Active sites characterization using adsorption microcalorimetry at reaction temperature

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Introduction:

Heterogeneous catalysis involves specific chemical interactions between the surface of a solid and the reacting gas (or liquid phase) molecules. The catalytic cycle is generally composed of absorption/desorption steps, and surface reaction processes. The knowledge about heat of adsorption of reactant on the surface of a catalyst at reaction temperature ($T_{react.}$) can contribute to a better understanding of the complex microkinetics. Since perhaps only a minor fraction of all surface atoms form active centers, the determination of their number, strength and energy distribution requires a sensitive analytical method. We focus here on adsorption microcalorimetry at reaction temperature [1] and present two projects i) the dynamics of Ag-O system depending on time/temperature/pressure studied by oxygen adsorption at 150°C and 230°C ($T_{react.}$) and ii) 1-hexyne adsorption at 80°C ($T_{react.}$) on supported ceria , being unexpectedly active in the three-phase semi-hydrogenation of 1-hexyne. [2]

Results and discussion

i) Based on XPS, DFT calculations and microcalorimetry we have developed a picture to explain the Ag-O dynamics during thermal treatments and ethylene epoxidation. Essential processes are surface reconstruction, oxygen dissolution to subsurface and surface oxide growth at pressure between 10^{-1} and 1 mbar O_2 and at 230°C. These reaction steps are characterized by a saturation concentration of oxygen of 1.5 $\mu molO_2/g_{Ag}$ and a differential heat of adsorption of >50 - 120 $kJmol^{-1}$.

ii) In order to correlate the catalytic performance with characteristic properties of ceria, the chemisorption of 1-hexyne at $T_{react.}$ = 80°C and r.t. was studied on two differently active 20wt%CeO2/TiO_2 catalysts. The 20wt%CeO_2/TiO_2-WI catalyst (wet impregnation) shows a much higher alkyne conversion than the 20wt%CeO_2/TiO_2-DI catalyst (dry impregnation). In both cases, the olefin selectivity is constant at 100%.

Figure 1 shows that for both catalysts the differential heat of adsorption profile as a function of 1-hexyne uptake reveals a very strong adsorption at the initial stage (up to 900 $kJmol^{-1}$) suggesting multiple dehydrogenation steps taking place [3] (formation of stable surface intermediates [4]). After approximately 0.01 $mmolg^{–1}$, the heat of adsorption stabilizes around 200 $kJmol^{–1}$. This heat of adsorption resembles the energy released upon a single dehydrogenation step of acetylene. [3] Further adsorption takes place with slowly decreasing heat evolution up to 0.22 $mmolg^{–1}$ for the more active 20wt%CeO^2/TiO^2-WI and up to 0.16 $mmolg^{–1}$ for the less active 20wt%CeO_2/TiO_2-DI. The chemisorption process is irreversible (Figure 1). The regeneration of the catalyst surface using H_2 (at 150°C) has been somewhat more successful for the more active catalyst. The more active catalyst is characterized by a higher amount of adsorption places for 1-hexyne and a slightly easier regeneration of the surface after 1-hexyne contact at reaction temperature. Furthermore, the obtained results indicate that under reaction conditions a significant portion of the surface sites is covered by dehydrogenated species and is not available for hydrogenation. This is in line with DFT calculations of acetylene adsorption on CeO_2(111) showing that the most preferred adsorption mode is dissociative with respect to the C–H bond. [3] Nevertheless, the remaining small number of surface sites is active and selective in alkyne hydrogenation.

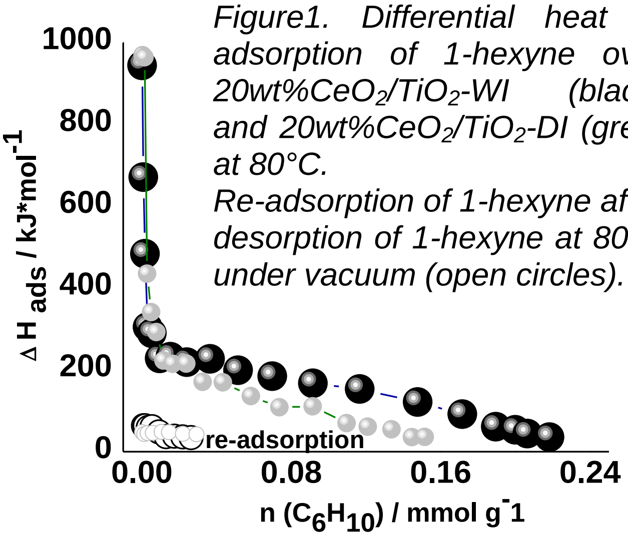

Figure1. Differential heat of adsorption of 1-hexyne over 20wt%CeO_2/TiO_2-WI (black) and 20wt%CeO_2/TiO_2-DI (grey) at 80°C.
Re-adsorption of 1-hexyne after desorption of 1-hexyne at 80°C under vacuum (open circles).

References:

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