Thermo-catalytic Decomposition of Methane Using Carbon as Catalysts

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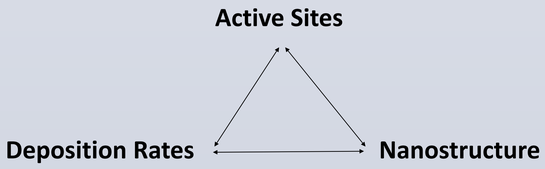
Introduction

Thermo-catalytic decomposition (TCD) is well-suited for the generation of hydrogen from natural gas. TCD provides a pathway to hydrogen economy, as it is a mid-term transition from fossil fuel to renewable hydrogen energy systems. In a decarbonization process for fossil fuel—pre-combustion—solid carbon is produced, with potential commercial uses including energy storage. TCD rates and active duration vary widely across carbons. In this study, TCD measurements were performed using a hot wall reactor and flat substrates of silicon and quartz. A test matrix encompassing a series of temperatures (700 – 1,100 ℃) and durations was performed, and deposition rates were measured periodically for determination of deposition rate by deposit thickness, using scanning electron microscopy (SEM). The nanostructure of the deposit was evaluated using transmission electron microscopy (TEM). At selected stages during TCD, samples were subjected to activated chemisorption in preparation for active site measurement. Active sites were quantified by measurement of chemisorbed oxygen using X-ray photoelectron spectroscopy (XPS).

Objectives

1. Investigate the relationship between TCD rates and active sites.
2. Understand how nanostructure connects to active sites
3. Explore the effect of nanostructure on initial deposition rates



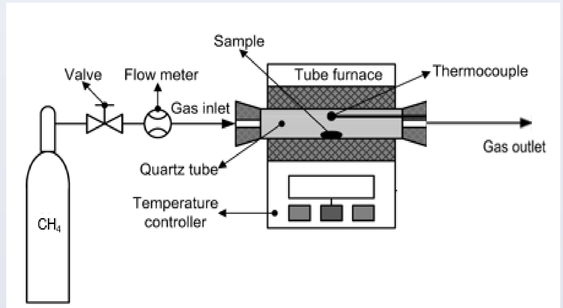
Temperature-Time Matrix

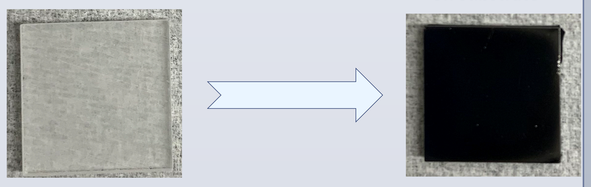
Temperature →			
Time (hrs.) ↓			

Materials and Methods

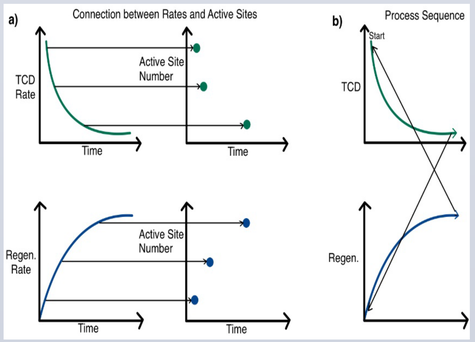
- Deposition studies: deposit thickness change with gas composition and temperature.
- Quantification of active sites by activated oxygen chemisorption and XPS
- Carbon nanostructure quantified through TEM and Fringe Analysis

Experimental Apparatus





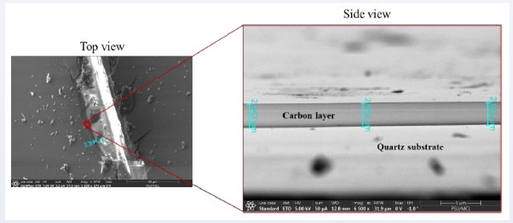
Deposition rates are evaluated gravimetrically with nanostructure quantification by HRTEM image analysis for lamellae length and tortuosity.



a) Connection between rates and active site number b) Anticipated coupling sequence between TCD and Regeneration.

Results and Discussion

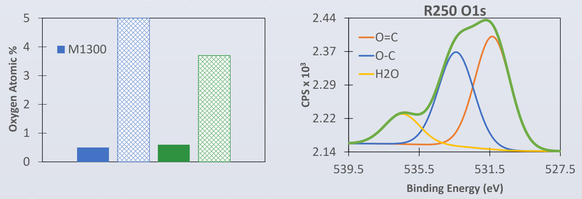
1. Deposition Rates



SEM images showing deposited carbon upon quartz substrate; top view (left) and side view (right).

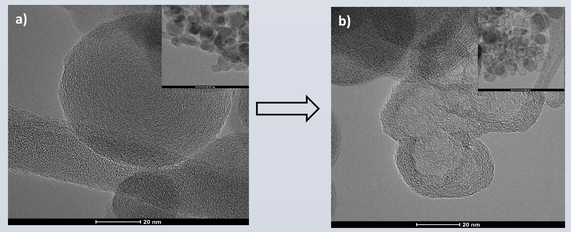
- SEM images of the TCD carbon deposit at the indicated viewing directions. Carbon deposition rate is measured by film thickness and can be translated to mass.

2. Active Site Measurement

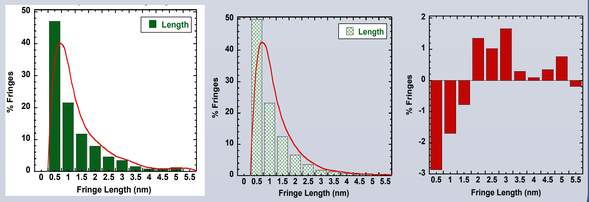


- Comparative increase in active sites upon partial oxidation as measured by O_2 chemisorption followed by XPS analysis.
- The high-resolution scan about the O1s region and deconvolution distinguishes the different oxygen functional groups formed during the activated chemisorption process.

3. Nanostructure



HRTEM images showing a) nascent carbon structure, and b) its change upon partial oxidation. The coarser structure observed along the particle perimeter is "visual" evidence of nanostructure change due to oxidation and corresponding increase in active (edge) sites (as per XPS) as lamellae regress in size.



- Fringe length distributions corresponding to the nascent and partially oxidized carbon.

Conclusions

- It is evident that partial oxidation can increase active sites number.
- The uniformity and 2D aspect of the TCD films is beneficial for XPS analysis of active sites compared to a packed bed.
- The connection between active sites and kinetic rates is yet to be made given the non-monotonic deposition rates.
- Active sites can be related to lamellae nanostructure.
- Project Outcome: If nanostructure can be correlated to active sites, a surrogate metric will be established by which to gauge carbon structure for reactivity under TCD and regeneration conditions.

References

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