlling the size of graphene oxide sheets produced via the graphite oxide route. *ACS Nano* 2011, 5, 4073-4083.

[97] D. Li, R.B. Kaner, Materials science. Graphene-based materials. *Science* 2008, 320, 1170-1171.

[98] W.S. Hummers, R.E. Offeman, Preparation of graphitic oxide. *J. Am. Chem. Soc.* 1958, 80, 1339.

[99] A.K. Geim, K.S. Novoselov, The rise of graphene. *Nat. Mater.* 2007, 6, 183-191.

[100] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, et al. Graphene and graphene oxide:

synthesis, properties, and applications. *Adv. Mater.* 2010, 22, 3906-3924.

[101] Z. Guo, M. Wang, Z. Huang, F. Kang, Preparation of graphene/carbon hybrid nanofibers and their performance for NO oxidation. *Carbon* 2015, 87, 282-291.

[102] J. Zhou, Z. Sui, J. Zhu, P. Li, D. Chen, Y. Dai, et al. Characterization of surface oxygen complexes on carbon nanofibers by TPD, XPS and FT-IR. *Carbon* 2007, 45, 785-796.

[103] Y.-W. Ju, S.-H. Park, H.-R. Jung, W.-J. Lee, Electrospun activated carbon nanofibers electrodes based on polymer blends. *J Electrochem Soc* 2009, 156, A489-A494.

[104] M. Bikshapathi, G.N. Mathur, A. Sharma, N. Verma, Surfactant-enhanced multiscale carbon webs including nanofibers and Ni-nanoparticles for the removal of gaseous persistent organic pollutants. *Ind. Eng. Chem. Res.* 2012, 51, 2104.

[105] A. Chakraborty, D. Deva, A. Sharma, N. Verma, Adsorbents based on carbon microfibers and carbon nanofibers for the removal of phenol and lead from water. *J. Colloid Interface Sci.* 2011, 359, 228.

[106] S. Lim, S.H. Yoon, Y. Shimizu, H. Jung, I. Mochida, Surface control of activated carbon fiber by growth of carbon nanofiber. *Langmuir* 2004, 20, 5559.

[107] H. Katepalli, M. Bikshapathi, C.S. Sharma, N. Verma, A. Sharma, Synthesis of hierarchical fabrics by electrospinning of PAN nanofibers on activated carbon microfibers for environmental remediation applications. *Chem. Eng. J.* 2011, 171, 1194.

[108] R.M. Singhal, A. Sharma, N. Verma, Micro-nano hierarchal web of activated carbon fibers for catalytic gas adsorption and reaction. *Ind. Eng. Chem. Res.* 2008, 47, 3700.

[109] P. Talukdar, B. Bhaduri, N. Verma, Catalytic oxidation of NO over CNF/ACF-supported CeO_2 and Cu nanoparticles at room temperature. *Ind. Eng. Chem. Res.* 2014, 53, 12537-12547.

[110] R.W. Pekala,Organic aerogels from the polycondensation of resorcinol with formaldehyde. *J. Mater. Sci.* 1989, 24, 3221-3227.

[111] P.V. Samant, F. Gonçalves, M.M.A. Freitas, M.F.R. Pereira, J.L. Figueiredo, Surface activation of a polymer based carbon. *Carbon* 2004, 42, 1321-1325.

[112] H.F. Gorgulho, F. Gonçalves, M.F.R. Pereira, J.L. Figueiredo, Synthesis and characterization of nitrogen-doped carbon xerogels. *Carbon* 2009, 47, 2032-2039.

[113] K. Jurewicz, R. Pietrzak, P. Nowicki, H. Wachowska, Capacitance behaviour of brown coal based active carbon modified through chemical reaction with urea. *Electrochimica Acta* 2008, 53, 5469-5475.

[114] M. Pérez-Cadenas, C. Moreno-Castilla, F. Carrasco-Marín, A.F. Pérez-Cadenas, Surface chemistry, porous texture, and morphology of N-doped carbon xerogels. *Langmuir* 2008, 25, 466-470.

[115] J.P.S Sousa, M.F.R. Pereira, J.L. Figueiredo, Carbon xerogel catalyst for NO oxidation. *Catalysts* 2012, 2, 447-465.

[116] E. Lam, J.H.T. Luong, Carbon materials as catalyst supports and catalysts in the transformation of biomass to fuels and chemicals. *ACS Catal.* 2014, 4, 3393-3410.

[117] Y. Shen, Carbothermal synthesis of metal-functionalized nanostructures for energy and environmental applications. *J. Mater. Chem. A* 2015, 3, 13114-13188.

[118] H.S. Kambo, A. Dutta, A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sust. Energ. Rev.* 2015, 45, 359-378.

[119] Y. Shen, Biochars as promising carbonaceous adsorbents or catalysts for tar elimination during biomass gasification. *Renew. Sust. Energ. Rev.* 2015, 43, 281-295.

[120] L. Dong, S. Gao, W. Song, G. Xu, Experimental study of NO reduction over biomass char. *Fuel Process. Technol.* 2007, 88, 707-715.

[121] M. Guerrero, A. Millera, M.U. Alzueta, R. Bilbao, Experimental and kinetic study at high temperatures of the NO reduction over Eucalyptus char produced at different heating rates. *Energy Fuels* 2011, 25, 1024-1033.

[122] W. Fan, Y. Lu, M. Xiao, Effect of peroxidation O_2 concentration on the reduction reaction of NO by char at high temperature. *Ind. Eng. Chem. Res.* 2013, 52, 6101-6111.

[123] X. Wu, Q. Song, H. Zhao, Z. Zhang, Q. Yao, Kinetic modeling of inherent mineral catalyzed NO reduction by biomass char. *Environ. Sci. Technol.* 2014, 48, 4184-4190.

[124] X. Wang, J. Si, H. Tan, Q. Zhao, T. Xu, Kinetics investigation on the reduction of NO using straw char based on physicochemical characterization. *Bioresour. Technol.* 2011, 102, 7401-7406.

[125] H. Chen, D. Chen, L. Hong, Influences of activation agent impregnated sewage sludge pyrolysis on emission characteristics of volatile combustion and De-NO_x performance of activated char. *Appl. Energy* 2015, 156, 767-775.

[126] S.C. Ma, J. Yao, X. Ma, L. Cao, M. Guo, Removal of SO_2 and NO_x using microwave swing adsorption over activated carbon carried catalyst. *Chem. Eng. Technol.* 2013, 36, 1217-1224.

[127] X. Wang, X. Ma, S. Zhao, B. Wang, C. Song, Nanoporous molecular basket sorbent for NO_2 and SO_2 capture based on a polyethylene glycol-loaded mesoporous molecular sieve. *Energy Environ. Sci.* 2009. 2, 878-882.

Graphical Abstract

This paper reviewed recent progress in catalytic oxidation of nitric oxide (NO) over various carbonaceous materials, such as activated carbon, carbon nanofibers with the aim of NO abatement.