



Active Sites Characterisation using Adsorption Microcalorimetry at Reaction Temperature



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INTRODUCTION

- The catalytic cycle is generally composed of adsorption/desorption steps, and surface reaction processes.
- The 1st step is the activation of the reacting molecules by adsorption. Thus, the study of ads. phenomena play an important role.
- The knowledge about heat of adsorption of reactant on the surface of a catalyst at reaction temperature 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 on: Adsorption Microcalorimetry at Reaction Temperature [1]

and present two projects:

- > the dynamics of Ag-O system depending on time/temperature/pressure studied by oxygen adsorption at 150°C and 230°C (T_{react})
- > 1-hexyne adsorption at 80°C (T_{react}) on supported ceria, being unexpectedly active in the three-phase semi-hydrogenation of 1-hexyne.

Adsorption Isothermal Microcalorimetry

HT1000 (rt-1000°C) and MS70 (rt-100°C) Tian-Calvet calorimeter of SETARAM combined with a custom-designed high vacuum and gas dosing apparatus. [2]

Adsorption microcalorimetry allows to determine:

- $\Sigma n_{\text{ads}} \text{ vs } p_{\text{eq}}$, $\text{mmol} \cdot \text{g}^{-1} \cdot \text{mbar}^{-1}$ Adsorption isotherm
- $q_{\text{diff}} = \frac{Q_{\text{diff}}}{n_{\text{ads}}} = \Delta H_{\text{ads}}$, kJ/mol Adsorption enthalpy
- $q_{\text{diff}} \text{ vs } n_{\text{ads}}$, kJ/mol Energetic distribution of ads. sites
- $K = K_0 \exp \frac{\Delta H_{\text{ads}}}{RT}$, hPa^{-1} Adsorption constant
- $S_{\text{sp,th}} = \frac{n_{\text{ads}}}{n_{\text{atoms}}} \cdot \text{Avogadro const.}$ Specific surface area
- $S_{\text{sp,Vol}} = \frac{n_{\text{ads}}}{V_{\text{cell}}} \cdot \text{Avogadro const.}$ $S_{\text{sp,Vol}}$ cross-section area $\frac{\text{mol}}{\text{m}^2}$ for porous [3]

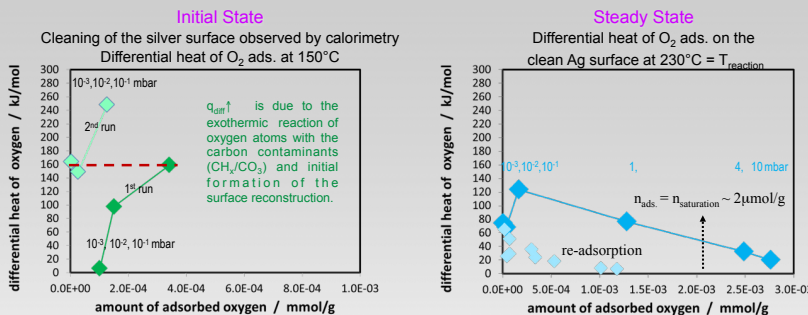
Calorimetric Element: Thermopile in series with thermopile has 2 functions: 1. heat transfer, 2. signal generation

The heat-flow detector gives an electrical signal "U" which is proportional to the heat transferred per time unit.

Dynamics of Ag-O system depending on time/temperature/pressure studied by oxygen adsorption at 150°C and 230°C (T_{react})

Silver: is used as a catalyst for the ethylene epoxidation and methanol oxidation.
Goal: is to safely translate the electronic signatures obtained by X-ray spectroscopies into structural information, which can be used to construct reaction mechanisms. The energetic data provided by calorimetry is essential to any reaction mechanism.
Catalyst: Ag powder <45micron #10519

Ag-O dynamics depend on temperature and pressure



T °C	pO ₂ mbar	n _{ads.} mmol _{O₂} /g _{Ag}	q _{diff} kJ/mol	Ag-O dynamics
T _{cleaning} 150	< 10 ⁻¹	0.5	> 120 - 260	> dissociative adsorption > cleaning the surface from CH _x /CO _x > initial formation of the surface reconstructions [7]
T _{reaction} 230	10 ⁻¹ - 1	1.5	> 50 - 120	> extensive structural changes * > oxygen begins to dissolve to subsurface ** > chemisorbed oxygen modified by a subsurface oxygen *** > Surface oxide growth = 60 - 80 kJ/mol [8]
T _{reaction} 230	> 1 - 10	1	< 50	> molecular oxygen adsorbed on surface vacancies **** > formation of electrophilic oxygen (weakly bound) *****

* Ag atoms moving from defects and edges to form the reconstructions. Isolated formation at low coverages.
** Formation of oxide like reconstruction and/or surface oxide layer.
*** Depends on time/temperature because its formation is limited by oxygen diffusion to subsurface.
**** Proposed by theory and calorimetry. In this case the time/temperature dependence is related to the defect formation.
***** The active site for epoxidation! Two interpretations are believed: O₂ stabilized on defects on O covered surface (DFT) or surface oxygen modified by sub-surface species (XPS)

Specific surface area of Ag for O₂ at T_{reaction} = 230°C

$$S_{\text{Ag-O}} = \frac{n_{\text{ads.}} \cdot \text{Avogadro constant}}{\text{Surface sites density } \Gamma_{\text{Ag, lattice, Ag}}} = \frac{2 \cdot 10^{-4} \text{ mol} \cdot 6.022 \cdot 10^{23} \text{ particles} \cdot \text{cm}^{-2}}{\text{g} \cdot 1.4 \cdot 10^{19} \text{ atoms} \cdot \text{mol}^{-1}}$$

$$S_{\text{Ag-O}} = 0.86 \text{ m}^2/\text{g}$$

BET_{N₂, 77K} = 0.72 m²/g
ΔS_{Calorimetry} / BET = 0.14 m²/g

The excess can be due to dissolving of oxygen into the Ag subsurface.

1-hexyne ads. at 80°C = T_{react.} on supported ceria, active in the three-phase semi-hydrogenation of 1-hexyne [9]

Goal: Does calorimetry offers the possibility to distinguish between catalysts of similar characteristic properties?
Catalyst: The 20wt%CeO₂/TiO₂-WI (wet impregnation; # 17380) shows a much higher alkyne conversion (X_{C₆H₁₀}) than the 20wt%CeO₂/TiO₂-DI (dry impregnation; # 17378). In both cases, the olefin selectivity (S_{C₆H₁₂}) is constant at 100%.

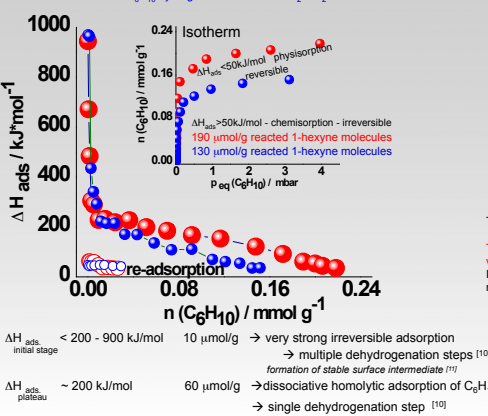
Yes, calorimetry is a useful tool to distinguish between catalysts of similar characteristic properties.

Key-note

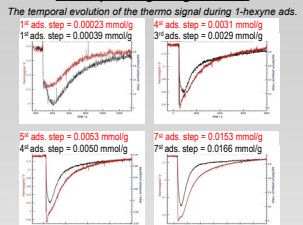
under reaction conditions a significant portion of the surface sites is covered by dehydrogenated species and is not available for hydrogenation. Nevertheless, the remaining small number of surface sites are active and selective in alkyne hydrogenation. This is in line with DFT calculations [10]

1-hexyne adsorption at 80°C = T_{reaction}

active in C₆H₁₀ hydrogenation 20wt%CeO₂/TiO₂-WI
less active in C₆H₁₀ hydrogenation 20wt%CeO₂/TiO₂-DI



Corresponding integral heats



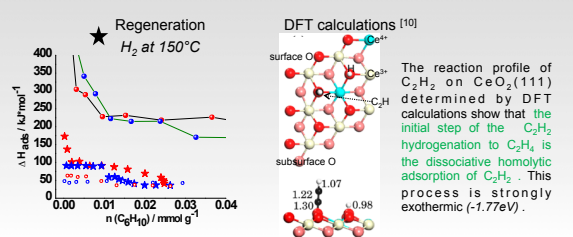
The adsorption signature is composed of two main contributions: physisorption / fast-signal & reaction / delayed signal. The most active catalyst has such sites that will hold 1-hexyne very weakly until the molecule chemisorbs stronger. In the less active catalyst the physisorbed molecule undergoes much faster side reactions or strong chemisorption.

The ads. of 1-hexyne at T_{react.} is composed of 2 main processes:

- 1) unspecific adsorption (physisorption <50kJ/mol)
- 2) time-consuming secondary process is due to single or multiple dehydrogenation steps and potentially oligomerization. [10] (>60 - 900 kJ/mol)

The most active catalyst is characterized by:

- higher amount of adsorption places for 1-hexyne 190 μmol/g
- slightly easier regeneration of the surface after 1-hexyne contact at T_{reaction}
- dynamic surface: pronounced trapped and phys. state of the adsorbates to find the most suitable place for reaction



References: [1] S. Wrabetz, R. Schlögl, J. Jenli et al., J. Catal. 269 (2010) 351-358. (b) Amalaks, W. Wrabetz, S. Knörner, J. Trojova-Müller, G. Schlögl, R. Tuschke, A. J. Am. Chem. Soc., 134 (28) (2012) 11462-11473. (c) B. Frank, S. Wrabetz, A. Turoňková, R. Schlögl et al., ChemPhysChem 12 (2011) 2709-2713. (d) R. Angino, S. Wrabetz, R. Schlögl et al., PCCP 14 (2012) 10523-10532. (e) G. Vilé, S. Wrabetz, L. Florjanczyk, M. E. Schuster, F. Girgsdes, D. Teschner, J. Pérez-Ramirez, Chem. Cat., 2014, DOI: 10.1002/cssc.201402124. [2] L. Jozefowicz, H. G. Karge, E. N. Coker, J. Phys. Chem., 98 (1994) 8053 - 8060; E. N. Coker, H. G. Karge, Rev. Sci. Instr. 68 (1997) 452; N. Cardona-Martinez and J. A. Dumescq, Advances in Catalysis, 38 (1992) 149-244. [3] A. L. McClellan et al., J. Chem. Soc. Faraday Trans. 2 (1979) 577. [4] A. Auroux, A. G. Goulet, P.C., 1981. Comparative study of the bond energy of oxygen at the surface of supported silver catalysts and of the activity of these catalysts for ethylene epoxidation. Thermochimica Acta, 47, pp.333-341. [5] Anderson, K.L., Piszczek, J.K. & Vannice, M., 1991. Heats of Adsorption of Oxygen, Ethylene, and Butadiene on Al₂O₃-Supported Silver. J. of Catalysis, 160, pp.148-160. [6] Anderson, K.L., Piszczek, J.K. & Vannice, M., 1991. Heats of Adsorption of Oxygen, Ethylene, and Butadiene on Al₂O₃-Supported Silver. Journal of Catalysis, 160, pp.148-160. [7] Charles T. Campbell, Chemistry Department, University of Washington, Seattle, USA; For Ag(110), reconstructions are formed at pressures as low as 10⁻⁶ mbar; but for Ag(111) they are formed only at 10⁻³ mbar. We have polycrystalline powder!