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An experimental and modeling study of the influence of flue gases recirculated on ethylene conversion

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The influence of those gaseous compounds that can be typically present in combustion processes with flue gas recirculation (FGR) techniques: CO_2, H_2O, CO, NO, NO_2, N_2O and SO_2, on ethylene conversion was analyzed through an experimental and modeling study. Ethylene oxidation experiments in the presence of the different gaseous compounds were carried out in the 700–1400 K temperature range, at atmospheric pressure, from fuel-lean to fuel-rich conditions, using N_2 as bath gas. These experiments were modeled by means of a detailed gas-phase chemical kinetic mechanism, which was used to identify the implications of the different gaseous compounds recirculated for the ethylene oxidation scheme, as well as for their own conversion. Overall, good agreement was obtained between the experimental data and the modeling, and thus the proposed mechanism can be successfully used to model the ethylene oxidation in the presence of flue gases recirculated (CO_2, H_2O, CO, NO, NO_2, N_2O and SO_2) in a wide range of operating conditions.

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1. Introduction

Combustion processes are typically considered as ones of the main responsible of the emission to the atmosphere of important air pollutants, such as NO_x, SO_2 and particulate matter. Flue gas recirculation (FGR) is an interesting technique for the reduction of nitrogen oxide (NO_x) emissions that can be applied to boilers or internal combustion engines. This technique includes the recirculation of part of the flue gases back to the combustion chamber, and may be responsible for various effects on combustion, pollutant formation and emissions. Thereby, it is of interest to analyze the role of the different main gases recirculated on the overall combustion scheme, as a first step toward the further development of flue gas recirculation strategies. In this context, it would be also interesting to develop a kinetic model able to describe properly the main features of hydrocarbon combustion together with flue gas recirculation strategies.

Although many combustion processes deal with solid fuels, a large part of the fuel conversion takes place in the gas-phase [1]. Therefore, it is interesting to progress in the knowledge of the oxidation of hydrocarbons in the presence of recirculated flue gases under combustion conditions. Some studies of the effect of CO_2 or H_2O on fuel oxidation have pointed out that both compounds, CO_2 and H_2O, participate in chemical reactions that modify the composition of the O/H radical pool: CO_2 mainly through reaction $CO_2 + H \rightleftarrows CO + OH$ [1–4], and H_2O mainly through reaction $H_2O + O \rightleftarrows OH + OH$ [5,6]. However, there are a number of literature results on the effect of the presence of CO_2 and H_2O on the oxidation of a given fuel, showing different results (e.g., [4,6]).

With respect to the recirculation of the main nitrogen oxides (i.e. NO, NO_2, N_2O), it is worth to mention that the hydrocarbon oxidation process in the presence of NO has been previously addressed in a number of works (see for example: [7–10]), covering a wide range of operating conditions and using different reaction systems. However, the implications of the presence of NO_2 or N_2O for fuel oxidation have not yet been fully described. Besides to the well known capacity of hydrocarbon radicals to reduce NO in reburn type reactions [8], the oxidation of hydrocarbons can also be promoted by the NO/NO_2 interconversion at low temperatures [11,12]. However, the role of NO or NO_2, as initial reactants, may differ. For example, Chan et al. [12] studied the differentiated effect of NO and NO_2 in promoting methane oxidation, at atmospheric pressure, in a flow reactor under fuel-lean conditions. They observed that the promotion by NO started at lower temperatures than with NO_2, while the sensitizing effect of NO_2, once initiated, became more active with the increase of the temperature. The authors attributed these different behaviors of NO and NO_2 presence, to the variation of the rate-controlling reactions in both NO and NO_2 systems. Meanwhile, in combustion processes N_2O is

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believed to be converted to N_2 through thermal decomposition, or by interaction with the radical pool, mainly by H reaction [13]. However, it can also react with hydrocarbon radicals (i.e. CH_3) leading to the formation of NO, as in hydrocarbon flames [14].

In the case of the recirculation of SO_2, even though it is known that SO_2 can interact with the radical pool during combustion affecting the combustion behavior [15], the effect of SO_2 on hydrocarbon oxidation is not completely understood. The mechanism for radical removal has been commonly recognized to be of the type: $X + SO_2 + M \rightarrow XSO_2 + M$ and $Y + XSO_2 \rightarrow XY + SO_2$, where X and Y may be H, O or OH [16]. However, in the last decade it has been reported that the inhibiting behavior of SO_2 can involve a number of interrelated and extended cycles [17].

In this context, this work includes an experimental and modeling study of the oxidation of C_2H_4 in the presence of recirculated flue gases (CO_2, H_2O, CO, NO, NO_2, N_2O and SO_2), to analyze the individual role of each flue gas in the process, under different operating conditions (i.e. by varying temperature and stoichiometry). The experimental results have been simulated and interpreted in terms of a literature detailed gas-phase kinetic mechanism that has been updated in the present work according to the present experimental data. The elementary steps involving ethylene conversion and the main gas products formation have been identified as a function of the different exhaust gases recirculated.

2. Experimental methodology

The experiments of the oxidation of ethylene in the presence of the different flue gases recirculated (CO_2, H_2O, CO, NO, NO_2, N_2O and SO_2) were carried out in an experimental installation that has been used with success by our group in a number of earlier works, addressing homogeneous gas-phase reactions (e.g., [18,19]). Reaction takes place in a quartz plug flow reactor, following the design of Kristensen et al. [20], which has a reaction zone of 8.7 mm inside diameter and 200 mm in length. The reactor is placed in an electrically heated oven, ensuring a uniform temperature profile throughout the reaction zone within ±5 K.

Gases are fed to the reactor, through mass flow controllers, in four separate streams: a main flow containing nitrogen and water, and three injector tubes containing C_2H_4, O_2 and the recirculated gases (CO_2, CO, NO, NO_2, N_2O or SO_2). The gases are premixed just before entering the reaction zone. Reactants and the nitrogen to balance are fed from gas cylinders, and water vapor is fed by saturating a nitrogen stream through a bubbling water system at the adequate temperature in order to get the desired concentration of H_2O in the reaction zone. The total flow rate in all experiments is 1000 mL(STP)/min, resulting in a gas residence time dependent on the reaction temperature of $195/T(\mathrm{K})$ seconds. Nitrogen is used to balance.

A constant concentration of 1000 ppm of C_2H_4 as fuel is introduced in all the experiments, and the amount of O_2 is varied depending on the stoichiometry of the reaction (λ), which has been ranged from fuel-rich to fuel-lean (i.e., $\lambda = 0.7$, 1 and 2). Each set of experiments is carried out at atmospheric pressure covering the 700–1400 K temperature range both, in the presence of a given flue gas recirculated (CO_2, H_2O, CO, NO, NO_2, N_2O and SO_2), and in the absence of it. Table 1 summarizes the conditions of the experiments performed. At the outlet of the reaction zone, the product gas is quenched by means of external refrigeration by cooling air.

The composition of the product gas from the reactor has been analyzed by a micro-gas chromatograph equipped with TCD detector, a Fourier Transform Infrared (FTIR) spectrometer, and continuous IR analyzers for CO, CO_2 and NO. The uncertainty of the measurements is estimated as ±5% in general, and ±10% for the FTIR analyzer, but not less than 10 ppm. Carbon-balance was checked for the experiments and, in general, was found to close within 100 ± 5%. A more detailed description of the experimental installation can be found elsewhere (e.g., [21,22]).

3. Detailed gas-phase chemical kinetic model

The gas-phase chemical kinetic mechanism developed in the present work was initially built from the work of Alzueta et al. [18], on the basis of previous work of Glarborg et al. [23] to describe the interactions among C_1/C_2 hydrocarbons and nitric oxide, and Skjøth-Rasmussen et al. for benzene formation [24]. Additional reactions were added from the ethanol oxidation mechanism of Alzueta and Hernández [22]. This compiled mechanism was previously used, with minor modifications and updates, for modeling CO oxidation in the presence of variable amounts of CO_2 and H_2O as representative of different exhaust gas recirculation conditions [25], and it was able to reproduce the main experimental trends and concentration results for CO. Subsequently, the sulfur subset taken from the work of Giménez-López et al. [15], based on the work of Alzueta et al. [16], was added. The resultant mechanism was tested against the experimental data obtained in this study, and minor modifications were introduced as listed as follows.

The modifications in the H/S/O subset involve the product channels of the $SO_2 + H$ reaction (HOSO and SO + OH), for which rate constants were adopted from Goumri et al. [26] and Blitz et al. [27], respectively, also used in the original mechanism of Alzueta et al. [16]. The modifications in the H/C/O subset include the addition of the $CH_2O + M \rightleftarrows CO + H_2 + M$ and $HCO + HO_2 \rightleftarrows CO_2 + OH + H$ reactions, for which rate constants were drawn from Glarborg et al. [23], who used the determinations of Kumaran et al. [28] and Tsang and Hampson [29], respectively. In the H/N/O subset, the reaction $NO_2 + HO_2 \rightleftarrows HONO + O_2$, which was found to be an important NO_x-related reaction [12], was included with the rate constant drawn from Hori et al. [11], which was also used in the work of Glarborg et al. [23].

The resultant mechanism, developed to describe the ethylene oxidation in the presence of flue gas recirculation gases (CO_2, H_2O, CO, NO_2, N_2O and SO_2) at atmospheric pressure, under a wide range of operating conditions, has been validated with the present experimental data. Thermodynamic data for the involved species are taken from the same sources as the origin mechanisms. This mechanism and the thermodynamic data are included as Supplementary material. The modeling study was performed using the

Table 1
Matrix of experimental conditions.[a]

Set	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$[C_2H_4]$	0.1 (%)															
λ	0.7	1	2	1	1	1	0.7	1	2	0.7	1	2	1	0.7	1	2
$[O_2]$ (%)	0.21	0.3	0.6	0.3	0.3	0.3	0.21	0.3	0.6	0.21	0.3	0.6	0.3	0.21	0.3	0.6
Gas recirc.	–	–	–	CO_2	CO	H_2O	NO	NO	NO	NO_2	NO_2	NO_2	N_2O	SO_2	SO_2	SO_2
(%)	–	–	–	25	0.5	10	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

[a] Water vapor was kept constant with a concentration of 5000 ppm in all of the experiments, with the exception of set 3 which contains 10% of H_2O.

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