

## SUPPORTING INFORMATION

Detection of some stable species during the oxidation of methane by coupling a jet-stirred reactor (JSR) to cw-CRDS

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### I. Detailed description of the experimental set up

The oxidation of methane was performed using a spherical quartz jet-stirred reactor. The same type of reactor has already been used recently to study the oxidation of large alkanes [28] and esters [29]. This is an isothermal and isobaric continuous flow reactor working at steady state which is well adapted to kinetic studies. It was designed to obtain homogeneous concentrations and temperature of the gas phase inside the reactor during residence times between 0.5 and 10 s [30]. Species exiting the reactor were analyzed using two different techniques: gas chromatography and cw-CRDS. A schematic view of the set-up is displayed in Figure 1.

#### I.1. Jet-stirred reactor

The jet-stirred reactor used in this study is spherical with a volume of about 85 cm<sup>3</sup>. It is preceded by an annular preheater in which the reacting mixture is progressively heated up to the reaction temperature. Then the reacting mixture enters the reactor through an injection cross providing four turbulent jets. The mixing of the gas phase is achieved through these four jets. The annular preheater and the reactor are made of fused silica. The heating is provided through Thermocoax resistances rolled around the preheater and the reactor. The reaction

temperature is measured with a type K thermocouple located in a glass finger (the intra-annular part of the preheater) at the center of the spherical reactor.

Mass flow controllers (Bronkhorst) are used to control the flow rates of the reactant ( $O_2$  and  $CH_4$ ) and of the inert gas (helium). The role of the inert gas is to dilute the reacting mixture in order to slow down the exothermicity of the reaction and to get a better control of the temperature. The pressure in the reactor (800 Torr = 106.7 kPa) is controlled using a manual valve located downstream.

## **I.2. Gas chromatography analyses**

Analyses were performed using two online gas chromatographs. Both apparatus were equipped with a six-gates sampling valve for the introduction of samples taken from the gas at the outlet of the jet-stirred reactor. The first gas chromatograph (Agilent 6820) was fitted with a Haysep D packed column and a flame ionization detector. The carrier gas was helium and the oven temperature profile was: 333.15 K during 10 min; ramp at a rate of  $5 \text{ K}\cdot\text{min}^{-1}$  up to 473.15 K; 473.15 K during 62 min. It was used for the quantification of methane,  $C_2$  and  $C_3$  hydrocarbons. The second gas chromatograph (Shimadzu 14A) was fitted with a Carbosphere packed column and a thermal conductivity detector. It was used for the quantification of oxygen and carbon oxides. The carrier gas was helium and the oven temperature profile was: 353.15 K during 10 min; ramp at a rate of  $10 \text{ K}\cdot\text{min}^{-1}$  up to 473.15 K; 473.15 K during 33 min. The calibration of the gas chromatographs was performed using gaseous standards provided by Air Liquide. The maximum relative uncertainty in the mole fractions was estimated to  $\pm 5\%$ . Limits of detection were 100 ppm for carbon oxides and 5 ppm for hydrocarbons.

## **I.3. cw-CRDS cell and analysis**

The cw-CRDS cell consists of a glass tube with an outer diameter of 8 mm and a length of 80 cm. The total volume of the cell including the sampling probe is estimated to be  $40 \text{ cm}^3$ . The cell is maintained through convection at ambient temperature and the pressure in the CRDS cavity is kept at around 10 Torr. The low pressure is obtained using a rotary vane pump (Alcatel 1015SD with a nominal flow rate of  $15 \text{ m}^3\cdot\text{h}^{-1}$ ).

CRDS analyses were carried out in the near infrared at wavelengths from  $6638 - 6643 \text{ cm}^{-1}$ . The near-infrared beam was provided by a fibred distributed feed-back (DFB) diode laser

(Fitel-Furukawa FOL15DCWB-A81-W1509) emitting up to 40 mW, the wavelength can be varied in the range  $6640 \pm 13 \text{ cm}^{-1}$  through changing the current applied to the diode laser. The diode laser emission is directly fibred and passes through a fibred optical isolator and a fibred acousto-optical modulator (AOM, AA Opto-Electronic). The AOM allows the laser beam to be deviated within 350 ns with respect to a trigger signal for a total duration of 1.5 ms. The zero order beam is connected to a fibred optical wave meter (228 Bristol Instruments) for monitoring the wavelength of the laser emission with an accuracy of  $0.01 \text{ cm}^{-1}$ . The main first order laser beam is coupled into the CRDS optical cavity through a short focal length lens ( $f = 10 \text{ mm}$ ) for mode matching so as to excite the fundamental  $\text{TEM}_{00}$  mode. Two folding micrometric mirrors allow easy alignment of the beam, as shown in Figure 1 (main text). After many round trips, the optical signal transmitted through the cavity is converted into current by an avalanche photodiode (Perkin Elmer C30662E). A home designed amplifier-threshold circuit converts the current signal to an exploitable voltage signal and triggers the AOM to deviate the laser beam (turn off of the first order) as soon as the cavity comes into resonance and the photodiode signal exceeds a user-defined threshold. The photodiode signal is connected to a fast 16 bit analogue acquisition card (PCI-6259, National Instruments) in a PC, which is triggered also by the amplifier-threshold circuit. The acquisition card has an acquisition frequency of 1.25 MHz and thus the ring-down signal is sampled every 800 ns and the data are transferred to PC in real time. The ring-down time  $\tau$  is obtained by fitting the exponential decay over a time range of seven lifetimes by a Levenberg-Marquardt exponential fit in LabView. The concentration of a species being formed or consumed during the hydrocarbon oxidation process in a jet-stirred reactor (JSR), can be obtained by measuring the ring-down time of the empty cavity  $\tau_0$ , i.e., the ring down time before heating the reactor, and the ring down time  $\tau$ , after turning on the heater:

$$\alpha = [A] \times \sigma = \frac{R_L}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (1)$$

where  $\sigma$  is the absorption cross section,  $R_L$  is the ratio between the cavity length  $L$ , i.e. the distance between the two cavity mirrors to the length  $L_A$  over which the absorber is present (see section on  $\text{CH}_4$  quantification),  $c$  is the speed of light. Knowing the absorption cross section  $\sigma$ , one can extract the concentration  $[A]$  of the target molecule.

## **REFERENCES:**

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