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 [1,2]. Recent studies have focused on the non-oxidative DH of butane over alumina-supported vanadia catalysts [3-5]. 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. For such materials THz-TDS spectra can be correlated with their catalytic performance in the oxidative dehydrogenation of ethylbenzene to form styrene.

Materials and Methods

The non-oxidative dehydrogenation of *n*-butane has been conducted over 3.5 wt. % VO_x/Al_2O_3 while the oxidative dehydrogenation of ethylbenzene has been conducted over a variety of CNFs (Applied Sciences Inc.). 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.

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 [5]. 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. A significant variation in the structure and electronic character of the deposited coke is observed, with greater absorption at higher reaction temperatures. 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. TEM micrographs, shown in Figure 2, reveal that at a reaction temperature of 700 °C the deposited carbon is in the form of highly ordered, curved, sheet-like structures which encapsulate the catalyst particles. Furthermore EPR spectroscopy reveals the presence of organic radicals at high temperature which are not present in coke deposited at lower temperatures.

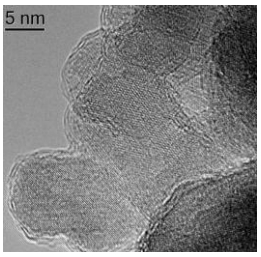

Figure 2. TEM micrograph of VO_x/Al_2O_3 after reaction at 700 °C.

That more highly ordered carbonaceous materials show greater absorption of THz radiation is confirmed by complementary studies of a series of CNFs, heat treated at progressively higher temperatures. 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. The electronic nature of the nanofibres can further be related to their catalytic performance in the oxidative dehydrogenation of ethylbenzene. Carbonaceous materials have previously been shown to be highly active in oxidative dehydrogenation reactions [7]. In the present work a greater selectivity towards styrene, as compared to other hydrocarbon products such as benzene, is observed over CNFs with a lower degree of order, *i.e.* a greater number of defect sites in their graphitic structure. This correlates well with the established mechanism of this reaction whereby quinolinic functionalities, which are the styrene-selective active sites, are formed *in situ* at defect sites on the surface of carbonaceous catalysts [7].

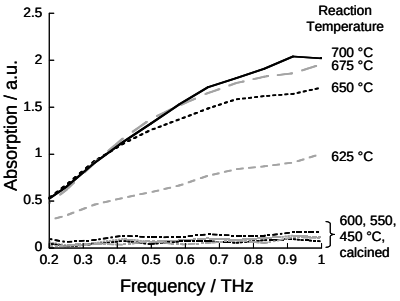

Figure 1. THz-TD spectra of VO_x/Al_2O_3 after reaction.

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 catalytic performance.

References

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