Kinetic modelling of NO heterogeneous radiation-catalytic oxidation on the TiO₂ surface in humid air under the electron beam irradiation

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Abstract. Theoretical study of NO_x removal from humid air by a hybrid system (catalyst combined with electron beam) was carried out. The purpose of this work is to study the possibility to decrease energy consumption for NO_x removal. The kinetics of radiation catalytic oxidation of NO on the catalyst TiO_2 surface under electron beam irradiation was elaborated. Program Scilab 5.3.0 was used for numerical simulations. Influential parameters such as inlet NO concentration, dose, gas flow rate, water concentration and catalyst contents that can affect NO_x removal efficiency were studied. The results of calculation show that the removal efficiency of NO_x might be increased by 8–16% with the presence of a catalyst in the gas irradiated field.

Keywords: electron beam • catalyst • reactions kinetics • NO_x removal • irradiation • modelling

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Introduction

Electron-beam flue gas treatment (EBFGT) technology has been applied in an industrial scale, EPS Pomorzany [1]. High removal efficiency of SO_2 (>90%) and NO_x (ca. 70%) was obtained at 8 kGy absorbed dose. NO_x removal needs much bigger energy consumption than that for SO_2. Therefore, there is a need to find a way to decrease energy consumption for NO_x removal in this process. Electron accelerators with high power are very expensive, the cost of accelerator is proportional to its power. It will be very costly to study the EBFGT process experimentally, especially in an industrial scale. Therefore, theoretical study of the process of electron-beam treatment of flue gas are first being looked for by many researchers. A hybrid system of a catalyst, combined with EB, might be one of the solutions [2]. In this case, the oxidation processes of NO_x and SO_2 take place on the catalyst surface in flue gas under the electron-beam treatment. As a result, a higher removal efficiency of NO_x from flue gas in the presence of catalyst can be expected at a lower irradiation dose. It provides a possibility that lower power accelerators at lower cost could be applied for EBFGT. It is a well-known fact that ionizing radiation might essentially affect kinetics and mechanism of reactions taking place on the surfaces of dispersive solid bodies. Ionic radiolysis products (free electrons and holes) play an essential role in such processes.

In 1966, the researchers in N. D. Zelinsky Institute for Organic Chemistry of the Academy

of Sciences, USSR found that the irradiation of heterogenic system molecular oxygen neodymium oxide with γ-radiation Co[60] at the temperatures up to 300°C resulted in an atomic re-arrangement in gaseous oxygen molecules [3]. The radiation-catalytic reaction occurs only at simultaneous exposure of ionizing radiation and heterogeneous catalysis at unequal mixture of isotope molecules of oxygen.

Minachev and Antoshin [3] studied the dependence of radiation-catalytic effect on the properties of the irradiated solid oxides, especially artificially synthesized zeolites. They found that the holes were favourably formed in the active center of the catalyst. A certain parallelism was observed in the intensity changes of the surface hole signals and activity, and the data of poison activity of irradiated samples with the release of hydrogen and carbon monoxide had confirmed the hole nature of catalytic active center.

Particles (free electrons and holes) might participate in the secondary reactions resulting in formation of radiolysis final products. The initial radiation-chemical yield of the divided electron-hole pairs determines the amount of radiolysis ionic products yield, and particularly enables the prediction of scale of possible acceleration of heterogeneous catalytic reactions under irradiation.

The catalytic oxidation of xylene in air using TiO₂ under electron beam irradiation [4] revealed that electron/holes pairs were formed as a result of direct impact of electrons on the TiO₂ surface; holes trapped the water molecules, which were adsorbed on the TiO₂ surface and generated OH radicals.

Cubillos Sanabria [5] and Yu *et al.* [6] found that the photo catalytic oxidation of NO on the TiO₂ surface results from an interaction with OH radicals. The rate of electron-hole pairs formation on the TiO₂ surface under the impact of photons according to Yu *et al.* [6] is 4.32×10^{-3} mol·dm⁻²·min⁻¹, according to Cubillos Sanabria [5] is 4.8×10^{-5} mol·dm⁻²·min⁻¹. The radiation-chemical yield of electron-hole pairs generation of 10 molecules/100 eV was obtained experimentally for MgO, BeO and Al₂O₃ [7]. In this case, the rate of formation of electron-hole pairs on the TiO₂ surface under the influence of electron beam was evaluated to be 3.29×10^{-3} mol· dm⁻²·min⁻¹ for Hakoda *et al.* work [4]. However, the energy band gap of TiO₂ is 2.5–3 times less than that of MgO, BeO and Al₂O₃. It could be expected that the radiation-chemical yield of electron-hole pairs formation for TiO₂ would be much higher than 10 and the real rate of electron-hole pairs formation on the TiO₂ surface under the impact of electron beam in the conditions of Hakoda *et al.* work [4] would be much higher than 3.29×10^{-3} mol·dm⁻²·min⁻¹.

This is the reason why we suggested that the process of radiation-catalytic oxidation of NO on the TiO₂ surface under the influence of electron beam in the wet air would go effectively; therefore, it should decrease the energy consumption for NOₓ removal by EBFGT process. In order to verify our assumption, a kinetic model of NO heterogeneous radiation-catalytic oxidation on the TiO₂ surface in humid air under the influence of electron beam was carried out in this work.

Kinetic modelling

The theory of EB-catalyst process was developed mainly based on the theory of heterogeneous photo catalytic oxidation of NO in the presence of TiO₂ proposed by Cubillos Sanabria [5] and Yu *et al.* [6]. The general theory for heterogeneous photo catalytic oxidation of NO in the presence of TiO₂ proposed in the papers [5] and [6] can be applied for electron beam oxidation of NO in the presence of TiO₂ mechanism description, except the generation of electron/hole pairs.

Under EB irradiation, the generation of electron-hole pairs under the influence of electron beam on the surface of catalyst is shown in Eq. (1)

$$(1) \qquad TiO_2 + \text{e-beam} \rightarrow e^- + h^+$$
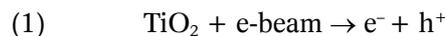
Holes formed according to Eq. (1) trap H₂O (which are adsorbed onto the active sites over TiO₂ surface) and generate OH radicals; the OH radicals oxidize NO (which are adsorbed onto the active sites over TiO₂ surface) to form HNO₂ until the final product being HNO₃ is obtained.

The kinetic model for NOₓ oxidation on the surface of catalyst TiO₂ has been discussed in detail by Cubillos Sanabria [5] and Yu *et al.* [6]. The rate of radiation-catalytic oxidation of NO and NO₂ can be referred to as the rate of photocatalytic oxidation of NO and NO₂ presented in [5], except the definitions of αE.

$$(2) \quad r_{NO} = \frac{-k_{NO}K_{NO}C_{NO}K_{H_2O}C_{H_2O}\beta \cdot \left(\sqrt{1 + \frac{4\alpha E \left(\begin{array}{c} 1 + K_{NO}C_{NO} + K_{NO_2}C_{NO_2} \\ + K_{H_2O}C_{H_2O} \end{array} \right)}{\beta K_{H_2O}C_{H_2O}}} - 1 \right)}{\left(4k_{NO}K_{NO}C_{NO} + 2k_{NO_2}K_{NO_2}C_{NO_2} \right) \cdot \left(1 + K_{NO}C_{NO} + K_{NO_2}C_{NO_2} + K_{H_2O}C_{H_2O} \right)}$$

$$(3) \quad r_{NO_2} = \frac{\left(k_{NO}K_{NO}C_{NO} - k_{NO_2}K_{NO_2}C_{NO_2} \right) K_{H_2O}C_{H_2O}\beta \cdot \left(\sqrt{1 + \frac{4\alpha E \left(\begin{array}{c} 1 + K_{NO}C_{NO} + K_{NO_2}C_{NO_2} \\ + K_{H_2O}C_{H_2O} \end{array} \right)}{\beta K_{H_2O}C_{H_2O}}} - 1 \right)}{\left(4k_{NO}K_{NO}C_{NO} + 2k_{NO_2}K_{NO_2}C_{NO_2} \right) \cdot \left(1 + K_{NO}C_{NO} + K_{NO_2}C_{NO_2} + K_{H_2O}C_{H_2O} \right)}$$

where: r_{NO}, r_{NO2} are the reaction rates at the active surface of catalyst for radiation-catalyst oxidation of NO and NO₂, respectively, [mol·dm⁻²·min⁻¹]; k_{NO}, k_{NO2} are the reaction rate constants for the oxidation of NO and NO₂, respectively, [dm²·mol⁻¹·min⁻¹]; K_{NO}, K_{NO2} and K_{H2O} are the adsorption equilibrium constants for NO, NO₂ and H₂O, respectively,

Table 1. Kinetic constants values

Parameter	Value [6]	Value [5]
k_{NO} [dm²·mol⁻¹·min⁻¹]	3.21×10^{-9}	6.30×10^{-10}
k_{NO2} [dm²·mol⁻¹·min⁻¹]	1.19×10^{-7}	5.94×10^{-9}
K_{NO} [dm³·mol⁻¹]	2.09×10^{4}	9.00×10^{4}
K_{NO2} [dm³·mol⁻¹]	5.38×10^{3}	1.47×10^{4}
K_{H2O} [dm³·mol⁻¹]	2.39	1.50×10^{-1}
β [mol·dm⁻²·min⁻¹]	6.20×10^{-8}	1.42×10^{-8}

[dm³·mol⁻¹]; β is a parameter relating to the reaction rate constants of the electrons and holes in the reaction, [mol·dm⁻²·min⁻¹]; C_{NO}, C_{NO2} and C_{H2O} are the concentrations of NO, NO₂ and water vapour in the air, respectively, [mol·dm⁻³]; αE: rate of electron-hole pair formation under the influence of electron beam on TiO₂ surface; E – intensity of irradiation on the catalyst surface, [W·dm⁻²]; α – parameter, [mol·W⁻¹·min⁻¹], related to radiation-chemical yield of electron-hole pairs formation on TiO₂ surface and the energy absorbed by catalyst at interaction with electron beam in a minute.

Based on Yu *et al*. [6], NO and NO₂ are consumed or generated along the reaction vessel as follows:

$$(4) \qquad v_{air}(dC_{NO}/dx) = (D_{TiO2}/H) \times r_{NO}$$

$$(5) \qquad v_{air}(dC_{NO2}/dx) = (D_{TiO2}/H) \times r_{NO2}$$

where, v_{air} is the linear gas velocity, [dm·min⁻¹]; D_{TiO2} is the catalyst content, [g·g⁻¹]. H is the distance between irradiation window of the reaction vessel and the upper face of the catalyst, [dm].

The concentration of NO and NO₂ along the reaction vessel was solved numerically using the program Scilab 5.3.0.

The values of constants k_{NO}, k_{NO2}, K_{NO}, K_{NO2} and K_{H2O}, for photo catalytic oxidation of NO, were defined in papers [5, 6] and listed in Table 1.

Results of calculation and discussion

NO heterogeneous radiation-catalytic oxidation on the TiO₂ surface in the humid air under the continuous electron beam accelerator

NO heterogeneous radiation-catalytic oxidation on the TiO₂ surface in the humid air under the continuous electron beam accelerator was studied. Irradiation was carried out with electron beam energy of 53 keV, current in the beam of 0.17 mA, and catalyst surface of 1.5×10^{-1} dm² [4]. The rate of electron-hole pair formation under the influence of electron beam on TiO₂ surface, i.e., αE, was calculated based on the conditions of Hakoda *et al*. [4].

If we assume that the catalyst is located at a distance of 1 cm from the irradiation window through which electron beam enters into a reaction vessel, then an electron with energy 53 keV during its movements in 1 cm depth of air will lose 5.7 keV energy in accordance to Baranov data [8]. Energy deposited in air (1 cm) and catalyst were 5.7 keV and 47.3 keV, respectively. Since electron beam current was 0.17 mA,

the number of electrons emitted per second were $0.17 \text{ mA} \times (6.24 \times 10^{15}) = 1.06 \times 10^{15}$ electrons/s; energy deposited in air was $5.7 \text{ keV} \times (1.06 \times 10^{15})$ $= 6.05 \times 10^{18}$ eV/s or 0.98 W and in catalyst 8.13 W.

Therefore, the ratio of absorbed EB energy between air and catalyst layer was approximately 1 W : 8 W.

The total geometry catalyst surface is 1.5×10^{-1} dm², so the intensity of irradiation on the catalyst surface E is:
$E = (8 \text{ W})/(1.5 \times 10^{-1} \text{ dm}^2) = 5.3 \times 10^{1}$ W·dm⁻².

If the radiation-chemical yield of the electron-hole pairs formation on TiO₂ surface equals to 10 for 100 eV, then $\alpha = ((10 /6.022 \times 10^{23})/(100 \times (1.6022 \times 10^{-19})) = 1.036 \times 10^{-6}$ mol·W⁻¹·s⁻¹ $= 6.216 \times 10^{-5}$ mol·W⁻¹·min⁻¹.

The NO oxidation was studied in the mixture: air, 3×10^{-6} mol·dm⁻³ NO, 1×10^{-9} mol·dm⁻³ NO₂, 1×10^{-5} mol·dm⁻³ H₂O.

Under this condition, the maximum expected reaction rate of the active surface for radiation-chemical oxidation NO on TiO₂ surface (r_{NO}) is 3×10^{-7} mol·dm⁻²·min⁻¹.

NO heterogeneous radiation-catalytic oxidation on the TiO₂ surface in humid air under the pulsed electron beam accelerator

NO heterogeneous radiation-catalytic oxidation on the TiO₂ surface in the humid air under the pulsed electron beam accelerator ILU-6M was theoretically studied. The configuration of EB-catalyst reaction vessel was presented in Fig. 1, and parameters used in the numerical simulation were listed in Table 2.

Temperature of the process is equal to 90°C.

αE, the average rate of electron-hole pair formation under the influence of electron beam on TiO₂ surface, is 8.4×10^{-2} mol·dm⁻²·min⁻¹ in the above described conditions; here, the radiation-chemical yield of the electron-hole pairs formation on TiO₂ surface was assumed to be 30 molecules/100 eV (three times higher), as the radiation-chemical yield of electron-hole pairs formation obtained experimentally for MgO, BeO, and Al₂O₃ [7].

Baranov [8] found that an electron with energy 900 keV during its traveling across 1 cm depth of air lost 1.66 keV. Its energy loss across 1 cm air is negligible, and all the energy of the electron is assumed to deposit on the catalyst surface. The distance between the catalyst layer surface and the irradiation windows was assumed to be 1 cm. The maximum residence time of flue gas inside
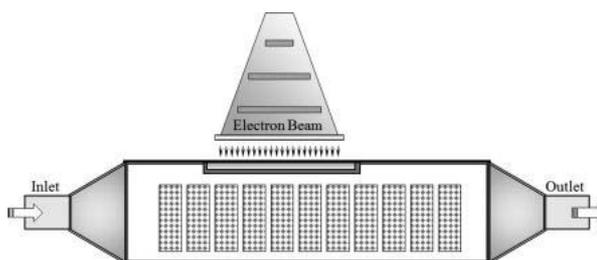
Fig. 1. A diagram of electron beam-catalyst reaction vessel.

Table 2. Parameters used in the numerical simulation

Accelerator	Reaction vessel	Flue gas	Catalyst
Electron energy – 900 keV Pulse current – 250 mA Pick power – 225 kW Pulse duration – 400 μs Pulse repetition rate – 2, 3, 5, 10, 15 and 25 Hz	Cylinder shape configuration: 2.0 dm (diameter) × 8.5 dm (length); Irradiation window: 3.5 dm (length) × 1.2 dm (width)	Flow rate: 5000 dm^3·h^{-1} constantly generated from an oil burner [9]; Gas mixture: air + 8.62% H_2O (V/V) + NO (200, 400, 800, 1000 or 1500 ppmV, respectively)	$TiO_2/\gamma Al_2O_3$ Ø 2–3 mm Specific surface area: 60–70 m^2·g^{-1} TiO_2 Catalyst content D_{TiO2}: 0.5 g·g^{-1}
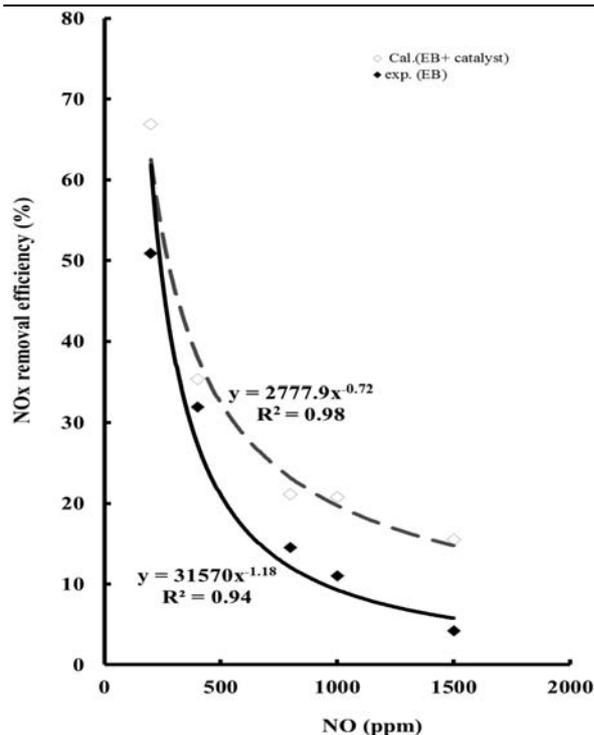
Fig. 2. Effect of the inlet NO concentration on the NO$_x$ removal efficiency (flow rate = 5 Nm^3/h, [C_{H2O}]$_{in}$ = 8.62% (V/V), dose = 44.1 kGy, D_{TiO2} = 0.5).

the reaction vessel at 5 Nm^3/h gas flow rate was 0.32 min. The influence of different parameters on the removal efficiency of NO$_x$ was considered.

Effect of the inlet NO concentration

The inlet concentration of NO influencing NO$_x$ (NO + NO$_2$) removal efficiency with the presence of TiO$_2$ catalyst was theoretically studied under electron beam irradiation with a dose of 44.1 kGy (0.32 min at 25 Hz); the results of calculation were present in Fig. 2 and were compared with the experimental results obtained in similar conditions without the presence of a catalyst [9].

From Fig. 2, it is seen that the removal efficiency of NO$_x$ decreased with increasing the inlet concentration of NO under EB irradiation; this tendency is similar to the experimental results [9]. The NO$_x$ removal efficiency was predicted to be increased by 8–16% with the presence of a catalyst. The removal efficiency of NO$_x$ is lower than that of NO due to NO$_2$ formation (Fig. 3). From Fig. 3, it is also seen that NO concentration decreased with increase of residence time of flue gas inside the catalytic reaction vessel under EB irradiation.
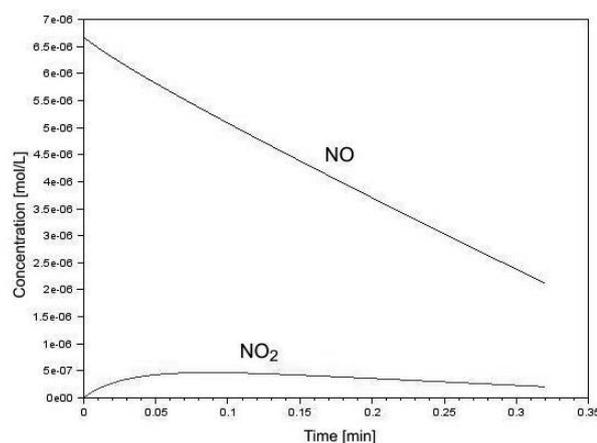
Fig. 3. NO and NO$_2$ concentration vs. residence time of the flue gas inside the catalytic reaction vessel under EB irradiation (gas flow rate = 5 Nm^3/h, [C_{H2O}]$_{in}$ = 8.62% (V/V), [C_{NO}]$_{in}$ = 200 ppm, D_{TiO2} = 0.5, pulse repetition rate = 25 Hz, corresponding dose was 44.1 kGy at 0.32 min).

Effect of the irradiation dose

Irradiation dose effect on the NO$_x$ removal efficiency with the presence of catalyst was theoretically studied for a 200 ppm inlet concentration NO. It was found that the removal efficiency of NO$_x$ increased with the absorbed dose increase (Fig. 4). Higher dose results in generating more electron/hole pairs,
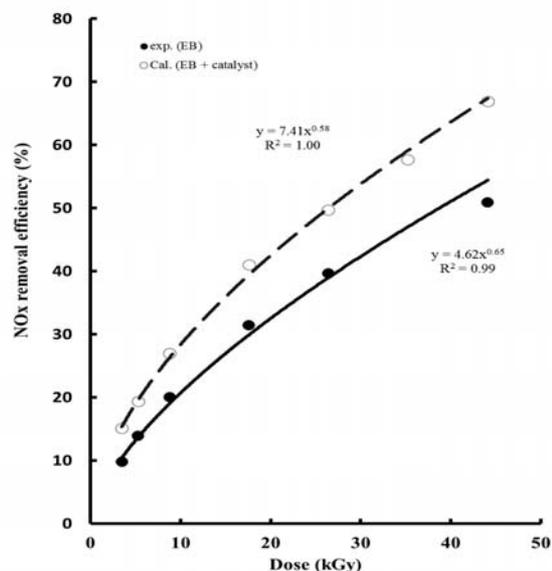
Fig. 4. Effect of the absorbed dose on the NO$_x$ removal efficiency (flow rate = 5 Nm^3/h, [C_{H2O}]$_{in}$ = 8.62% (V/V), [C_{NO}]$_{in}$ = 200 ppm, D_{TiO2} = 0.5).
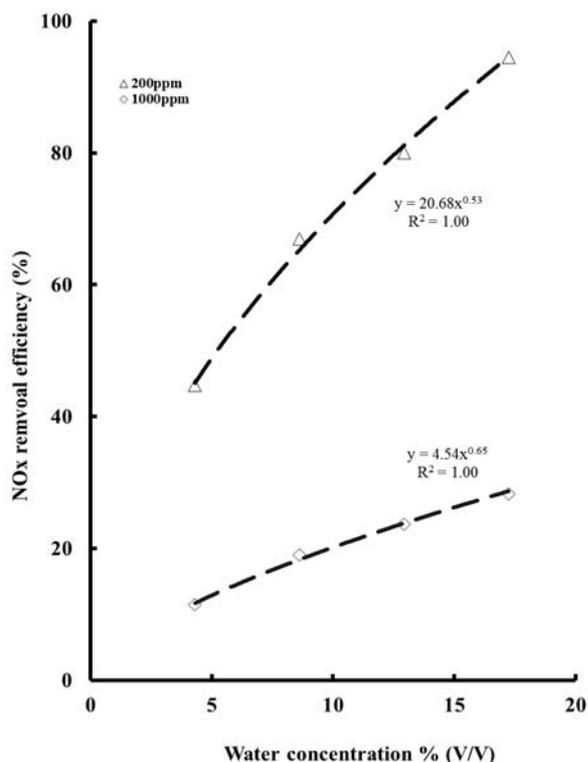
Fig. 5. Effect of water vapour concentration on the NO$_x$ removal efficiency (dose = 44.1 kGy, flow rate = 5 Nm^3/h, D$_{TiO2}$ = 0.5).

thus giving rise to the formation of more hydroxyl radicals; hence, leading to oxidation of NO into NO$_2$ and finally into HNO$_3$ [6]. This phenomenon agrees well with the experimental results carried out in the same conditions without the presence of a catalyst [9]. NO$_x$ removal efficiency increased by 16% at 44.1 kGy with the presence of catalyst under EB irradiation.

Effect of water vapour

Water vapour concentration plays a very important role in NO$_x$ removal. Our previous study [10] revealed that NO$_x$ removal efficiency increased at higher water vapour concentration. Water is a main source for hydroxyl radical formation during water molecules bonding with generated holes on the catalyst surface under EB irradiation. Water influence on NO$_x$ removal efficiency was studied at 44.1 kGy dose for the inlet concentration of NO being 200 and 1000 ppm, respectively. It is found that at higher water vapour concentration, the removal efficiency of NO$_x$ increased (Fig. 5). At the lower inlet concentration of NO, this phenomenon was more apparent.

Effect of gas flow rate

Gas flow rate has an influence on the NO$_x$ removal efficiency because it determines the residence time of flue gas inside the catalytic reactor; longer residence time results in a better mass transfer and adsorption NO onto the catalyst surface, which leads to higher NO$_x$ removal efficiency. Gas flow rate varied from
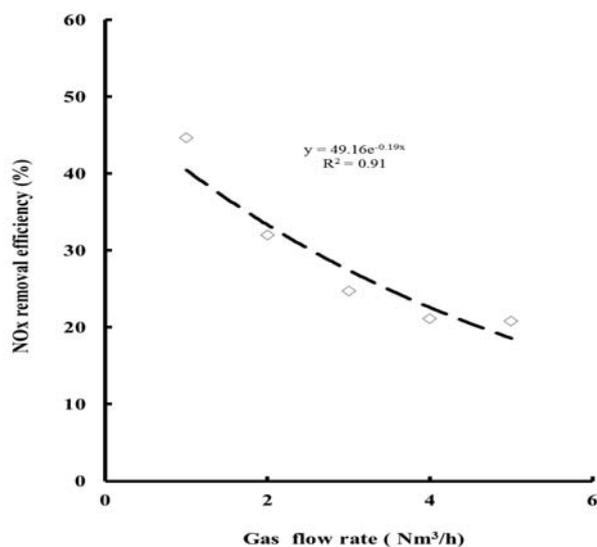
Fig. 6. Effect of gas flow rate on the NO$_x$ removal efficiency (dose = 44.1 kGy, [C_{H2O}]$_{in}$ = 8.62% (V/V), [C_{NO}]$_{in}$ = 1000 ppm, D$_{TiO2}$ = 0.5).

1, 2, 3, 4 and 5 Nm^3/h corresponding to the gas residence time of inside the catalyst reactor being 1.6, 1.28, 0.96, 0.64 and 0.32 minutes, respectively. Figure 6 shows that when the gas volumetric flow rate decreased from 5 Nm^3/h to 1 Nm^3/h, the NO$_x$ removal efficiency increased from 20.8% to 44.7% for the 1000 ppm inlet concentration of NO at 44.1 kGy absorbed dose.

Effect of the catalyst content

Catalyst content has a direct impact on the radiation--catalytic oxidation of NO on the catalyst surface. Electron/hole pairs are generated on the catalyst surface (which is proportional to the catalyst mass applied) under EB irradiation. Figure 7 shows the calculated results of TiO$_2$ content effect on the NO$_x$ removal efficiency for 200 ppm NO at 44.1 kGy dose. It is found that the NO$_x$ removal efficiency is
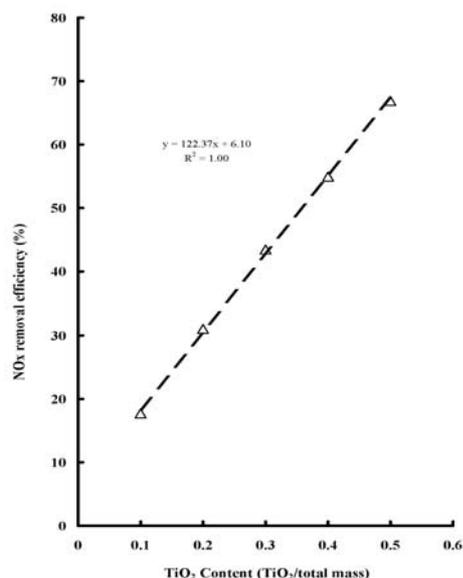
Fig. 7. Effect of catalyst content on the NO$_x$ removal efficiency (flow rate = 5 Nm^3/h, [C_{H2O}]$_{in}$ = 8.62% (V/V), [C_{NO}]$_{in}$ = 200 ppm, dose = 44.1 kGy).

linearly increased with increase of the TiO_2 content, which is in line with Yu *et al.* [6]. Even without the catalyst presence, about 6.1% NO_x can be removed from flue gas under EB irradiation.

Conclusions

NO_x removal from a humid air in the radiation--catalytic reactor was theoretically studied using numerical simulation. Based on the computer modelling simulation, the NO_x removal efficiency in a gas mixture could be enhanced with the presence of a catalyst. The removal efficiency of NO_x increase in the presence of TiO_2 catalyst was predicted to be in the range of 8–16% under EB irradiation. NO_x removal efficiency decreases with increase of the inlet concentration of NO and the volumetric gas flow rate, as well as increase for higher gas humidity and energy dose absorbed. These results agree with tendencies reported on the basis of the experimental results obtained for NO_x removal in the absence of a catalyst [10]. NO_x removal efficiency linearly increases with the rising amount (surface) of the applied catalyst (TiO_2). NO_2 formation from NO oxidation was below 12% due to the desorption and mass transfer of NO_2 from the surface of TiO_2 catalyst to the ambient air [6]. The final product of the radiation-chemical oxidation of NO was HNO_3 molecule.

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