

Chemistry and Emissions of Nitrogen Oxides (NO, NO₂, N₂O) in Combustion of Solid Fuels

I. Heterogeneous Reactions – NO + NO₂

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Nitrogen oxides (NO + NO₂) belong to the most important gaseous pollutants from combustion processes. This review is focused on the mechanism and reaction kinetics of fuel nitrogen conversion to NO in combustion of solid fuels (coal, peat, wood). Mechanism and kinetics of heterogeneous catalyzed and gas-solid noncatalyzed reactions of NO formation in solid fuel devolatilization and char combustion have been studied in terms of NO-precursor release (NH₃ + HCN), precursor oxidation and decomposition. Destruction reactions (interactions and reduction reactions) of NO, mainly caused by char, CO and H₂, are very important for final emissions of NO in combustion of solid fuels. Application of heterogeneous mechanisms and kinetics of fuel N → NO formation and NO destruction is mainly in fluidized bed combustion, partly in pulverized coal combustion (where thermal NO formation may be significant).

Fossil fuel combustion in stationary sources is estimated to produce about 25 mass % of the global emissions of NO_x and combustion of coal contributes more than half of this [1, 2]. The nitrogen oxides (NO, NO₂, and N₂O) are harmful to the environment in several ways: acid deposition, photochemical smog, greenhouse effect, and ozone layer destruction.

The emissions of NO, NO₂, and N₂O from combustion processes have their origin in three main sources [3]:

- thermal NO formation by Zeldovich mechanism,
- prompt NO formation mechanism in flame by contribution of carbohydrate radicals,
- fuel nitrogen oxidation (NO, NO₂, N₂O).

The thermal NO formation and partly the prompt NO formation are strongly temperature-dependent. Lowering the combustion temperature leads to lower equilibrium concentrations of thermal NO, as shown in Fig. 1. The NO₂ and N₂O concentrations in flue gas (emissions) are generally small (negligible) at temperatures above 1000°C.

The overall nitrogen oxide emissions result as differences between formation and destruction reactions of these compounds in a combustion system. In those ones with solid particles (*e.g.* combustion of coal and biomass) both homogeneous and heterogeneous reac-

tions are generally important. The combustion of majority of solid fuels is schematically characterized by the following stages:

- devolatilization – rapid pyrolysis (often with partial gasification),
- homogeneous and/or catalyzed, heterogeneous gas-phase combustion of volatiles,
- char combustion with heterogeneous reactions.

The path of fuel nitrogen to emissions of NO_x in combustion is characterized by formation and destruction reactions with overlapping sets of homogeneous and heterogeneous catalyzed and noncatalyzed reactions. Simplified scheme of important reactions and intermediates for the formation and reduction of NO and N₂O in coal combustion is shown in Fig. 2.

Forms and Release of Nitrogen Species from Solid Fuels

Coals have the nitrogen involved in the macromolecular organic structures as pyridinic, pyrrolic, amino and quaternary functionalities. Inorganic nitrogen has been found only in anthracites [3]. Typically, coals contain 1–2.5 mass % of nitrogen (under *daf* = dry, ash-free conditions). The nitrogen in coals is mainly (50–80 mass %) pyrrolic, 20–40 % pyri-

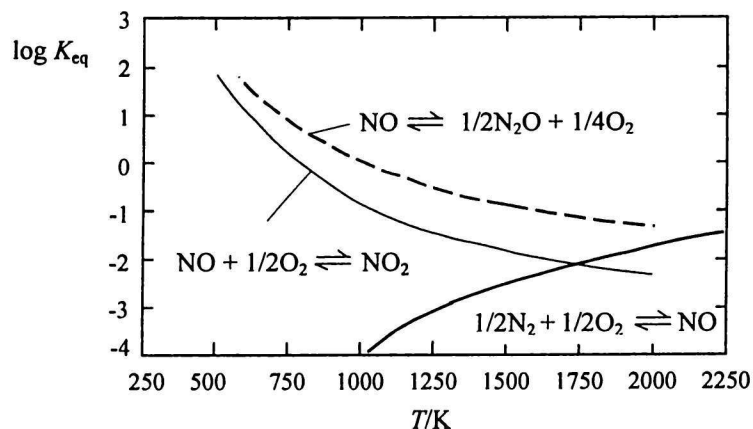


Fig. 1. Equilibrium constants of nitrogen reactions as functions of temperature.

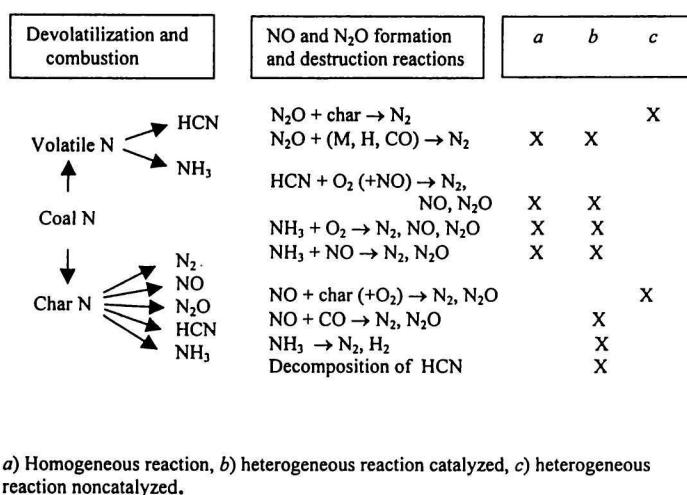


Fig. 2. Simplified reaction scheme for NO and N₂O formation and destruction in combustion, especially in fluidized bed combustion.

dinic, 0–20 % quaternary N, with small amount of amino and pyridone functionality for some coals. During pyrolysis, gasification, and combustion the spectrum of nitrogen functionalities changes. At temperatures above 900 K the pyrrolic N gradually disappears.

The conversion of pyrrolic nitrogen to pyridinic and quaternary N is a function of pyrolysis temperature and residence time. During the condensation process of pyrolysis the nitrogen atoms in char are incorporated into the graphene layers [3, 4] (mostly as pyridinic and quaternary N). Similar evolution and transformation of nitrogen functionalities was observed during pyrolysis of polymeric model N-substances [5] (e.g. poly(vinyl carbazole)).

The type of nitrogen and the molecular structure of the precursor are not factors determining the distribution of N-functionalities in the char after pyrolysis/gasification. Factors like temperature, heating rate, and composition of gaseous atmosphere are decisive for resulting N-functionality and nitrogen loss by devolatilization. The fraction of coal nitrogen loss in

pyrolysis and gasification in a fluidized bed is approximately linearly dependent on fraction of carbon loss [6].

Release and Heterogeneous Reactions of Nitrogen at Pyrolysis and Gasification

Partitioning of coal nitrogen into volatiles and char depends on factors like pyrolysis temperature, heating rate, coal type and particle size, formation of porous char structure, equipment, etc. Intermediate temperature of pyrolysis and short residence time usually lead to char with a higher N-content than the parent coal. At high pyrolysis temperature (typical for pulverized coal combustion) the N-content in the char is lower. The primary devolatilization involves release of tar, with similar N-content as the original coal. The secondary devolatilization involves the release of such gases like methane and hydrogen and this usually increases N/C mole ratio ($\psi = n(N)/n(C)$) in a char. The typical pyrolysis stages of a bituminous coal with

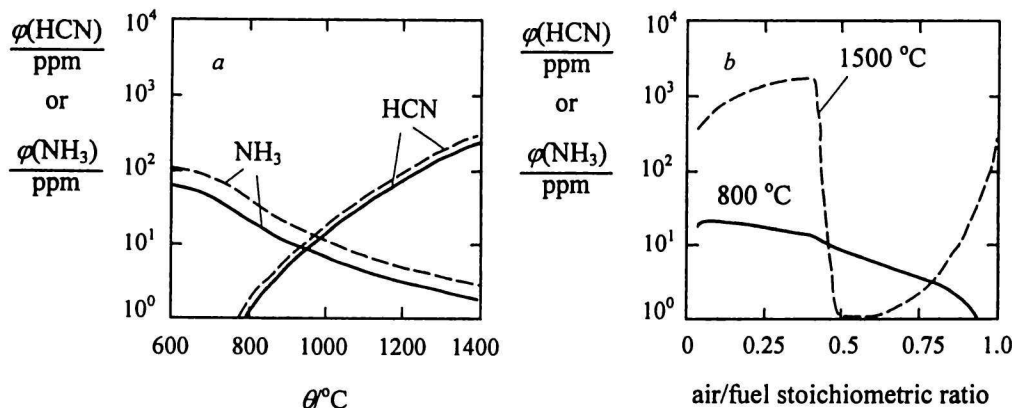


Fig. 3. a) The calculated equilibrium concentrations of HCN and NH₃ as functions of temperature at pyrolysis of peat (—) ($w(\text{C}^{\text{daf}}) = 56.9$ mass %, $w(\text{H}^{\text{daf}}) = 5.9$ mass %, $w(\text{N}^{\text{daf}}) = 1.9$ mass %, $w(\text{O}^{\text{daf}}) = 35$ mass %) and bituminous coal (---) ($w(\text{C}^{\text{daf}}) = 82.3$ mass %, $w(\text{H}^{\text{daf}}) = 5.3$ mass %, $w(\text{N}^{\text{daf}}) = 1.1$ mass %, $w(\text{O}^{\text{daf}}) = 10.2$ mass %). b) The calculated equilibrium volume fraction of (HCN + NH₃) as a function of air/fuel stoichiometric ratio for partial gasification at 800 and 1500 °C for the same bituminous coal [9] and for total pressure $P = 0.1$ MPa. The volumetric concentrations (HCN + NH₃) are normalized for conditions of air/fuel stoichiometric ratio = 0.4.

release of nitrogen compounds [7, 8] involve primary (gas + tar) and secondary pyrolysis (gas + soot).

The enrichment of nitrogen in the char reaches a maximum [3] in the temperature range 1000–1300 K. Further pyrolysis (at higher temperatures) results in the release of NH₃ and HCN, leading to a decrease in N/C mole ratio ψ at higher temperatures. Secondary pyrolysis and gasification of tar *N*-compounds gives rise to HCN and NH₃. A small part of coal nitrogen is incorporated into soot particles. Gasification of char *N*-compounds leads to HCN and NH₃. Heterogeneous combustion of char probably produces directly mainly NO and N₂ through the formation of surface species (e.g. —C(NO)) with a minority of N₂O.

Equilibrium C—H—O—N—S chemistry at peat and coal pyrolysis and gasification was studied by global equilibrium analysis based [9] on Gibbs energy minimization (program SOLGASMIX). The calculated equilibrium concentrations of nitrogen species for pyrolysis showed that N₂ is the main component. Minorities are NH₃ and HCN. Their ratio is a function of temperature (Fig. 3), HCN being prevailing at high temperatures. The air/fuel stoichiometric ratio at partial gasification/incomplete combustion dramatically changes total equilibrium volume fractions of (NH₃ + HCN), especially at temperatures [9] above 1000 °C (Fig. 3).

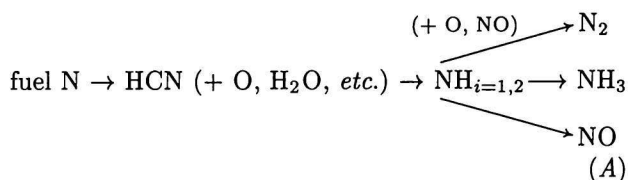
The amount of NH₃ and HCN released during pyrolysis of solid fuels depends upon a number of parameters. The most important are: coal (fuel) type, volatile matter release $w(\text{V}^{\text{daf}})$, heating rate, final temperature, and residence time. The majority of experimental results support the general statements:

The release of ammonia and the ratio of mole concentrations of NH₃ and HCN in released gases for lower-rank coals is mostly larger than for higher-rank coals.

The experiments with smaller coal particles (75–100 μm), higher heating rates (10⁴ K s⁻¹), and lower gas residence time (0.3–0.5 s) have shown much higher HCN yield than the experiments with bigger particles (0.15–0.2 mm), lower heating rate, and longer residence time [7].

Typical temperature trends for NH₃ and HCN yields in pyrolysis of coals with high and low values of $w(\text{V}^{\text{daf}})$ are demonstrated [8] in Fig. 4.

There are two possible routes for HCN and NH₃ formation in pyrolysis/gasification: parallel reactions of the same order, with kinetic ratio $R(\text{NH}_3)/R(\text{HCN}) = k(\text{NH}_3)/k(\text{HCN})$, giving the relative distribution of N between NH₃, HCN, and a scheme with consecutive and parallel reactions [7, 10]



The kinetic scheme with parallel reactions for NH₃ and HCN is probably more valid for small fuel particles and short gas residence time. The kinetic constants $k(\text{HCN})$ for HCN and $k(\text{NH}_3)$ for NH₃ formation by the first-order reactions in pyrolysis of coal are [7, 11]

$$k(\text{HCN})/\text{s}^{-1} = 0.17 \times 10^{14} \cdot \exp[-30000 \text{ K}/T]$$

$$k(\text{NH}_3)/\text{s}^{-1} = 0.12 \times 10^{13} \cdot \exp[-27300 \text{ K}/T]$$

Kinetic parameters for secondary pyrolysis of tar *N*-compounds can be estimated from kinetic data [12] for pyridine and pyrrole pyrolysis (Table 1).

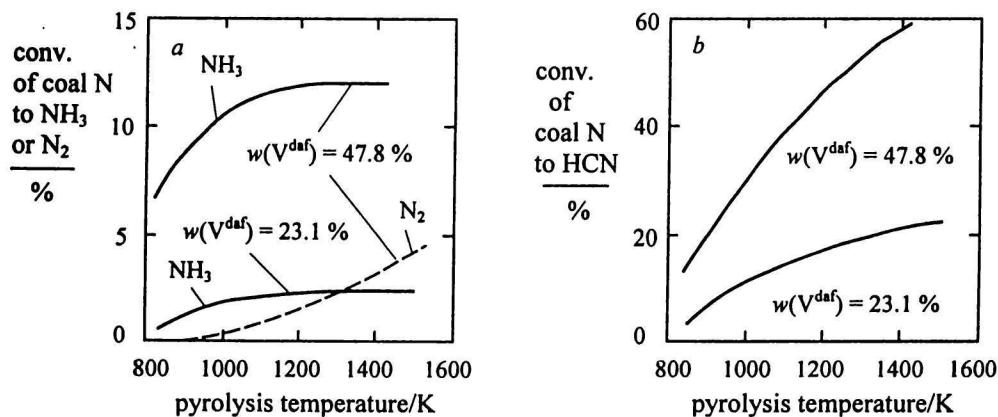


Fig. 4. a) Variation of NH_3 and N_2 yields (in mass % of the mass content of nitrogen in coal) with pyrolysis temperature for typical coals with higher and lower volatile content $w(\text{V}^{\text{daf}})$ [8]. b) Variation of HCN yields with pyrolysis temperature for the same typical coals with higher and lower volatile content.

Table 1. Kinetic Data [12] for Pyrolysis of Model *N*-Compounds

$-dc/dt = k \cdot c^n = A \cdot c^n \cdot \exp(-E/RT)$			
Compound	Reaction order n	A/s^{-1}	$E/(kJ \text{ mol}^{-1})$
Pyridine	1	3.8×10^{12}	293
Pyrrole	1	7.5×10^{15}	356

The main product of *N*-compounds pyrolysis in inert gas at temperatures over 1000°C is HCN. With increasing moisture of coal or a solid fuel NH_3 formation is more significant. Active free alkalies in fuels mineral (ash) matter like CaO , KOH , etc. exhibit at lower temperatures ($400\text{--}800^\circ\text{C}$) increasing rate of NH_3 formation [13].

Biomass fuels (wood, straw) produce in pyrolysis and partial gasification generally more NH_3 than coals. The main reason is probably the reaction of oxygen compounds (H_2O , CO_2) with HCN. Pressurized pyrolysis and gasification of coal, peat, and biomass usually lead to higher conversions of fuel N to NH_3 and lower conversions of fuel N to HCN comparing with atmospheric conditions.

Oxidation and Destruction of NH_3 and HCN from Volatiles

Oxidation of HCN

Tar nitrogen compounds in volatiles are transformed and partially oxidized to a mixture of HCN, NH_3 , NO , N_2O , and N_2 [14] (neglecting the nitrogen in soot). HCN and NH_3 are the most important precursors of NO and N_2O emissions. Oxidation of HCN and NH_3 from volatiles to products (N_2 , NO , and N_2O)

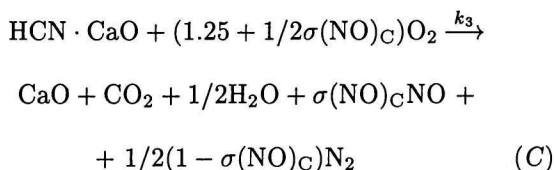
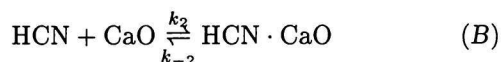
can proceed as homogeneous and/or heterogeneous, catalyzed reactions. The homogeneous reactions are typical rather for high-temperature combustion with radicals in flame and low concentrations of solid particles.

Heterogeneous catalytic oxidation reactions are at lower temperatures (below 1000°C) usually much faster than corresponding homogeneous reactions [15].

Catalytic oxidation of HCN gives as main products NO and N_2 . Nitrous oxide and ammonia are minor "by-products" of HCN oxidation. Calcined limestone, char, and Fe_2O_3 were recognized and proved [1, 15] to be efficient catalyst for HCN oxidation.

The selectivity of NO formation over calcined limestone is 50–70 %. The NO formation selectivity over fully sulfated limestone attains 15–25 % only. The selectivity of NO formation increases with rising temperature, increasing O_2 concentration, and decreasing HCN concentration (influence of NO –HCN reaction). An example of dependence of NO and N_2O formation selectivities at catalytic oxidation of HCN over reactive lime is illustrated in Fig. 5.

The main mechanisms and kinetics of HCN catalytic oxidation over lime are described in a kinetic model for HCN oxidation over calcined limestone and solved for limiting situations by Jensen [1, 16]. The following model reactions were proposed



where $\sigma(\text{NO})_C$ denotes selectivity of NO formation

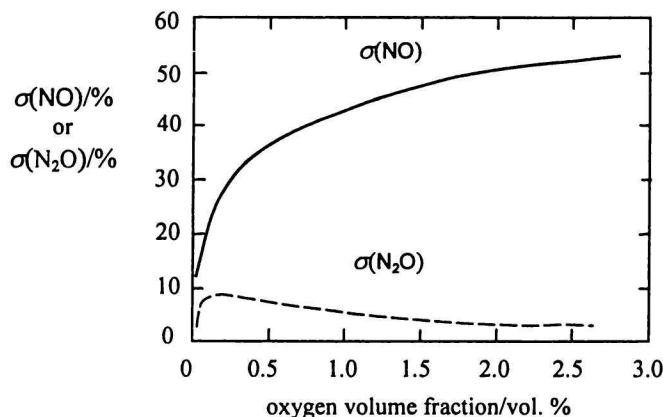
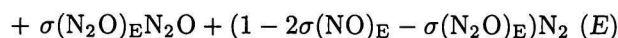
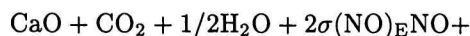
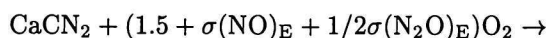


Fig. 5. Effect of oxygen concentration on oxidation of HCN in terms of selectivities σ for formation of NO and N₂O [16] over reactive lime (chalk) particles ($d_p = 0.25\text{--}0.3$ mm), inlet HCN volume fraction 400–420 ppm, temperature 1025 K.

by oxidation of HCN · CaO according to the chemical reaction (C), $\sigma(\text{NO})_C = \text{moles of NO formed by HCN} \cdot \text{CaO oxidation} / \text{moles of HCN} \cdot \text{CaO oxidized}$.



where $\sigma(\text{NO})_E$ and $\sigma(\text{N}_2\text{O})_E$ are selectivities for NO and N₂O formation in reaction (E).

Under conditions of low HCN concentrations and relatively high O₂ concentrations only the chemical reactions (B) and (C) are relevant (formation of CaCN₂ is neglected). If further kinetic equations for steady-state conditions are considered (*i.e.* $x_r(\text{HCN} \cdot \text{CaO}) = \text{const}$ or $r(\text{HCN} \cdot \text{CaO}) = dx_r(\text{HCN} \cdot \text{CaO})/dt = 0$), then the following kinetic equations can be written

$$-r(\text{HCN})/s^{-1} = k_2 \cdot c(\text{HCN}) \cdot x_r(\text{CaO}) - k_{-2} \cdot x_r(\text{HCN} \cdot \text{CaO}) \quad (1)$$

$$r(\text{HCN} \cdot \text{CaO}) = k_2 \cdot c(\text{HCN}) \cdot x_r(\text{CaO}) - k_{-2} \cdot x_r(\text{HCN} \cdot \text{CaO}) - k_3 \cdot [c(\text{O}_2)]^{n_3} \cdot x_r(\text{HCN} \cdot \text{CaO}) = 0 \quad (2)$$

where $n_3 = (1.25 + 1/2\sigma_{\text{NO,C}})$ denotes the reaction order with respect to oxygen (from the reaction (C)).

The sum of concentrations of reacting species $x_r(\text{CaO})$ and $x_r(\text{HCN} \cdot \text{CaO})$ is equal to $x_{r,\Sigma}$

$$x_{r,\Sigma} = x_r(\text{CaO}) + x_r(\text{HCN} \cdot \text{CaO}) \quad (3)$$

where $x_{r,\Sigma}$ is the total site relative mole fraction ("to-

tal site concentration") and $x_r(\text{CaO})$, $x_r(\text{HCN} \cdot \text{CaO})$ are the relative mole fractions ("surface concentrations") of CaO and HCN · CaO. After substitution for $x_r(\text{CaO})$ from eqn (3) into eqn (2) and arrangement the following expression for $x_r(\text{HCN} \cdot \text{CaO})$ is gained

$$x_r(\text{HCN} \cdot \text{CaO}) = k_2 \cdot c(\text{HCN}) \cdot x_{r,\Sigma} / (k_2 \cdot c(\text{HCN}) + k_{-2} + k_3 \cdot [c(\text{O}_2)]^{n_3}) \quad (4)$$

From eqns (1) and (2) a rate expression for HCN oxidation can be derived

$$-r(\text{HCN}) = k_3 \cdot [c(\text{O}_2)]^{n_3} \cdot c(\text{HCN} \cdot \text{CaO}) = x_{r,\Sigma} \cdot k_2 \cdot k_3 \cdot [c(\text{O}_2)]^{n_3} \cdot c(\text{HCN}) / (k_2 \cdot c(\text{HCN}) + k_{-2} + k_3 \cdot [c(\text{O}_2)]^{n_3}) \quad (5)$$

where the rate expression for HCN oxidation $-r(\text{HCN})$ is in s⁻¹. In limits, the rate eqn (5) forecasts the following reaction orders for HCN and O₂

$$\lim_{c(\text{HCN}) \rightarrow 0} (-r(\text{HCN})) = K_1 \cdot c(\text{HCN})^1 \quad (6)$$

and

$$\lim_{c(\text{HCN}) \rightarrow \infty} (-r(\text{HCN})) = K_2 \cdot c(\text{HCN})^0$$

$$\lim_{c(\text{O}_2) \rightarrow 0} (-r(\text{HCN})) = K_3 \cdot [c(\text{O}_2)]^{n_3} \quad (7)$$

and

$$\lim_{c(\text{O}_2) \rightarrow \infty} (-r(\text{HCN})) = K_4 \cdot [c(\text{O}_2)]^0$$

where the oxygen exponent n_3 varies between 1.25 and 1.75 (for $\sigma_{\text{NO,C}}$ values between 0 and 1) and K_1 – K_4 are terms derived from eqn (5) in the limiting cases.

Table 2. Typical Ranges of the Pseudo-First-Order Constants for Catalytic Reactions of NH₃ and HCN at 1100 K, $\varphi(\text{O}_2)=0.04\text{--}0.06$

Reaction	Catalyst	Rate constant (per mass unit of catalyst)/(m ³ kg ⁻¹ s ⁻¹)					
		10 ⁻³	10 ⁻²	10 ⁻¹	10 ⁰	10 ¹	10 ²
Oxidation HCN + O ₂ → NO, N ₂ , N ₂ O	Calcined limestones Sulfated limestones				—	—	
Oxidation NH ₃ + O ₂ → NO, N ₂ , N ₂ O	Calcined limestones Sulfated limestones Char Coal ash Fluidized bed material		—		—		
Decomposition HCN → N ₂	Calcined limestone		—				
Decomposition NH ₃ → N ₂ + H ₂	Calcined limestones (various Fe content) Sulfated limestones Coal ash Fluidized bed material		—		—		
Reaction HCN + NO → CO, CO ₂ , N ₂ , H ₂ O	Calcined limestones		—				
Reaction NH ₃ + NO → N ₂ , H ₂ O $\varphi(\text{NH}_3) = 350\text{--}450$ ppm	Calcined limestones Sulfated limestones Char Coal ash Fluidized bed material		—		—		

Under oxygen lean conditions and relatively higher HCN concentrations the formation and destruction of CaCN₂ are important. In steady-state analysis [1] the limiting reaction orders for HCN and oxygen are the same as in the foregoing simplified model solution.

Char exhibits approximately the same catalytic activity as lime, but N₂O formation has not been observed [14]. The selectivity for NO formation is about 50 %. The measured values of selectivities for NO formation may be influenced by reduction of NO by C, CO, and HCN.

The heterogeneous catalytic oxidation reactions of HCN are important in fluidized bed combustion and in systems with higher solid particle concentrations at relatively lower temperatures. In high-temperature pulverized coal combustion/reburning the homogeneous reactions of HCN with reactive radicals are prevailing.

For comparison, the typical values for the pseudo-first order constants k_{kin} (1100 K) for catalytic oxidation and decomposition reactions of HCN and NH₃ (in a transformed form $r = k \cdot c(i)$) are summarized [15] in Table 2.

Oxidation of Ammonia

In oxidation of ammonia coal ash, char, lime/limestone, stainless steel, transition and noble metals are known as catalysts. The main products from NH₃ oxidation are N₂ and NO with minor amount of N₂O.

The selectivity for NO production over lime catalyst at 1100 K is high (50–90 %) and increases with temperature. Stainless steel (Ni-based alloys) exerts very high NO selectivity (over 90 %) in NH₃ oxidation at temperatures over 750 °C.

The selectivity for N₂O formation is very low: 3–7 % at temperatures below 1100 K and negligible at temperatures over 1200 K. Catalytic activity of limestone decreases with increasing degree of sulfation and consequently NO selectivity decreases. Char is a very active catalyst for NH₃ oxidation (see Table 2) with attainable conversions to NO 80–90 % at 850 °C in a differential reactor.

A detailed single-particle model for NH₃ oxidation during lime sulfation was developed by *Kiil et al.* [17]. A simplified model for NH₃ oxidation, decomposition, and destruction reaction with NO was presented by *Lin* [18].

The kinetics of NH₃ oxidation is generally described by power-law kinetics ($-r(\text{NH}_3) = k \cdot c(\text{NH}_3)^a \cdot [c(\text{O}_2)]^b$) or by the equations of the Langmuir–Hinshelwood type [1], *e.g.*

$$-r(\text{NH}_3) = k(\text{NH}_3, \text{O}_2) \cdot c(\text{NH}_3) \cdot c(\text{O}_2) / (k_a + c(\text{O}_2)) \quad (8)$$

Typical values of the constants $k(\text{NH}_3, \text{O}_2)$ and k_a for two basic oxidation reactions of NH₃

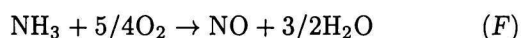
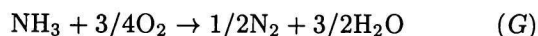


Table 3. Values of Constants $k(\text{NH}_3, \text{O}_2)$ and k_a in Eqn (8) for Catalytic Oxidation of NH_3 over Char and Mixture of Ash, Sand, and Lime Particles from Fluidized Bed Combustion (Reaction Rate r per Volume Unit of Catalyst [$\text{mol m}^{-3} \text{s}^{-1}$])

Solid catalytic material	Reaction	Kinetic rate constant $k(\text{NH}_3, \text{O}_2)$ per volume unit of catalyst	Ads.-kin. constant k_a
		$\text{m}^3 \text{ m}^{-3} \text{ s}^{-1}$	mol m^{-3}
Char	(F)	$6.75 \times 10^6 \exp(-10000K/T)$	0.054
Char	(G)	$2.89 \times 10^6 \exp(-10000K/T)$	0.054
Mixture of fluidized bed material	(F)	$3.1 \times 10^6 \exp(-10000K/T)$	0.054
	(G)	$4.96 \times 10^6 \exp(-10000K/T)$	0.054



are presented for temperature around 1125 K [1] in Table 3.

Catalytic Decomposition of Ammonia and HCN

The major products of NH_3 decomposition in inert gases are N_2 and H_2 . Limestone, coal ash, Fe- and Ni-materials [19], and quartz sand are common catalysts for the decomposition (Table 2). Ammonia is due to relatively higher equilibrium concentrations of hydrogen at higher temperatures an efficient reduction agent. Sulfated limestones react with ammonia at higher temperatures under formation of $\text{CaO} + \text{SO}_2 + \text{H}_2\text{O}$ and/or $\text{CaS} + \text{H}_2\text{O}$. Activation energy E_a for the catalytic decomposition reaction of ammonia on metallic catalysts, considering the pseudo-first-order reaction, is around 90 kJ mol^{-1} [20]. Pressurized processes (gasification, combustion) shift the NH_3/H_2 mole ratio towards higher values.

Equilibrium calculations for gas—solid reactions between HCN and CaO proved [1] that CaCN_2 , CO, CO_2 , H_2 , N_2 , and in the presence of H_2O also NH_3 are the main products of HCN decomposition and reactions with lime-based materials. The range of kinetic constant values for HCN catalytic decomposition over calcined limestones is given in Table 2. Sulfated limestones (CaSO_4) are decomposed or reduced by HCN to CaO or CaS.

Catalyzed Reduction Reactions of NO with NH_3 , HCN, CO, and H_2

The reduction reactions of NO (both homogeneous and heterogeneous) lead to nitrogen as the main product and N_2O as the minor product. Heterogeneous (catalyzed) reactions of NO with NH_3 and HCN accompany commonly the oxidation reactions of NH_3 and HCN and cause, especially at lower oxygen concentrations, substantial decrease of NO selectivities in the oxidation reactions [15, 16, 18].

The catalyzed NO + CO reactions are especially important at char surface. Catalyzed reactions of NO

with hydrogen are usually in practical systems less important, because of very fast oxidation of H_2 to H_2O .

Reactions of NO with Ammonia and HCN

The main product from catalyzed reaction of NH_3 with NO is N_2 (N_2O being quite minor by-product). The main catalysts for the reaction are: calcined limestone, char, and coal ash. Catalytic activity of calcined limestones based on experimental data or calculations is relatively low when compared with their activities in other reduction and oxidation reactions. The catalytic activity further decreases during reaction of CaO with SO_2 to CaSO_4 (as shown in Table 2). A part of NH_3 (in a mixture with NO) is parallelly decomposed to N_2 and H_2 [18]. In the presence of oxygen in heterogeneous catalytic systems at high temperatures, the mixture of $\text{NH}_3 + \text{NO}$ is preferentially oxidized over efficient catalyst lime [15, 18] to NO. Supposing the formal kinetic equation of the second order for catalytic reaction of NH_3 with NO in the form

$$-r(\text{NO}) = k_2 \cdot c(\text{NH}_3) \cdot c(\text{NO}) \quad (9)$$

the reaction rate per mass unit of catalyst is in $\text{mol kg}^{-1} \text{ s}^{-1}$. The k_2 values at 850°C for various calcined limestones were found to range [18] between $70\text{--}600 \text{ m}^6 \text{ kg}^{-1} \text{ mol}^{-1} \text{ s}^{-1}$. Char (*e.g.* in a fluidized bed) is a very active catalyst for reduction of NO with NH_3 . The activity is 10 times higher than for reduction of NO with CO.

The reaction of NO with HCN is catalyzed by limestone and coal ash. The activity of calcined limestone under conditions of fluidized bed combustion is about the same as for reduction of NO by NH_3 [15]. The main product of the NO—HCN heterogeneous reaction is N_2 , with minor N_2O . Under conditions of O_2 absence the mechanism of NO—HCN reaction over lime surface involves two main routes: adsorption to $\text{CaO} \cdot \text{HCN}$ complex and reaction [16] of a part of HCN with CaO to CaCN_2 , which is in a further step oxidized/decomposed by NO back to CaO.

Presence of SO_2 and sulfation reaction of CaO cause the decrease of both overall conversion of HCN

Table 4. Pseudo-First-Order Rate Constants for Catalytic Reduction of NO by CO and H₂ [15] at 1100 K

Reaction	Catalyst	Rate constant (per mass unit of catalyst)/(m ³ kg ⁻¹ s ⁻¹)					
		10 ⁻³	10 ⁻²	10 ⁻¹	10 ⁰	10 ¹	10 ²
Oxidation NO + CO → 1/2N ₂ + CO ₂	Calcined limestones						
	Sulfated limestones						
	Sulfided (CaS) limestones						
	Char						
	Coal ash						
	Fluidized bed material						
NO + H ₂ → NH ₃ , N ₂ , H ₂ O	Calcined limestones						
	Char						

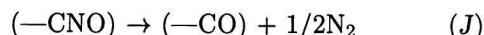
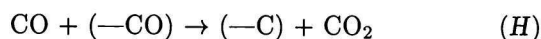
and selectivity of NO formation. Presence of low concentrations of oxygen elevates the NO and N₂O selectivity in NO—HCN reaction.

Reaction of NO with CO and H₂

NO—CO reaction is catalyzed by calcined limestone, char, and brown coal ash.

The reaction is inhibited by small O₂ concentrations (about 1 vol. %) at low CO/NO mole ratios, but can proceed if the CO/O₂ mole ratio is higher than 1.5. The rate of CO—NO reaction is slower in the presence of oxygen. The main product of the reaction is N₂ with minor N₂O possible production. Sulfation of CaO to CaSO₄ decreases catalytic activity, but reduction of calcium sulfate to CaS restores and even elevates the original catalytic activity of CaO. The usual range of kinetic constants for NO—CO catalyzed reaction for the pseudo-first-order reaction of NO at 1100 K is shown in Table 4.

Char-catalyzed reaction between NO and CO accompanies the heterogeneous reaction C(s)—NO. The reaction mechanism, especially at lower temperatures (below 900 °C), is following the adsorption-reaction kinetics of the Langmuir—Hinshelwood type. A part of carbon monoxide is adsorptively bound at C-surface and can react with gaseous CO to CO₂. The carbon active-surface centre (—C) then reacts with NO to elementary nitrogen.



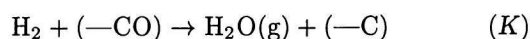
The apparent kinetics is described either by power-law kinetic equation

$$-r(\text{NO}) = k(\text{NO—CO}) \cdot [c(\text{NO})]^m \cdot [c(\text{CO})]^n \quad (10)$$

or (depending on overall conditions) by a reaction kinetic equation of the Langmuir—Hinshelwood type [1]. An increase of CO volume fraction from 0 % to

3 vol. % elevates the reaction rate 4—5 times.

The char-enhanced reaction of NO with H₂ is probably similar in reaction mechanism with the reaction of CO (eqn (H))



The reaction rates were measured at rather lower temperatures (below 950 K) and the values presented in Table 4 are extrapolated. The selectivity for NH₃ formation decreases with increasing temperature and at 1173 K attains ≈ 10 %. The major product of NO reduction by hydrogen is nitrogen. Limestone is as well a very active catalyst for NO—H₂ reaction with similar characteristics for NH₃ selectivity as char.

The reaction over limestones is somewhat slower than reaction over char (Table 4).

Oxidation of Char Nitrogen and Reaction Kinetics of NO—Carbon Reaction

During char oxidation nitrogen is released mainly as NO, N₂, and N₂O. HCN and NH₃ are quite minor species [15, 21]. The nitrogen compounds from char and volatiles are subjected to interactions with many gaseous species and radicals, to catalytic reactions on solid particle surfaces (char, ash, limestone), and to gas—solid reactions (char, etc.).

The formation of NO in combustion of a single coal particle was modelled by *Visona* and *Stanmore* [22, 23]. The most important interaction is probably the reduction of NO by char (carbon) [21] and by reactive species on carbon surface (—O, —CO, —CN, etc.).

Oxidation of Char Nitrogen

The conversions of char N to NO and N₂O during combustion of char vary typically between 20 % and 80 % for NO (as shown in Fig. 6) and between 1.5 % and 16 % for N₂O. The variation of the conversions is due to the use of different experimental techniques, due to various devolatilization temperature, coal rank, particle size, nitrogen content, char annealing, ash catalytic effects, etc. Chars have been usually found to be most

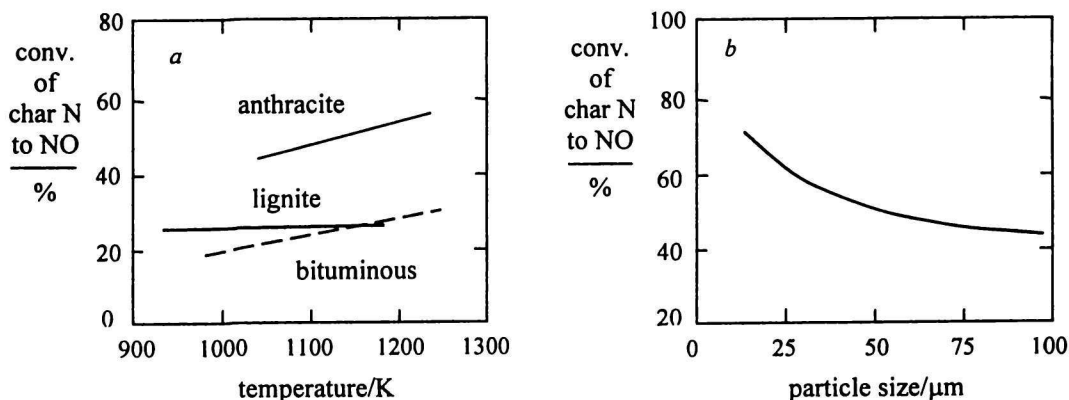


Fig. 6. a) Mass fractional conversion of char N to NO during combustion of chars from coals of different rank as a function of temperature [15]. b) Effect of particle size on mass fractional conversion of char N to NO for char from lignite [23], temperature 1750 K, 20 vol. % O₂.

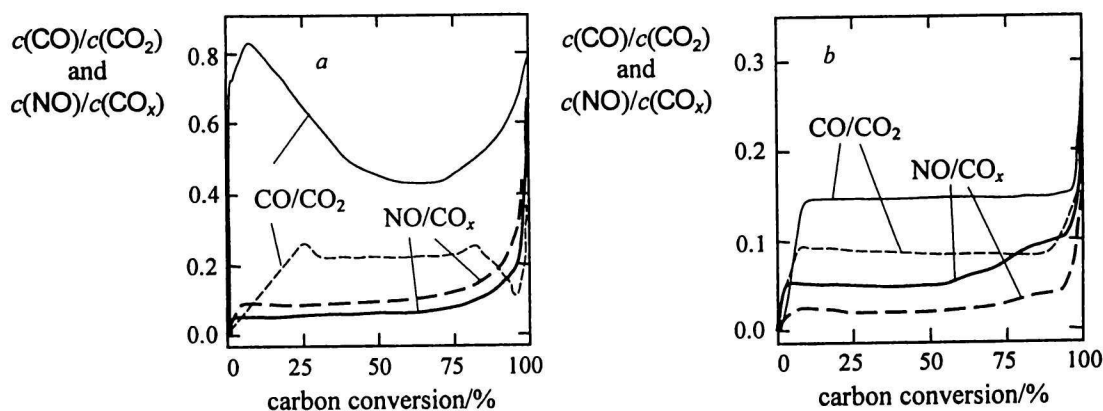


Fig. 7. Gas evolution in thermogravimetric isothermal char combustion at 600°C and 1000°C for two different coal chars (lignite and anthracitic coal) [24] in 20 vol. % O₂ (+ Ar). — Anthracitic char, --- lignite char. The values of $c(\text{NO})/c(\text{CO}_x)$, where $\text{CO}_x = \text{CO} + \text{CO}_2$, for lignite char are multiplied by 50, the values for anthracitic char are multiplied by 20. a) 600°C, b) 1000°C.

active for reduction of N₂O and this can be the reason for relatively lower conversions of char N to N₂O.

The reduction of NO and N₂O takes place within the pore system of the char (on the diffusing path to the char surface) and/or the nitrogen oxides may be also reduced by contact with other char particles. Experimental results have shown that when the char content in a fluidized bed increased 10 times, the conversion of char N to NO decreased roughly on one half of the initial value. The highest conversions of char N to NO were measured in differential reactors with small char particles or at the end of burning of bigger char particles [15, 21] because of limited reduction reactions of NO with C, CO, and NH₃. The char N to NO conversions increase with increasing temperature, oxygen concentration, decreasing particle size, and operating pressures illustrated in Fig. 6. With increasing nitrogen content of chars, conversions of fuel N to NO decrease, but conversions to N₂O usually increase. The growing oxygen gas concentration elevates the conver-

sion of char N to NO, but at higher concentrations of oxygen. The more reactive and porous char is available (e.g. after low-temperature devolatilization and activation), the more efficient reduction of NO by char carbon is usually found.

Thermogravimetric analysis of small coal-char samples ($d_p = 0.37\text{--}0.75$ mm) at temperature 600°C (regime of chemical kinetic control) and 1000°C (char pore diffusion important) derived from various, different coals revealed [24] that with higher coal rank (decreasing content of volatiles in coals), the char N to NO conversions increase. With higher temperature of combustion the conversion to NO mostly slightly decreases [24] and the $c(\text{CO})/c(\text{CO}_2)$ ratio decreases in the temperature range 600—1000°C.

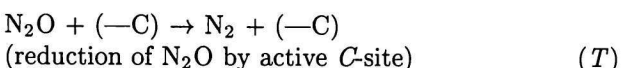
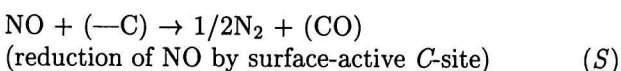
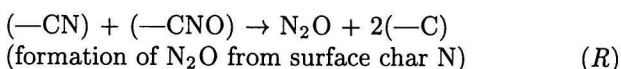
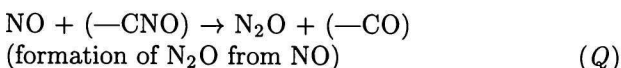
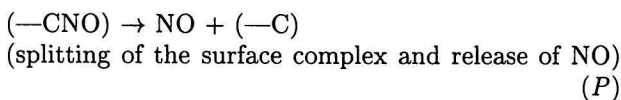
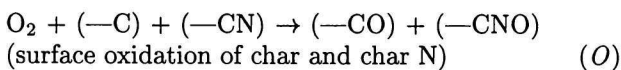
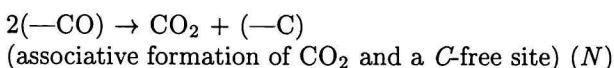
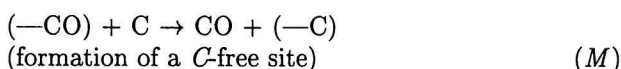
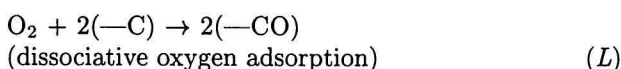
Higher $c(\text{CO})/c(\text{CO}_2)$ ratios were generally detected in combustion of higher rank coal-chars (from bituminous and especially from anthracitic coals). The experimental results from thermogravimetric combustion in a gaseous atmosphere (20 % O₂, 80 % Ar) at

Table 5. Evaluated Values [25] for Pre-Exponential Factors A and Activation Energies E_a for Selected Kinetic Constants $k_i = A_i \exp(-E_i/RT)$ for Two Levels of Total (System) Pressure

Reaction	Total, system pressure/MPa	$A/(\text{kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1})$	$E_a/(\text{kJ mol}^{-1})$
(O)	0.2	8×10^{-6}	58
	1.0	1.4×10^{-6}	55
(P)	0.2	$16 \times 10^{-2} \text{ kg m}^{-2} \text{ s}^{-1}$	42
	1.0	$22 \times 10^{-2} \text{ kg m}^{-2} \text{ s}^{-1}$	43
(Q)	0.2	6	121
	1.0	3	118
(S)	0.2	3×10^{-6}	71
	1.0	6×10^{-6}	83
(T)	0.2	5×10^{-5}	78
	1.0	7×10^{-5}	91

600°C and 1000°C gained for lignite and anthracitic coal derived chars are compared in Fig. 7.

The mechanism of heterogeneous reactions occurring during char combustion and leading to NO probably accords with the following reaction schemes [25]



In a kinetic model solution [25] all the above reactions except those involving O₂ (reactions (L) and (O)) were assumed to be first-order with respect to gaseous reactants (NO, N₂O). The reaction (R) was considered to be improbable and negligible. The sum S of all active sites in a char was assumed to be

$$S = n(-\text{C}) + n(-\text{CO}) + n(-\text{CN}) + n(-\text{CNO}) \quad (11)$$

The mole fractions of individual active sites are defined as

$$x_S(\text{C}) = n(-\text{C})/S$$

$$x_S(-\text{CO}) = n(-\text{CO})/S \quad (12)$$

$$x_S(-\text{CN}) = n(-\text{CN})/S$$

$$x_S(-\text{CNO}) = n(-\text{CNO})/S$$

The expressions for surface emissions rs (kg m⁻² s) of e.g. CO, CO₂, and NO from char combustion are

$$rs(\text{CO}) = k_M \cdot [x_S(-\text{CO})] \quad (13)$$

$$rs(\text{CO}_2) = k_N \cdot [x_S(-\text{CO})]^2 \quad (14)$$

$$rs(\text{NO}) = k_P \cdot x_S(-\text{CNO}) - k_Q \cdot [x_S(-\text{CNO})] \cdot p_{\text{NO}} - k_S \cdot [x_S(-\text{C})] \cdot p_{\text{NO}} \quad (15)$$

Experimental measurements of char burning kinetics in a fixed bed reactor have enabled [25] evaluation of kinetic constants k_i and their dependences on temperature from Arrhenius plots. The typical values of A and E_a for two levels of the total (system) pressure and for the same partial pressure of reacting gaseous species are summarized for selected reactions in Table 5. The reaction rates are mostly (with the exception of reaction (P)) slightly lower at higher total pressures at the same partial pressure of reacting gases. At conditions of only compressing the gases (practically the same mole fraction of reacting gases) the relevant reaction rates are slightly higher due to pressure (prevailing effect of increasing partial pressures of reacting gaseous species.)

It was found [25] both theoretically and by experimental measurements that the global emissions of NO in char combustion decrease when the total pressure increases and reduction of NO to N₂O becomes more significant compared to NO reduction to N₂, with increasing total (system) pressure in combustion. In-

creasing total pressure in combustion causes mainly faster reduction of NO on char and higher selectivity for N₂O formation in this reduction. Increasing partial pressure of H₂O and CO₂ effects the reaction mechanism of formation and destruction of nitrogen oxides under higher pressures (above 0.5 MPa).

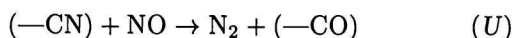
Nitric Oxide—Carbon Reaction

The reaction of NO in char pore surface with C and CO belongs to the most important routes for destruction of NO and lowering NO emissions [21]. The kinetics of NO—C(s) gasification reaction usually exerts a two-regime Arrhenius behaviour. The transition ($T = 850\text{--}1075\text{ K}$) is of chemical kinetic origin. The activation energy for low-temperature regime is typically $< 100\text{ kJ mol}^{-1}$ and that for high-temperature regime is between $100\text{--}250\text{ kJ mol}^{-1}$, depending on many factors (coal rank, pore structure and carbon reactivity, thermal char annealing, mineral matter, gas composition, *etc.*). The reaction of NO with C(s) is a first-order one with respect to NO, but the kinetic measurements, especially in fixed bed reactors and arrangements are commonly complicated by NO—CO reaction catalyzed by C(s) surface. Generally, the presence of oxidizing gases (O₂, CO₂, and H₂O) can have an important effect on the kinetics of NO—C(s) reaction [21].

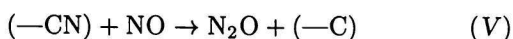
The mechanism of the NO—C reaction and nature of the surface sites reacting with NO is not completely known. It is agreed [26], however, that at temperatures above 500°C NO is irreversibly adsorbed on the reactive carbon surface (denoted (—C)) and that both (—CO) and (—CN) are formed. Three different N₂ formation paths should be considered:

- catalytic reaction of CO with NO on C(s) surface (without (—CN) participation),
- reaction between two (—CN) adjacent adsorbed N-species forming N₂ and (—C),
- heterogeneous gas—solid reaction between (—CN) and NO(g).

On the basis of recent experimental studies with isotopically labelled C and NO it is now clear that the rate of N₂ formation during NO—C reaction between 600°C and 950°C is proportional to the NO and surface concentration of (—CN) and that the heterogeneous g—s mechanism [26, 27]



is the main route for NO reduction by char. The reaction kinetics is practically of the first order with respect to the both species, NO and (—CN). The minor product, with a maximum yield at 800°C, is nitrous oxide



The accumulation of nitrogen in C-surface in the form (—CN) is increasing with increasing temperature (600—1000°C) [26].

The presence of surface oxygen species (—CO)s was proved to enhance the char reactivity towards NO. The formation of free reactive sites by CO desorption seems to be the most probable mechanism of this effect [27].

The kinetic constant for NO reduction should be based on unit solid surface area. In reality the initial (measured) and the final surface area can be measured. But the surface area changes in the course of the reaction may be significant and without tracking the area during the reaction it is impossible to estimate “real” values of the area. Besides this, not the total surface pore area is active in the reaction (active sites are edges, spots with imperfect structure, *etc.*).

Differences among reactivities of various carbons, chars, graphites, active chars, and other C-materials to NO reduction, expressed in terms of kinetic constant k_{sa} ($\text{g m}^{-2}\text{ h}^{-1}\text{ MPa}^{-1}$) attain several orders of magnitude. Graphites belong generally to the less reactive C-materials. Lignite coal chars and activated carbons cluster towards the higher limits of reactivities [21]. In experimental measurements of reaction kinetics of NO—C reaction, it seems there are two sources of difficulties: active site blockage by oxide intermediates (other kinetic results are obtained after removal of the surface oxygen species (effect of surface oxide cleaning)) and effect of simultaneous reactions of C(s) and CO with NO.

The apparent reaction order in gasification of C by NO is strongly influenced by the presence of CO in the reactant gas stream (*e.g.* fixed bed experiments). In the presence of CO the apparent order with respect to NO decreases (from values ≈ 1 to ≈ 0.5 for higher CO concentrations) – as illustrated in Fig. 8. The effect of CO has been observed to decrease with increasing temperature in the high-temperature regime. Other oxidizing gases (O₂, H₂O, CO₂) might affect to some extent the NO—C kinetics. Due to the fact that CO is a product of NO—C reaction, the interpretation of NO—C kinetics depends on experimental arrangements (differential reactor, fixed bed reactor, size of particles, single/multiparticle measurements, thermogravimetric measurement, *etc.*).

Presence of water vapour exerts mostly inhibiting effect on the NO—C reaction kinetics. Oxygen has a significant effect on the rate of the NO—C reaction. The oxygen enhancement of reaction rate is often coupled with catalytic effect of mineral matter.

The effect of heat treatment (thermal history) of a char on reactivity towards NO is not completely in various relations known. It is clear that high-temperature annealing of a char decreases the reactivity to both oxygen and NO (Fig. 8).

Ash (mineral matter) has generally catalytic effect

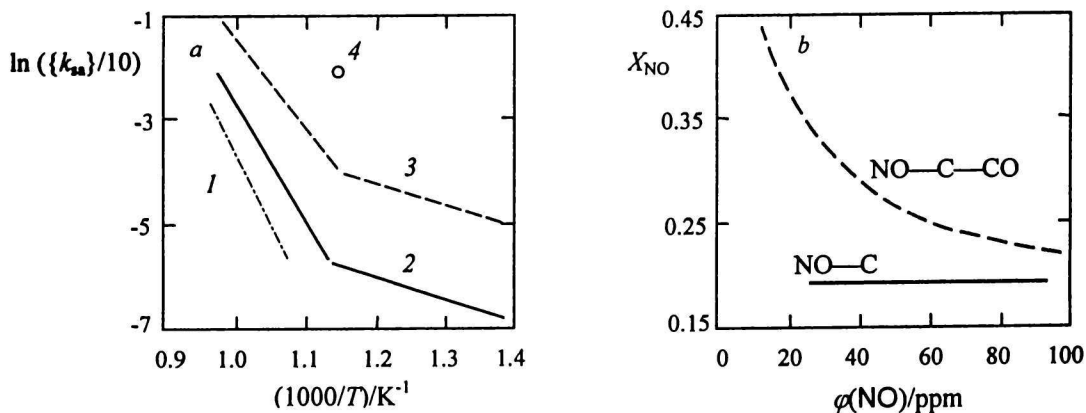


Fig. 8. a) Effect of thermal history (heat treatment) of a coal char on reaction with pure NO in a fixed bed, $p_{NO} = 10$ Pa. 1. Samples of a coal char heated for 24 h at 1273 K, 2. coal char heated for 2 h at 1273 K, 3. coal char heated at 30 K min^{-1} to 1273 K and then cooled, 4. coal-char sample heated at 333 K s^{-1} to 1273 K and immediately cooled [21]. b) Effect of CO on the apparent reaction order X_{NO} of the NO—graphite reaction. Conditions: 1073 K, fixed bed reactor, 0 ppm and 275 ppm CO in the gas inlet.

on gasification reactions of gases with C. Predicting of reaction kinetics for catalyzed NO—C reaction is still difficult and rather unreliable, because of still insufficient knowledge of the *in situ* catalytic effects.

Mass transfer (char pore structure and gas pore diffusion) affects experimental kinetic measurements and especially in the case of bigger coal-char particles (above $100\text{--}150\ \mu\text{m}$) the mass transport limitation leads to lower values of experimentally determined activation energy in high-temperature regime of NO—C reaction. The size of particles at the onset of mass transport limitations is typically between $100\ \mu\text{m}$ and $1000\ \mu\text{m}$ for coal derived chars (depending on starting coal materials, preparation conditions, burnout, porosity, mineral matter, etc.).

Impacts of Heterogeneous Reactions on Emissions of Nitrogen Oxides from Combustion Technologies

The transport phenomena, reaction mechanisms, and kinetics coupled with combustion of solid fuels (coal, peat, wood) are still not completely understood. The three classes of reactions (homogeneous, heterogeneous gas—solid noncatalyzed, and gas reactions heterogeneously catalyzed) are in practical situation often very closely coupled.

The kinetics of homogeneous radical and gas reactions is described quantitatively on a good level. For the purpose of better understanding and minimization of emissions from basic combustion modes (stove, grate, fluidized bed, and pulverized coal combustion) specific models for NO, N_2O , CO, and SO_2 emissions were constructed and solved. Attention is paid here to minimization of NO emissions from the most industrially used combustion technologies: fluidized bed and pulverized combustion.

Emissions of NO from Fluidized Bed Combustion

Fluidized bed combustion (FBC) is marked by relatively low combustion temperature ($800\text{--}950^\circ\text{C}$) within a particle bed with temperatures of burning particles being often $50\text{--}150^\circ\text{C}$ higher than the “bulk” temperature of the bed. SO_2 is captured *in situ* by means of limestone addition. The fluidized bed contains typically over 90 mass % of a mixture of ash and partly reacted particles of calcined limestone ($CaO + CaSO_4$).

“Catalytic deactivation” of CaO by reaction with SO_2 decreases conversion of fuel nitrogen to NO and the oxidation of CO to CO_2 is partly hindered [17, 28]. As it was proved experimentally and theoretically [29—32], both formation and destruction reactions are important for controlling of NO + N_2O emissions. Air staging, optimal combustion temperature, reburning by gaseous fuels and pressurized combustion generally lead [29, 30, 32, 33] to reduction of NO emissions. Coal ash, especially from lignite and subbituminous coals, has mainly positive catalytic influence to the reduction of nitrogen oxides at typical temperatures for FBC [34]. In the case of wood or biomass material FBC the combustion of volatiles is more important for emissions than char combustion. The optimized air staging [35, 36] and/or flue gas recirculation/reburning [35, 36] is probably the best and cheapest method for NO_x emission abatement in biomass combustion.

Pulverized Coal Combustion

Pulverized coal combustion (PCC) is characterized [37—39] by very fast combustion of coal powders ($d_p < 60\ \mu\text{m}$) at relatively high temperatures ($T > 1450\text{ K}$). The heating rates attain commonly values over

10^5 K s^{-1} and the "lifetime" of coal/char particles is very short in comparison with FBC. The contribution of char N to the total NO emissions is mainly related to temperature through char yield, because at temperatures above 1100°C the influence of temperature on char $\text{N} \rightarrow \text{NO}$ reaction is rather weak. Because of high temperatures thermal formation of NO may be significant. The concentrations and reactions of reactive gaseous radicals are more important and catalytic phenomena and reactions are less important.

The air staging with fuel-rich combustion in one stage remains still one of the main assumptions for low NO emissions in pulverized coal combustion. Low NO_x emissions combined with sufficient burnout of char particles require long particle residence times in the burner, internal recirculation zone with a "back flame", and optimization of the inlet coal particle size distribution [37, 39, 40].

CONCLUSION

The heterogeneous reactions in combustion of solid fuels (devolatilization, formation of NO_x emission precursors $\text{NH}_3 + \text{HCN}$, catalyzed oxidation of HCN and NH_3 to NO and N_2O , catalyzed reactions of NO with reducing gases like NH_3 , HCN, CO, H_2 , CH_4 , etc., and g—s reaction of NO with solid carbon) play a very important role in formation and destruction of NO and N_2O emissions. At high temperatures the prevailing precursor of NO is HCN. At lower combustion temperatures, under higher H_2O vapour concentrations and in combustion of biomass NH_3 is the main nitrogen oxide precursor.

At pyrolysis and gasification of solid fuels and biomass the NH_3 yield is substantially higher than in devolatilization/gasification process in air or flue gas.

At temperatures below 1000°C the catalyzed oxidation reactions of NH_3 and HCN are much faster than homogeneous corresponding reactions. The selectivity for NO formation in NH_3 and HCN catalytic oxidation (commonly exceeding 50 %) increases with rising temperature, increasing O_2 concentration, and decreasing HCN concentration (influence of NO—HCN reaction). The selectivity for N_2O formation is substantially lower than for NO. Efficient catalysts for the oxidation reactions are char, calcined limestone, and coal ash.

The destruction (reduction) reactions of NO are coupled mainly with the presence of NH_3 , HCN, CO, H_2 , and char carbon. Reactive chars with developed rich porous structure and high specific pore surface area (e.g. from lignite and subbituminous coals) are very efficient in NO reduction. CaO, CaS, and char were recognized and proved to be the most common catalysts for reduction reactions in real combustion systems. Decreasing operating temperature and increasing pressure lead in combustion systems to lower emissions of NO (but simultaneously to somewhat

higher emissions of N_2O). The overall conversions of fuel N to NO do not exceed in staged FBC 15 % and in the case of pulverized coal combustion 20 %.

Ca/S mole (stoichiometric) ratio affects lime-catalyzed reactions through CaO/CaSO₄ mole ratio and available, catalytically active, surface. Higher Ca/S mole ratios cause somewhat higher NO emissions and simultaneously somewhat lower N_2O emissions (thermal catalytic destruction). The effect of the Ca/S ratio is bigger in combustion of low-ash bituminous coals.

Mechanism of catalytic reactions at temperatures below 950°C involves, at least as a transient period, formation of C-surface adsorbed and reacting species (like —CO, —CN, —CNO, etc.).

Acknowledgements. This study was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Project No. A 407 2801).

SYMBOLS

A	frequency factor	s^{-1}
c	concentration	mol m^{-3}
(—C)	active site on carbon (char) surface	
(—CO)	active site-surface complex containing oxygen	
(—CN), (—CNO)	active site-surface complexes containing nitrogen and (oxygen + nitrogen)	
conv.	conversion = mass fraction of total char N or coal N converted to NH_3 or NO	
d_p	diameter of solid particles	m
daf	dry, ash-free conditions for coals	
E_a	activation energy of reaction	kJ mol^{-1}
k	kinetic rate constant [s^{-1} for the 1st-order reactions; $\text{mol m}^{-3} \text{s}^{-1}$ for the 2nd-order reactions; $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$ for catalytic reactions, or as given in the text of the paper]	
k_a	adsorption-kinetic rate constant in eqn (8)	mol m^{-3}
k_{sa}	kinetic constant for surface reaction of C-containing matter with NO	$\text{g m}^{-2} \text{h}^{-1} \text{MPa}$
K_{eq}	equilibrium constants for nitrogen and NO reactions (in Fig. 1)	
m	mass	kg
$n(\text{Y})$	amount of substance of species Y	mol
n_3	reaction order for reaction of oxygen according to the scheme (C) in eqns (2, 4, 5, 7)	
$p_i, p(i)$	partial pressure of species i	Pa
P	total pressure	Pa
$r(\text{Y})$	net rate of formation for species Y	$\text{mol m}^{-3} \text{s}^{-1}$
$\mathbf{r}(\text{Y})$	net rate of formation for species Y in reaction of HCN with lime, eqns (1—7)	s^{-1}
rs	surface emission rate in eqns (13—15)	$\text{kg m}^{-2} \text{s}^{-1}$

R	reaction rate (volumetric)	$\text{mol m}^{-3} \text{s}^{-1}$
R	gas constant	$= 8.31433 \text{ J mol}^{-1} \text{ K}^{-1}$
S	sum of all active sites in a char, defined by eqn (11)	mol
T	absolute temperature	K
t	time	s
V	volume	m^3
$w(\text{V}^{\text{daf}})$	mass fraction of volatiles in coal for daf conditions	
$w(\text{C}^{\text{daf}})$	mass fraction of carbon in coal for daf conditions	
$w(\text{H}^{\text{daf}})$	mass fraction of hydrogen in coal for daf conditions	
$w(\text{O}^{\text{daf}})$	mass fraction of oxygen in coal for daf conditions	
$w(\text{N}^{\text{daf}})$	mass fraction of nitrogen in coal for daf conditions	
$x_r(\text{Y})$	relative mole fraction of solid species Y ("surface concentration")	
$x_{r,\Sigma}$	sum of relative mole fractions of reactive species given by eqn (3)	
x_S	mole fraction of individual active sites defined in eqn (12)	
φ	volume fraction	
ψ	mole ratio $[n(\text{N})/n(\text{C})]$	
$\sigma(\text{NO})$	selectivity for NO formation by oxidation of HCN or NH_3 (moles of NO formed by HCN or NH_3 oxidation/moles of HCN or NH_3 oxidized)	
$\sigma(\text{N}_2\text{O})$	selectivity of N_2O formation by oxidation of HCN or NH_3	

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