



MAX-PLANCK-GESELLSCHAFT



## The structure and mechanistic impact of carbon deposits in dehydrogenation reactions

James McGregor<sup>1\*</sup>, JA Zeitler<sup>1</sup>, EPJ Parrott<sup>1,2</sup>, LF Gladden<sup>1</sup>, JP Tessonier<sup>3</sup>, TW Hansen<sup>3</sup>, D Su<sup>3</sup>, and R Schlögl<sup>3</sup>

<sup>1</sup>University of Cambridge, Department of Chemical Engineering and Biotechnology, Cambridge CB2 3RA, UK

<sup>2</sup>University of Cambridge, Cavendish Laboratory, Cambridge CB3 0HE, UK

<sup>3</sup>Fritz-Haber Institut der MPG, Berlin, D-14195, Germany

\*jm405@cam.ac.uk

### Introduction

The catalytic dehydrogenation (DH) and oxidative dehydrogenation (ODH) of light alkanes is widely studied as a route to the formation of alkenes and di-alkenes, important precursor molecules for synthetic rubbers, plastics and a variety of other products [1-4]. Recent studies have focused on the non-oxidative DH of butane over alumina-supported vanadia catalysts [5-7]. In the present work, we provide a detailed understanding of both the role and structure of coke deposited on  $\text{VO}_x/\text{Al}_2\text{O}_3$  during reaction. A range of characterisation techniques have been employed including the first application of terahertz time domain spectroscopy (THz-TDS) to the study of coke. Complementary THz-TDS characterisation of carbonaceous materials including carbon nanofibres (CNFs) has also been conducted.

### Experimental

The non-oxidative dehydrogenation of *n*-butane has been conducted over 3.5 wt. %  $\text{VO}_x/\text{Al}_2\text{O}_3$ . Reactions have been conducted in a flow-through quartz reactor connected to an on-line GC. Catalyst characterisation has been conducted by THz-TDS, EPR, Raman, NMR, NEXAFS and X-ray photoelectron spectroscopies and TEM. Additionally, CNFs have been studied by THz-TDS as model coke compounds.

### Results and Discussion

Figure 1 shows THz-TD spectra of the carbonaceous deposits present on  $\text{VO}_x/\text{Al}_2\text{O}_3$  after reaction at various temperatures. Previous studies of coke in such systems have employed a variety of techniques, including  $^{13}\text{C}$  NMR spectroscopy [7]. NMR spectroscopy however, cannot probe ordered conducting coke structures, or materials with a high density of paramagnetic species. THz-TDS however, is ideally suited to analysis of such deposits. THz-TDS is a relatively new technique and probes intermolecular vibrational modes, such as phonon vibrations, and free electron density. As such, in the case of carbonaceous deposits, greater absorption in the THz region may be assigned to coke with a higher degree of graphitic order. Consider-

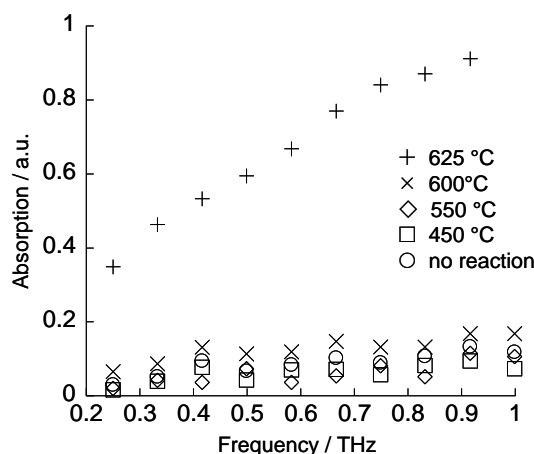


Figure 1. THz-TD spectra of  $\text{VO}_x/\text{Al}_2\text{O}_3$  after reaction.

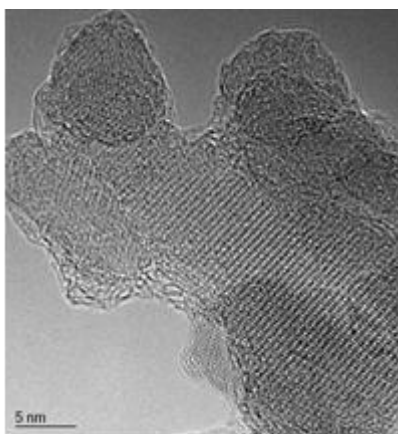


Figure 2. TEM micrograph of catalyst after reaction at 550 °C

ing the data shown in Figure 1. Below a reaction temperature of 600 °C little absorption of THz radiation occurs. Much more significant absorption however is observed at higher reaction temperatures. This corresponds to a significant change in the structure and electronic character of the deposited coke. That this equates to an increase in the order of the deposited coke is confirmed through complementary techniques including Raman, NMR, NEXAFS and X-ray photoelectron spectroscopies, and TEM analysis. For example, Figure 2 shows that at a reaction temperature of 550 °C carbon platelets cover mainly individual support particles. The extent of this coverage increases at higher temperature. The change in the electronic nature of the coke is supported by  $^{13}\text{C}$  NMR spectroscopy studies which reveal detuning of the NMR probe due to the formation of conducting coke structures. Similar  $^{13}\text{C}$  NMR phenomena have previously been observed by other workers [8]. Additionally, the presence of organic radicals at high temperature is revealed by EPR spectroscopy. Such radicals are not present in coke deposited at lower temperatures.

That more highly ordered carbonaceous materials show greater absorption of THz radiation is confirmed by complementary studies of a series of CNFs. CNFs share many of the same structural characteristics as the coke deposited at high reaction temperatures over  $\text{VO}_x/\text{Al}_2\text{O}_3$ . In this work, CNFs which have been heat treated at progressively higher temperatures have been investigated. This heat treatment has removed any disordered carbon on the nanofibre surface, with higher temperatures forming more-ordered structures. In agreement with studies over  $\text{VO}_x/\text{Al}_2\text{O}_3$  the material with the most ordered structure exhibits the greatest absorption.

## Conclusions

Carbonaceous deposits play a key role in catalytic reaction mechanisms, in particular with regard to catalyst deactivation. In the present study THz-TDS has been applied to the study of these materials for the first time. THz-TD spectra are shown to be directly related to the structure of the deposited carbon, demonstrating that this is a valuable new resource in the catalyst characterisation toolkit. Complementary studies reveal a correlation between the electronic nature of CNFs, as revealed by THz-TDS, and their structural characteristics demonstrating that THz-TDS also has potential applications in the study of such materials.

## References

1. Bañares, M.A. *Catal. Today*, 51, 319 (1999)
2. Blasco, T. and Nieto, J.M.L. *Appl. Catal. A: Gen.* 157, 117 (1997)
3. Su, D.S., Maksimova, N., Delgado, J.J., Keller, N., Mestl, G., Ledoux, M.J. and Schlögl, R. *Catal. Today*, 102, 110 (2005).
4. Cavani, F. and Trifiro, F. *Appl. Catal. A*, 133 219 (1995)
5. Wu, Z.L. and Stair, P.C. *J. Catal.*, 237, 220 (2006).
6. Jackson, S.D. and Rugmini, S. *J. Catal.*, 251 59 (2007)
7. McGregor, J., Huang, Z., Shiko, G., Gladden, L.F., Stein, R.S., Duer, M.J., Wu, Z., Stair, P.C., Rugmini, S., Jackson, S.D. *Catal. Today*, doi:10.1016/j.cattod.2008.07.022
8. Meinhold, R.H. and Bibby, D.M. *Zeolites*, 10, 121 (1990)