The nature and role of carbonaceous overlayers in ethylbenzene dehydrogenation over alumina supported catalysts

Sara Gomez Sanz1, Liam McMillan1, Maria Mediero-Munoyerro1, Paul A. Midgley2, Nabil Al-Yassir3, James McGregor4*, Sulaiman Al-Khattaf1 and Lynn F. Gladden1

1. University of Cambridge, Chemical Engineering and Biotechnology, Cambridge CB2 3RA (UK)
2. University of Cambridge, Materials Science and Metallurgy, Cambridge CB2 3RA (UK)
3. King Fahd University of Petroleum & Minerals, Chemical Engineering, Dhahran 31261 (Saudi Arabia)
4. University of Sheffield, Chemical and Biological Engineering, Sheffield S1 3JD (UK)

*james.mcgregor@sheffield.ac.uk

Introduction
Carbon deposition takes place during many catalytic reactions and is usually an undesired process. Various elementary reactions lead to coking and can cause poisoning, resulting in a loss of activity and selectivity [1]. Understanding the role of carbonaceous overlayers (or coke), and the influence of different reaction pathways on how such layers are deposited is therefore of great importance. Here, ethylbenzene dehydrogenation is used as a model system to understand such issues and to investigate the catalytic features that lead to carbon build-up. The reaction was performed over fresh CrO$_2$/Al$_2$O$_3$ and catalysts pre-cooked with different precursor molecules. Thereby, the source of coke can be identified allowing such deposits to be exploited in order to enhance catalytic activity and selectivity. To this end, a range of characterisation techniques including elemental analysis, temperature programmed desorption and oxidation (TPD/TPO), Raman, FTIR and terahertz spectroscopies and transmission electron microscopy (TEM) have been employed.

Materials and Methods
Alumina-supported chromia with a chromium loading of 10 wt. % was prepared by wet impregnation using Cr(NO$_3$)$_3$·9H$_2$O (Sigma-Aldrich, 99%). Ethylbenzene dehydrogenation was performed in the gas-phase employing a fixed-bed reactor connected to an on-line GC (Agilent 6890N Series, FID, column Agilent HP-5).

Results and Discussion
Figure 1a) shows two distinct periods of activity in the dehydrogenation of ethylbenzene over CrO$_2$/Al$_2$O$_3$ at different times-on-stream: (i) a cracking period (high selectivity to benzene and toluene) and; (ii) styrene breakthrough after around 3 hours. Most of the coke deposited in the reaction is found to occur at reaction times below 3 hours, indicating that it arises due to the cracking reaction.

Ethylbenzene dehydrogenation was also performed over CrO$_2$/Al$_2$O$_3$ after pre-cooking with different agents: benzene, toluene, styrene and ethylene. Figure 1b) shows the reaction profile of ethylbenzene dehydrogenation over CrO$_2$/Al$_2$O$_3$ pre-cooked with benzene. It can be observed that the induction period required for styrene to be formed is no longer present. Also, selectivity to cracking products and coke is reduced. Pre-cooking with benzene will impact both on the surface coverage of carbonaceous deposits and potentially on Cr oxidation state. Both of these parameters have been investigated.

TPD measurements of CrO$_2$/Al$_2$O$_3$ pre-cooked with benzene showed that the catalyst has two adsorption sites (desorption at 600 and 800 °C) and benzene is strongly chemisorbed over the high energy adsorption centre. Therefore, by pre-cooking the catalyst with benzene, the strongest acid sites are poisoned, hence preventing cracking. Additionally a higher selectivity to styrene, the desired product, is obtained under steady-state conditions over the benzene pre-cooked catalyst as compared to the fresh catalyst.

The nature of carbonaceous deposits has been probed by different characterisation techniques. Elemental analysis showed higher C/H ratio for the catalyst pre-cooked with benzene than styrene, reflecting the presence of more ordered coke structures. These finding agrees with TPO measurements where carbon deposits from benzene pre-cooked CrO$_2$/Al$_2$O$_3$ exhibited the highest oxidation temperature (495 °C), which is indicative of a higher degree of polyaromaticity. Furthermore, coke deposited after adsorption of benzene over CrO$_2$/Al$_2$O$_3$ showed higher THz absorption coefficient as compared to other pre-cooked catalysts, indicative of more ordered carbon structures [2]. Similar D1/G ratio but higher D1/D3 ratio for the catalyst pre-cooked with benzene were observed from Raman spectra. These results suggest that benzene is the precursor molecule of more graphic coke which has a beneficial effect on the catalytic performance by suppressing the initial cracking stage of the reaction.

Significance
It has been demonstrated that tailored carbon deposition can be employed as a novel approach to modify catalysts in order to optimize catalytic activity and selectivity.

References