Electronic Supplementary Information for

Thermal cracking of CH₃Cl leads to auto-catalysis of deposited coke

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Materials

As the thermal cracking of CH_3Cl was reported to be a radical route, two types of inert surface were used to initiate the $CH_3^\bullet$ and $Cl^\bullet$ radicals. The first one consisted of glass beads purchased from Carl Roth (Ref. A555.1) with a size ranging between 1.25 and 1.65 mm and with a geometric area of 2 m^2/kg. The second inert surface was SiO_2-432 from Grace Davison, crushed and sieved between 50 and 400 μm before the CH_3Cl cracking. Its specific surface area (SSA) was 310 m^2/g and it contained 0.1 wt% of Cl. Black Carbon was a Vulcan 3 (Cabot) powder sample with SSA of 75 m^2/g.

Catalytic testing for the thermal cracking

The CH_3Cl cracking tests were performed in a fixed-bed reactor with a height and a diameter of 3 and 1 cm, respectively. All the tests were performed at a pressure of 0.4 MPa (similar to the DS) and six temperatures were set: 375, 400, 450, 475, 500 and 550 °C.

Before each test, the reactor was flushed under 100 mls/min of pure Ar at atmospheric pressure while temperature was increased from room temperature to the desired one with a rate of 5 °C/min and maintained under Ar for 1 h. The argon flush was then stopped. CH_3Cl/Ar (10/90) mixed with N_2, with respective flow of 5.22 and 3.18 mls/min, were introduced during ca 15 h. N_2 was used as an internal standard.

During the CH_3Cl cracking, the output gases N_2, CH_3Cl, H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, n-butane and isobutene were analyzed by Shimazu GC-2014 and treated with the LabSolutions software. HCl selectivity was determined using a trap with NaOH and by measuring the initial and final pH.

The selectivity to A product was calculated by (eqn. S1).

$$Sel\,(A) = \frac{n(A)_{output}}{n(CH_3Cl)_{input} - n(CH_3Cl)_{output}} \times 100$$

(eqn. S1)

where $n(A)_{output}$ corresponds to the amount of A product at the output of the fixed bed reactor and $n(CH_3Cl)_{input}$ and $n(CH_3Cl)_{output}$ correspond to the amount of CH_3Cl reagent on the input and output of the fixed bed reactor, respectively.

The consumption rate of CH_3Cl was calculated by (eqn. S2) with $X(CH_3Cl)$ the conversion of CH_3Cl and $F(CH_3Cl)$ the input flow of CH_3Cl ($mol.s^{-1}$). A first-order of reaction was assumed for the calculation of the reaction rate, because of the low partial pressure of CH_3Cl.

$$r_{CH_3Cl\ consumption} = X(CH_3Cl)\ x\ F(CH_3Cl) \qquad\qquad (eqn.\ S2)$$

The activation energy of thermal cracking was determined from the rates determined after two hours of reaction assuming a first order reaction. For glass beads, the experiments performed at 400 ° and 500 °C were discarded because the conversion was too low and limitation occurred, respectively. For silica particles, the experiment performed at 550 °C was not considered for the calculation because diffusion resistance was suspected.

Characterization methods

In addition to gases, the amount of coke deposited on silica was determined by elemental analysis on carbon with a Thermo Scientific, Flash 200 organic elemental analyzer.

Raman spectra reported in this work were performed at ambient atmosphere with a LabRam HR (Jobin Yvon-Horiba) spectrometer. The exciting line at 633 nm of a He-Ne laser was used. The power measured at the sample was around 1 mW. The spatial resolution is ca 4 microns and the spectral resolution is 4 cm^{-1}. For each sample, the spectrum corresponds to the mean of ca 20 spectra recorded on different analysis areas.

The X-Ray Fluorescence analysis was performed with a Panalytical, Epsilon 4 instrument equipped with an Ag source. The Cl content was determined from a semi-quantitative method (Omnian).
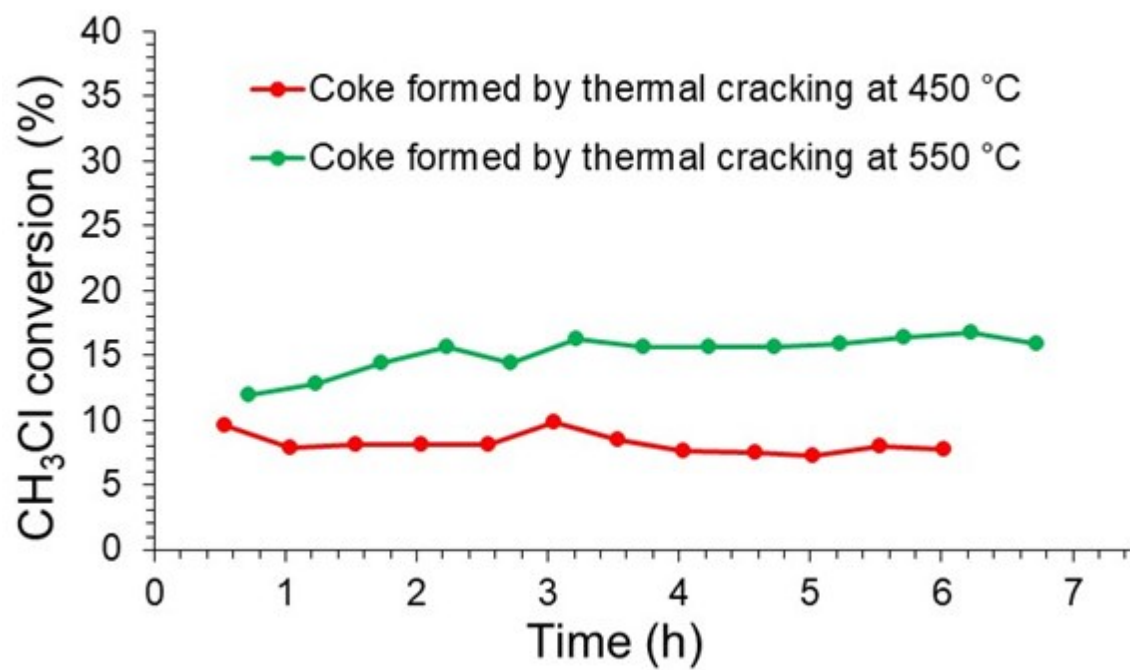
Fig. S1: Conversion of CH_3Cl at 400 °C on coke obtained by thermal cracking on 0.8 g of SiO_2 at 450 and 550 °C, at 0.4 Mbar and with a residence time of 0.3 min.