

# Time Resolved (2 s) Study of the Initial Steps of the Catalytic Hydrogenation of CO: From Branched Isomers to Unsaturated Molecules

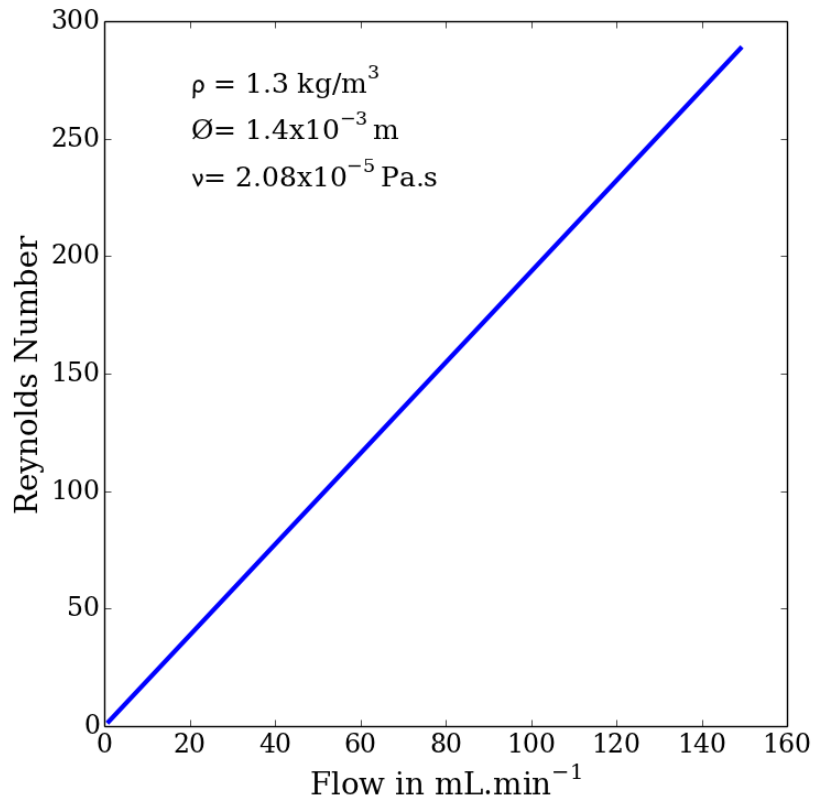
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## **Supporting Information**

The behavior of flow in the pipes from the delivery system to the reactor and from the reactor to the analytical system was evaluated using the dimensionless Knudsen and Reynolds numbers. The former, calculated at room temperature for 1/8" stainless steel tubing, shows that our system is in a *viscous flow* (i.e. mean free path of molecules ( $\lambda$ )  $\gg$  than inner diameter of the pipe). The Reynolds number was evaluated for different flow rates as presented in Figure S1.



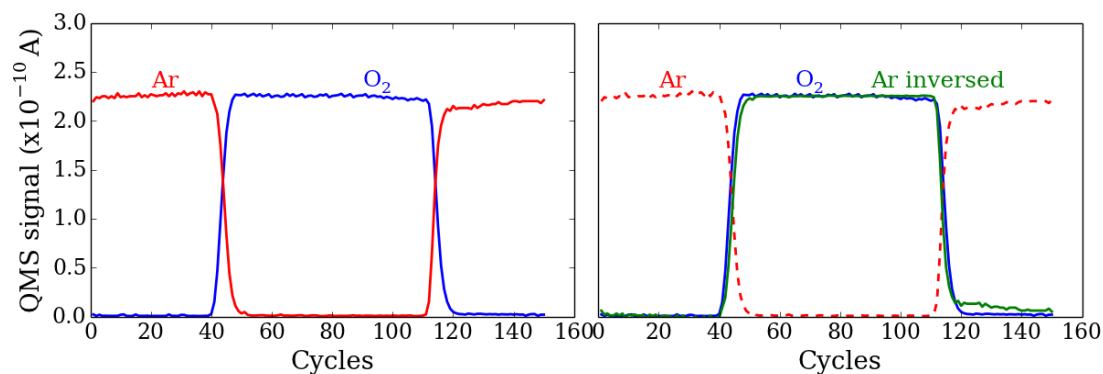
**Figure S1: Evaluation of Reynolds number for our transient system; calculation was done using O<sub>2</sub> at room temperature for a flow in the range of 1 to 150 mL.min<sup>-1</sup>**

From the calculated value, it can be seen that the Reynolds is well below the number for a cylindrical pipe ( $Re \approx 2000$ ), which indicates that our flow is *viscous laminar* flow.

The laminar sublayer thickness ( $\delta_s$ ) was calculated for the range of flow rates. It was determined that for a flow between 20 and 100 sccm,  $\delta_s$  is an order of magnitude smaller than the inner diameter of the pipe. This indicates that the flow behavior is close to a plug flow where the velocity of the fluid is assumed to be constant across any cross-section of the pipe perpendicular to the axis of the pipe.

Verification for a well-mixed reactor was done by executing a switch between pure argon (in circuit 1) and pure oxygen (in circuit 2) while the reactor is opened.

The mass/charge ( $m/z$ ) ratio is monitored at the online-quadrupole mass spectrometer. The results of this experiment are presented in Figure S2.

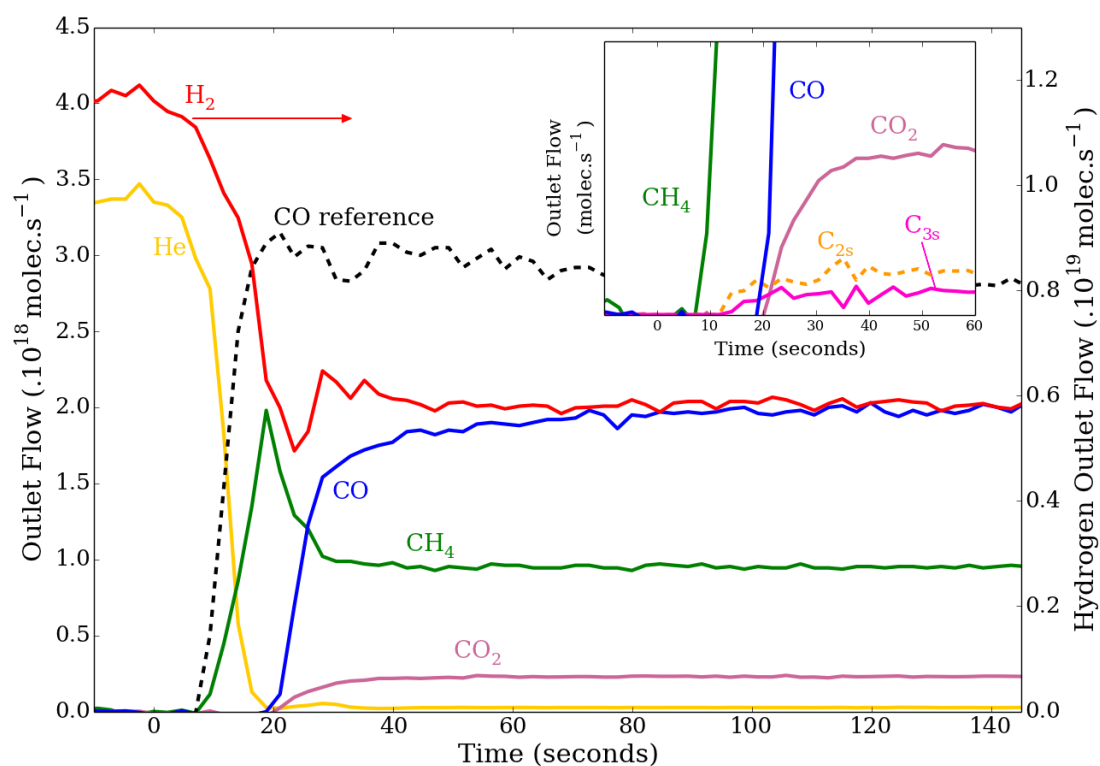


**Figure S2: Online-quadrupole mass spectrometer signal (left) and normalized signal (right) obtained during Ar → O<sub>2</sub> → Ar switch at room temperature and a total flow of 25 sccm**

As is seen in Figure S2, the O<sub>2</sub> and Ar inversed are perfectly overlapped showing that the residence time of the gases in the reactor are identical. Moreover, the mass spectrometer signals exhibit the characteristic exponential time dependence of a well-mixed reactor.

Finally, the different processes such as reactor filling, adsorption/desorption, variation of CO concentration (i.e. partial pressure in the reactor), etc. are deconvoluted from each other thanks to the use of different reference gases. We are co-feeding argon with CO (mixed 10% in Vol. in the CO cylinder) which allows accounting for the behavior of CO if it was not reacting with the catalyst. The argon signal at the mass spectrometer is normalized and scaled up to produce the *CO reference* curves presented in the different Figures. Subsequently, we are adding neon at the outlet of the reactor but before the MS. Since the neon does not flow through the reactor, its behavior is independent from the phenomenon occurring in the reactor and allow for the evaluation of the total instantaneous volumetric flow rate.

Figure S3 depicts the data obtained from the online-MS after the catalyst was submitted to a switch from H<sub>2</sub>:He to H<sub>2</sub>:CO. All timing is referenced to the theoretical CO onset (“CO reference” in Figure S3), such that a time of zero corresponds to the appearance of argon at the online-MS.



**Figure S3:** Outlet flows in molecules per second during the transient experiment ( $T = 230\text{ }^{\circ}\text{C}$ , atmospheric pressure, total volumetric flow rate of  $40\text{ cm}^3\text{ min}^{-1}$ ,  $\text{H}_2\text{:CO} = 3\text{:}1$ ). The inset provides a zoom allowing for identification of delay times.