



Full paper/Mémoire

Diesel soot oxidation by nitrogen dioxide, oxygen and water under engine exhaust conditions: Kinetics data related to the reaction mechanism[☆]

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ABSTRACT

Experimental studies on diesel soot oxidation under a wide range of conditions relevant for modern diesel engine exhaust and continuously regenerating particle trap were performed. Hence, reactivity tests were carried out in a fixed bed reactor for various temperatures and different concentrations of oxygen, NO₂ and water (300–600 °C, 0–10% O₂, 0–600 ppm NO₂, 0–10% H₂O). The soot oxidation rate was determined by measuring the concentration of CO and CO₂ product gases. The parametric study shows that the overall oxidation process can be described by three parallel reactions: a direct C–NO₂ reaction, a direct C–O₂ reaction and a cooperative C–NO₂–O₂ reaction. C–NO₂ and C–NO₂–O₂ are the main reactions for soot oxidation between 300 and 450 °C. Water vapour acts as a catalyst on the direct C–NO₂ reaction. This catalytic effect decreases with the increase of temperature until 450 °C. Above 450 °C, the direct C–O₂ reaction contributes to the global soot oxidation rate. Water vapour has also a catalytic effect on the direct C–O₂ reaction between 450 °C and 600 °C. Above 600 °C, the direct C–O₂ reaction is the only main reaction for soot oxidation. Taking into account the established reaction mechanism, a one-dimensional model of soot oxidation was proposed. The roles of NO₂, O₂ and H₂O were considered and the kinetic constants were obtained. The suggested kinetic model may be useful for simulating the behaviour of a diesel particulate filter system during the regeneration process.

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R É S U M É

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Une étude expérimentale sur l'oxydation des suies diesel a été menée dans des conditions opératoires proches du fonctionnement des échappements Diesel et de la régénération continue des filtres à particules. Les tests de réactivité ont été effectués dans un réacteur à lit fixe pour différentes températures et concentrations d'oxygène, de NO₂ et de vapeur d'eau (300–600 °C, 0–10 % O₂, 0–600 ppm NO₂, 0–10 % H₂O). La vitesse d'oxydation des suies a été déterminée à partir des concentrations des espèces CO et de CO₂ formées. L'étude paramétrique montre que l'oxydation des suies par un mélange gazeux contenant NO₂, O₂ et H₂O peut être décrite par trois réactions d'oxydation distinctes : une réaction directe C–NO₂, une réaction directe C–O₂ et une réaction coopérative C–NO₂–O₂. Les

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réactions C–NO₂ et C–NO₂–O₂ sont les principales réactions d'oxydation des suies se déroulant entre 300 et 450 °C. La vapeur d'eau agit comme un catalyseur sur la réaction directe C–NO₂. Cet effet catalytique diminue avec l'augmentation de la température jusqu'à 450 °C. Au-dessus de 450 °C, la réaction directe C–O₂ contribue à la vitesse globale d'oxydation des suies. La vapeur d'eau exerce également un effet catalytique sur la réaction directe C–O₂ pour des températures comprises entre 450 °C et 600 °C. À partir de 600 °C, la réaction directe C–O₂ est la seule réaction responsable de l'oxydation des suies. À partir du mécanisme réactionnel obtenu, un modèle monodimensionnel de l'oxydation des suies a été établi. Les rôles de NO₂, O₂ et H₂O ont été pris en compte et les constantes cinétiques ont été obtenues. Le modèle cinétique établi peut être utile pour simuler le comportement d'un système de filtre à particules diesel pendant le processus de régénération.

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1. Introduction

The improved performance and the low specific fuel consumption of diesel engines caused an increasing demand, during the last years, of cars powered by diesel engines. However, diesel engines produce NO_x and particles of carbonaceous soot (PM), which consist of unburned organic compounds and other solid and liquid material. NO_x and particulates from diesel engines have been identified to generate harmful effects on human health and the environment. To satisfy European and US regulations, extensive efforts have been focused on how to reduce emissions of pollutants, by controlling the combustion process and by developing efficient after-treatment systems. Currently, diesel particulate filters (DPF) are considered very effective a solution to attain the particulate matter (PM) emission standards since they have proved to meet serious diesel engine pollution reduction limits with filtration efficiencies exceeding 90 %. However, soot retained from exhaust gases should be removed to prevent back pressure and therefore a DPF regeneration is necessary. In the diesel exhaust emissions, NO₂ and O₂ are the main oxidants in presence. Hence, soot oxidation by these oxidants is an alternative to regenerate the filters. Several studies focused on the investigation of the uncatalyzed and catalyzed soot oxidation reaction by O₂ and/or NO₂ in the presence or absence of H₂O. Many mathematical models were proposed to simulate these processes in order to understand thoroughly the inherent mechanisms, to predict the behaviour of DPF during its usage and to contribute to the improvement of the design process. Jeguirim et al. [1] studied the adsorption and reduction of NO₂ at low temperatures (50 °C) on activated carbon and evidenced the formation of surface complexes such as –C(ONO₂), –C(NO₂) and –C(O). Gao et al. [2] found similar results. Muckenhuber and Grothe [3] proposed a reaction mechanism where two oxygen atoms from two different NO₂ molecules are transferred onto the carbon surface. In this case, NO₂ reacts directly with the carbon surface to form an acidic functional group, of acyl-nitrite type, as intermediate only. Du et al. [4] studied the oxidation by oxygen of uncatalyzed and calcium-catalyzed soot by means of Thermogravimetric Analysis (TGA) and Temperature-Programmed Desorption (TPD). They concluded that the products of the reaction, CO and CO₂, are generated via different mechanisms and that CO₂ was

formed on sites different from CO ones. They formulated a model where the carbon structure is the controlling factor for the uncatalyzed oxidation and where calcium dispersion on the carbon surface is that for the catalyzed reaction. He et al. [5] simulated the CO/CO₂ ratio obtained during char combustion by taking into account the pore model, the gas diffusion inside the pores and the reaction between carbon and oxygen. They concluded that the secondary reactions and pore structure significantly influenced the CO/CO₂ ratio. Biggs and Agarwal [6] investigated the ratio CO/CO₂ on a porous char particle in a fluidized bed and suggested a relationship between the CO/CO₂ ratio and the char particle size. Floess et al. [7] found that the reactivity of char is a function of particle size for particles between 50 and 200 μm in diameter. This effect is not observed for macroporous char networks. Neef et al. [8] studied the kinetics of the uncatalyzed oxidation, in oxygen/argon atmosphere with or without water, of two types of soot: flame soot (Printex U) and diesel soot, in the temperature range 450–550 °C in a flow reactor. A kinetic model, taking into account the conversion factor, was proposed and discussed. Jacquot et al. [9] and Jeguirim et al. [10–12] studied the kinetics of the reaction between NO₂ and carbon in the presence of O₂ and H₂O in a fixed bed reactor. The rate increase of carbon consumption by NO₂ in the presence of O₂ was attributed to the reaction between NO₂ and the intermediate species formed by the adsorption of oxygen on the carbon surface. Water presence increases the rate of carbon consumption because of the formation of intermediate nitric and nitrous acids which enhance the rate of C–NO₂ reaction. However, the oxygen of water is not consumed and thus water is considered as a catalyst for the carbon oxidation reaction [12]. A monodimensional model was developed and kinetic parameters were extracted for the temperature range 300–400 °C [9–11]. Carbon oxidation by O₂–NO₂–H₂O in a flow reactor was also studied at 250–500 °C by Jung et al. [13] who proposed reaction mechanisms and extracted kinetic constants. Schejbal et al. [14] developed a model for the soot deposition on the DPF and its regeneration based on the detailed kinetics of catalyzed and uncatalyzed soot combustion by O₂ and NO₂ developed by Jeguirim et al. [12]. The role of NO₂ and O₂ in the combustion of soot was also investigated by Setiabudi et al. [15] on three kinds of soot in the temperature range 100–450 °C in a flow reactor system and by thermogravimetry. The intermediates of

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