Calorimetric Study of Propane and Ethylbenzene on Active Surface on Carbon-Based Catalysts

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1 Introduction

The use of carbon materials instead of (mixed) metal oxides in selective oxidation catalysis could emerge to be of basic interest for the catalysis community. Low dimensional carbon allotropes such as multiwalled carbon nanotubes (CNTs) with high structural homogeneity provide the characteristics of model catalysts with well defined active sites as compared with polyvalent transition metal oxides featuring complex electronic and spin structures. The oxydehydrogenation (ODH) reaction over carbon has been discovered in 1979 by Alkhazov *et al.*[1] From the mechanistic point of view, quinone groups are believed be the active site. These nucleophilic oxygen species can selectively abstract hydrogen atoms and the formed phenol groups are subsequently reoxidized by O_2.

We choose the ODH of propane and ethylbenzene (EB) as the model reactions. Propane is widely investigated as a substrate in this reaction and mechanistic models for the reaction sequence over metal oxide catalysts are numerously suggested. It is equipped with a high C–H bond strength (410.5 kJ mol^{-1}). In contrary to the alkane, the weak C-H bond in benzylic position (357.3 kJ mol^{-1}) makes the molecule highly reactive for ODH.

2 Experimental

Nitric acid washed multiwalled carbon nanotubes (CNTs) were chosen as the model catalyst for ODH. *Kinetic measurements* were conducted in the ranges of T = 623-673 K, $p(O_2)$ = 1-5%, p(HC)=2-10% at differential conversions. *XPS* was performed under 0.5 mbar HC, HC/O_2 (1:1), and O_2 atmospheres, respectively, at T = 423-623 K.

An apparatus and a procedure were developed to characterize the adsorption sites on the surface of a catalyst in any state along the reaction profile by *microcalorimetry*.[2] The calorimeter cell is used as a fixed bed reactor containing the catalyst under propane or EB ODH reaction conditions. After reaching steady state performance, the cell was cooled to room temperature. The sealed cell was transferred into a SETARAM MS 70 calorimeter connected to a volumetric system, and evacuated at 313 K, where adsorption was performed. $T_{ads.}$ was chosen lower than $T_{reaction}$ to separate the adsorption process from the catalytic reactions.

3 Results and discussion

The ODH reaction induces the formation of a variety of surface oxygen groups (Fig. 1). The nucleophilic branch of the O1s range from 531.5 to 529 eV evidences a substantial fraction of ketones and quinones on the carbon surface, which are believed to be the active sites in ODH reactions. The gap between these two regions indicates a minor fraction of more or less neutral fragile lactone, ether, and hydroxyl groups, which are likely oxidized by O_2. Differences in the spectra are evident. The O1s spectra notably differ in the intensity of redox-active nucleophilic C=O groups. Their highest fraction within the assembly of oxygen surface groups can be detected in O_2/C_3H_8 and in pure O_2, respectively, and their intensity gradually decreases in O_2/EB, whereas they are almost absent in pure EB vapour. This impressively illustrates the impact of chemical potential of the different hydrocarbon molecules and reaction conditions on the dynamic catalyst surface: the higher their reactivity, the lower the concentration of active sites in steady state.

The adsorption of propane on the active catalyst surface of the carbon catalysts is completely reversible as shown by microcalorimetry.[3] A similar experiment was performed for EB (Fig. 3). The shape of the adsorption profile (Fig. 1) and the extracted site classification are very similar. An almost equal number of homogeneous high-energy adsorption sites, 8 µmol g^{-1}, most likely the quinone sites active in ODH catalysis, exist on the CNT catalyst. This plateau is followed by a steady decay range with a capacity of approx. 100 µmol g^{-1} comprising a broad variety of oxygenated and energetically inhomogeneous adsorption sites. Beyond this range hydrocarbon adsorption occurs with comparably low energy. The most significant difference in comparison with propane is the partial irreversibility of EB adsorption in the high-energy range probably due to the higher reactivity of the benzylic C-H bond

in this probe molecule. The reaction of EB with the active surface of the CNT catalyst considerably changes the properties of the latter similar to its interaction with propylene (Fig. 4).[3] In the re-adsorption experiment high energy sites are totally absent, however, the total capacity for EB adsorption increases by factor of 10. This can be explained by the considerable formation of H_2O during initial reaction, which blocks active sites and turns the surface more hydrophilic, thus hindering the adsorption of large amounts of non-polar EB molecules. In the re-adsorption, which is performed after evacuation of the calorimeter cell, the interaction is totally reversible and no H_2O is formed. However, from energetic and quantitative point of view microcalorimetry reveals an astoishing analogy of active catalyst surfaces equilibrated in propane and EB ODH reactions, respectively.

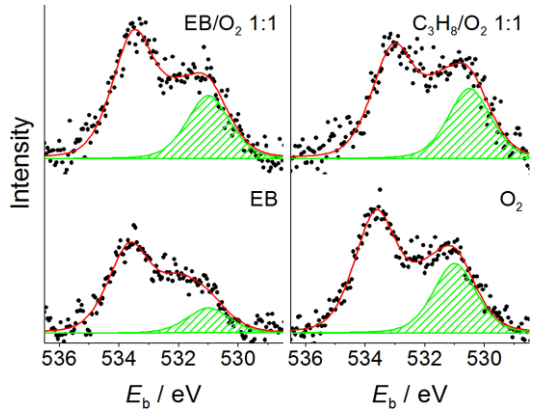

Figure 1. O1s ranges of in situ XP spectra of a CNT catalyst under different atmospheres, measured at 350°C (O_2: 150 °C). Nucleophilic C=O groups are highlighted as green shaded curves and originate from three-component fits (red lines) of the spectra, respectively.

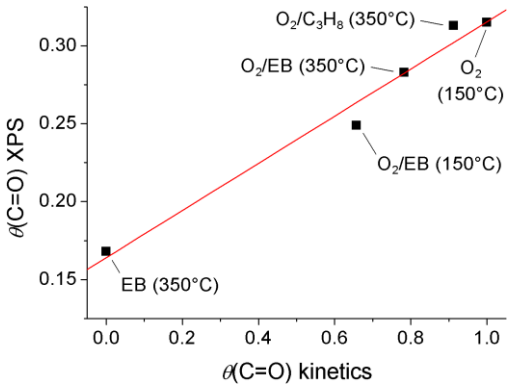

Figure 2. Correlation of kinetic and spectroscopic approaches of active site quantification on a CNT catalyst.

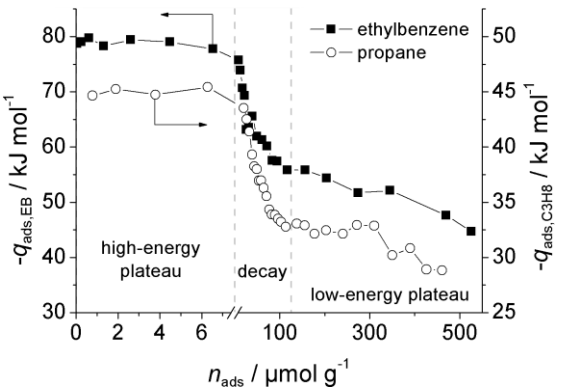

Figure 3. Differential heats of adsorption of ethylbenzene (■) and propane (○) on the active surfaces of CNT catalysts.

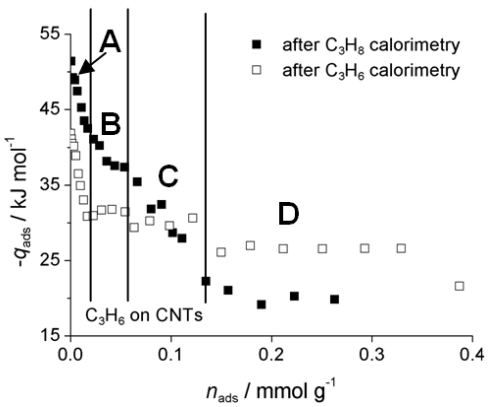

Figure 4. Differential heats of adsorption of propene on oCNT used in oxidative dehydrogenation of propane.
Assignments [3]: A to ketone and quinone groups, B to carboxylic anhydrides, C to lactone/ester, phenol, and ether sites, and D to adsorption on the basal plane of graphitic carbon

A two-site redox kinetic approach was chosen to separate the reaction of the hydrocarbon with the quinone sites from the subsequent reoxidation of formed phenol groups by O_2. This mechanism is supported by previous experiments with alternating feed. Higher activation barriers in the reduction step of the redox model well correlate with the higher stability of the aliphatic C-H bond in propane over the benzylic C-H bond in EB. Furthermore, the redox model gives access to the surface coverage of active sites being in active state θ, i.e., nucleophilic C=O sites, which most likely can be related to the O1s band located at around 531 eV in the XP spectra. A linear correlation for both ODH substrates C_3H_8 and EB is found under high-pressure XPS conditions (Fig. 2) indicating perfect agreement between the kinetics and *in-situ* XPS.

References

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