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Full Length Article

Effect of CO_2 atmosphere and presence of NO_x (NO and NO_2) on the moist oxidation of CO

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A B S T R A C T

The role of CO_2 on the moist oxidation of CO in the CO-NO and CO-NO_2 systems is analyzed from both experimental and modelling points of view, under flow reactor conditions, at atmospheric pressure, over the temperature range of 700–1400 K and at fuel-rich ($\lambda = 0.5$) and fuel-lean ($\lambda = 2$) environments. Sensitivity and reaction rate analyses were used to identify the role of CO_2 in this process. Additionally, the effect of the presence of NO and NO_2 on CO oxidation is considered. Results indicate significant differences in combustion characteristics between CO oxidation in a 0% or 25% CO_2 atmosphere, in the presence of both NO or NO_2. In particular, at high temperatures, either NO or NO_2 promote the CO oxidation in CO_2 atmosphere, through a specific NO-NO_2 interconversion system, which is catalysed by the CO_2 presence. However, in the 1075–1150 K range and independent of the CO_2 atmosphere, the CO oxidation is strongly inhibited by NO_2 presence. The effect of CO_2 and NO_x presence on CO conversion is quite similar for both O_2 levels.

1. Introduction

Carbon dioxide (CO_2) capture and storage (CCS) roughly consist of producing a concentrated CO_2 output stream from industrial and energy-related sources and its further storage, for a long-term isolation from the atmosphere, or its use in industrial processes [1]. Among the different technologies proposed for CO_2 capture, the oxy-fuel combustion process implies the use of nearly pure oxygen for combustion instead of air, using recirculated gases to control temperature. Therefore, during this process, the reactants are diluted in CO_2, and the high CO_2 concentration may modify the formation and consumption of other atmospheric pollutants, such as CO and nitrogen oxides (NO_x). Even though the oxy-fuel combustion represents an opportunity to minimize CO emissions to very low levels because of the high concentration of oxygen, the CO-CO_2 equilibrium may become a source of CO emissions. In addition, the distribution of nitrogen oxides between NO and NO_2 may also be affected by the oxygen rich environment and their subsequent relative impact on the CO oxidation by the high CO_2 levels. While the individual CO-CO_2 and CO-NO_x systems have been investigated previously in a number of works e.g. [2–7], considerably lower work has been made to characterize the effect of CO_2 on the CO-NO_x oxidation system.

NO_x can significantly impact the CO oxidation; both NO_2 and NO have the capacity, under given conditions, to inhibit or boost the moist CO oxidation [4]. This way, the overall effect of NO and NO_2 depends on the radical pool composition and their specific ability to remove radicals. In general, NO catalyses the recombination of radicals through the reaction sequence: $X + NO + M \rightarrow XNO + M$ and $Y + XNO \rightarrow XY + NO$ [2], while NO_2 acts as a H/O radical sink through reactions of the type: $X + NO_2 \rightarrow OX + NO$, where X and Y may be the O, H or OH radicals [2]. These reactions are usually reported to inhibit the fuel oxidation in flames, although, under given conditions of temperature and NO_x concentration, they can also promote its consumption [4]. Additionally, a CO_2 atmosphere may also modify the reaction scheme and consequently affect the CO-NO_x system. Actually, CO_2 is reported to inhibit the moist CO oxidation by modifying the O/H radical pool [6]. However, as in the case of the NO_x, the extent of this suppressing effect depends on the given reaction environment [6].

In this context, in the present work an experimental and modelling study of the effect of a CO_2 atmosphere on the conversion of moist CO-NO_x mixtures at fuel-rich and fuel-lean conditions, in the 700–1400 K range, is systematically performed.

2. Experimental and modelling methodology

2.1. Experimental

The experiments were performed in an experimental installation

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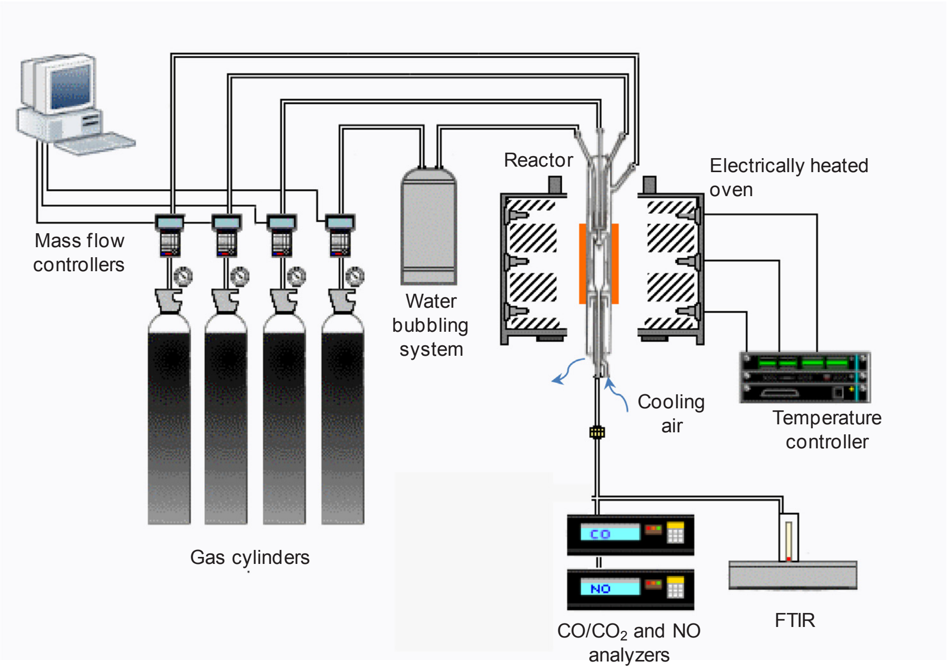

Fig. 1. Experimental set-up used for studying the gas-phase oxidation of fuel mixtures.

used with success in a number of early works addressing gas-phase reactions (see for instance [6,8]). Fig. 1 shows an scheme of the experimental installation.

The reaction system is constituted by a quartz plug flow reactor, according to the design of Kristensen et al. [3], located inside a three-zone electrically heated oven. Reactant gases are fed to the reactor, through mass flow controllers, in up to four separate streams which are mixed just before entering to the reaction zone. The mass flow controllers present a full scale error of 1.5%. However, each flow rate was manually checked with a flow meter, reducing the uncertainty of the flow rates to negligible values. The configuration of the injection system has been designed following the investigations of Alzueta et al. [9]. The reaction zone has 8.7 mm inside diameter and 200 mm in length, and it has a uniform temperature profile within ± 5 K. The temperature in the reaction zone was measured with a type K fine-wire thermocouple placed into a thin tube along the reactor without contact with reactants. The uncertainty in temperature measurements with the type K thermocouple was estimated to be ± 1.5 K. At the outlet of the reaction zone, the product gas is efficiently quenched by means of external refrigeration with cooling air and, then, directed to the gas analysis system. The CO, CO_2 and NO concentrations have been measured by Uras 14/IR analysers and the NO_2 concentration by a Fourier Transfer Infrared (FTIR) analyser. The uncertainty of these measurements is estimated within 5%.

Experiments are performed under diluted conditions (0.5% CO), at atmospheric pressure, over the temperature range of 700–1400 K, at fuel rich ($\lambda = 0.5$) and fuel lean ($\lambda = 2$) conditions, in the presence of 0.1% H_2O, variable amounts of CO_2 (0 and 25% CO_2), and in the presence of either 0.1% NO or 0.1% NO_2. In all the experiments, N_2 is used to balance up to obtain a total flow rate of 1000 mL (STP)/min. The experiments are performed under moist conditions to provide a source of H and OH radicals; nevertheless, the above concentration of water is relatively low so as not to hinder the specific role of CO_2 in this process.

CO, CO_2, O_2, NO, NO_2 and N_2 are fed to the reaction system from gas cylinders, and H_2O is fed by saturating a nitrogen stream through a bubbling water system at room temperature. The reactant concentrations are shown in Table 1. In addition to the experiments performed in the present work, Table 1 includes selected experiments from a previous work of the authors [6], which corresponds to the moist oxidation of CO-CO_2 mixtures in the absence of NO_x. These experiments (sets 1, 3, 5 and 8 in Table1) were performed in the same experimental installation as the one used in the present work, and are used to isolate the specific effect of NO_x in the CO-CO_2 system.

The experimental procedure followed to perform the experiments is well established [6,8,9]; the overall experimental uncertainty is dominated by the uncertainty in the gas concentration measurements and is estimated to be ± 5%.

Table 1
Matrix of experimental conditions. All the experiments are run at a given flow rate of 1000 mL (STP)/min and using nitrogen to balance. P.w. denotes present work.

Set	λ	CO (%)	O_2 (%)	NO (%)	NO_2 (%)	H_2O (%)	CO_2 (%)	Ar (%)	
1	0.5	0.5	0.125	–	–	0.1	–		[6]
2	0.5	0.5	0.125	0.1	–	0.1	–		P.w.
3	0.5	0.5	0.125	–	–	0.1	25		[6]
4	0.5	0.5	0.125	0.1	–	0.1	25		P.w.
5	2	0.5	0.5	–	–	0.1	–		[6]
6	2	0.5	0.5	0.1	–	0.1	–		P.w.
7	2	0.5	0.5	–	0.1	0.1	–	50	P.w.
8	2	0.5	0.5	–	–	0.1	25		[6]
9	2	0.5	0.5	0.1	–	0.1	25		P.w.
10	2	0.5	0.5	–	0.1	0.1	25	50	P.w.