The role and structure of carbonaceous materials in dehydrogenation reactions

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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 VO_x/Al_2O_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.

Materials and Methods

The non-oxidative dehydrogenation of *n*-butane has been conducted over 3.5 wt. % VO_x/Al_2O_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

The structure of carbonaceous deposits in DH and ODH reactions has previously been studied extensively. The techniques employed include ^{13}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. THz-TD spectra of VO_x/Al_2O_3 catalysts after reaction at various temperatures are 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 corresponds 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}C NMR spectroscopy studies which reveal detuning of the NMR probe due to the formation of conducting coke structures. Similar ^{13}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.

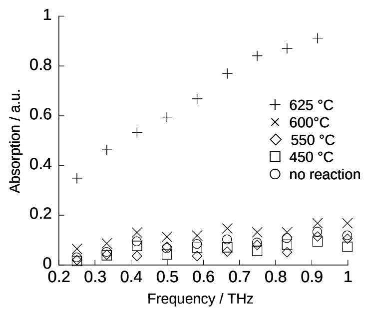

Figure 1. THz-TD spectra of VO_x/Al_2O_3 after reaction.

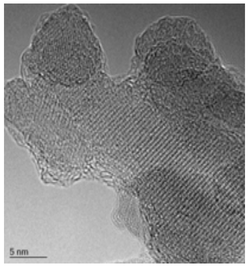

Figure 2. TEM micrograph of catalyst after reaction at 550 °C

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 VO_x/Al_2O_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 VO_x/Al_2O_3 the material with the most ordered structure exhibits the greatest absorption.

Significance

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

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