# Effects of adsorbed oxygen containing molecules on the XANES of Pt in supported Pt / $SiO_2$ catalysts

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The variation of the X-ray absorption coefficient above the Pt-$L_{III}$ edge after adsorption of crotonaldehyde, butyraldehyde, crotylalcohol and butanol on a Pt/$SiO_2$ catalyst was studied by means of X-ray absorption spectroscopy. The adsorption of these molecules caused the intensity of the white line to decrease in the order CrHO > CrOH $\sim$ BuHO $\gg$ BuOH. From this we concluded that adsorbed unsaturated compounds donate electrons from their double bonds to Pt. The magnitude of the observed effects was approximately equal for the C=O and the C=C group. Over the Pt/$SiO_2$ catalysts studied, crotonaldehyde was concluded to be adsorbed via both double bonds. The interaction of the free electron pairs of the oxygen was concluded to be significantly weaker than the interaction of the electrons in the $\pi$-bonds.

**Keywords:** Pt-catalysts; adsorption of aldehydes and alcohols; XANES

## 1. Introduction

The selectivity for hydrogenation of multiple unsaturated organic molecules as, e.g., crotonaldehyde ($CH_3$–CH=CH–CHO), was proposed to depend critically upon the adsorption structure of the reactant molecules [1–3]. For elements with partially filled d-states (group VIII elements) the interaction of these reactant molecules arises mainly from the overlap of orbitals of the adsorbed reactant with occupied or unoccupied d-states of the surface atoms [4]. The variations in the X-ray absorption near edge structure (XANES) and the threshold energy (edge position) of the Pt-$L_{III}$ edge were shown to be a suitable tool for studying the density of d-states of Pt / $SiO_2$ catalysts under hydrogenation conditions [5].

To understand better the interactions between unsaturated hydrocarbons and the metal particles, the changes in the density of unoccupied Pt d-states upon the adsorption of crotonaldehyde, butyraldehyde, crotylalcohol and butanol were studied. We monitored the Pt-$L_{III}$ edge, i.e., transitions of Pt $2p_{3/2}$ states into unoccupied $6s_{1/2}$, $5d_{3/2}$and $5d_{5/2}$ states above the Fermi level [6]. Because for Pt the unoccupied final states with a total angular momentum quantum number $J = 5/2$ contribute about 14 times more to d final states than those with $J = 3/2$ [7], the Pt-$L_{III}$ edge represents almost exclusively the transition from $2p_{3/2}$ into $5d_{5/2}$ states.

## 2. Experimental

### 2.1. CATALYST PREPARATION

A 1.5 wt% Pt/$SiO_2$ catalyst ($SiO_2$ Degussa Aerosil 200 $m^2/g$) was prepared by ion exchange in a $Pt(NH_3)_4(OH)_2$ solution ($10^{-2}$ molar) at 298 K for 12 h [8]. The catalyst was filtered, washed with water and dried in air at 373 K. A H/M ratio of 0.82 was determined by $H_2$ chemisorption after reduction at 573 K.

### 2.2. X-RAY ABSORPTION SPECTROSCOPY

X-ray absorption experiments were carried out at the National Brookhaven Laboratory (Beamline X18B) in transmission mode, using a Si (220) double crystal monochromator. At the Pt-$L_{III}$ edge (11564 eV) the resolution was about 0.5 eV. In order to obtain an energy calibration of the spectra, a thin Pt foil was measured simultaneously with a third ionization chamber. The precursor of the catalyst was pressed into self-supporting wafers and placed inside a stainless steel cell that permitted collection of the spectra in situ during the adsorption of the hydrocarbons. The weight of the sample was selected to achieve an absorption of less than $\mu x = 2.5$ for the reduced catalyst to optimize the signal to noise ratio [9]. The actual height of the edge step was approximately $\Delta\mu_0 x = 0.2$ to avoid non-linear variations of $\mu x$ induced by the thickness of the pellet [10]. During all measurements a continuous stream of hydrogen saturated with the sample molecules (at 300 K) was passed over the catalyst. This ensured full surface coverage for all molecules studied as determined in separate volumetric experiments.

Before each adsorption, the catalyst was reduced in $H_2$ at 573 K and an X-ray absorption spectrum (XAS) was recorded at 298 K as reference for the changes in the XANES after saturating $H_2$ with the sorbate molecules. The edge positions of the XAS were determined at the maximum of the first derivative of the edge and aligned using the maximum of the first derivative of the edge of the internal Pt reference foil. A third order polynomial function was used to approximate the variation of the total absorption coefficient due to the background scattering (support, ionization chambers and window material). The scattering coefficient of the edge metal was determined from the Victoreen coefficients up to 700 eV above the edge [11]. The mass areal loading, representing the product of metal concentration and sample thickness, was calculated using [12]

$$(\mu t)_{\mathrm{tot,exp}} = B + C\lambda + D\lambda^2 + E\lambda^3 + \ldots + N\lambda^n + \left(\frac{m}{A}\right)\left(\frac{\mu}{\rho}\right)_{\mathrm{edge}},$$

where $\mu$ is the total linear absorption coefficient, $\rho$ the density of the metal, $\lambda$ the wavelength, $t$ the sample thickness, $m/A$ the mass areal loading, and $B$–$N$ are coefficients to construct the background.

To estimate the area of the peak above the absorption edge, the continuum step was modelled by an arctan function and subtracted from the XANES [13]. The inflection point of the arctan function was positioned at the half height of the absorption edge. The height of the modelled step was aligned by a least square fit of the XANES starting at 40 eV above the edge. The intrinsic width of the step was obtained by adjusting the model function to the shape of the absorption edge of bulk Pt. An example of the simulation of the continuum step is shown in fig. 1. The grey shaded area was integrated numerically.

## 3. Results and discussion

The adsorption of crotonaldehyde, butyraldehyde, crotylalcohol and butanol did not change the threshold energy of the absorption edge to a measurable extent. Note, that the resolution of the monochromator at 11563 eV was approximately 0.5 eV. The variations of the intensity of the white line after adsorption of the hydrocarbons compared to the intensity of the white line of the reduced catalyst, measured before the adsorption experiment, are compiled in fig. 2.

The area under the peak above the Pt-$L_{\mathrm{III}}$ absorption edge decreased about 11% during adsorption of crotonaldehyde, 3.8% during adsorption of butyralde-

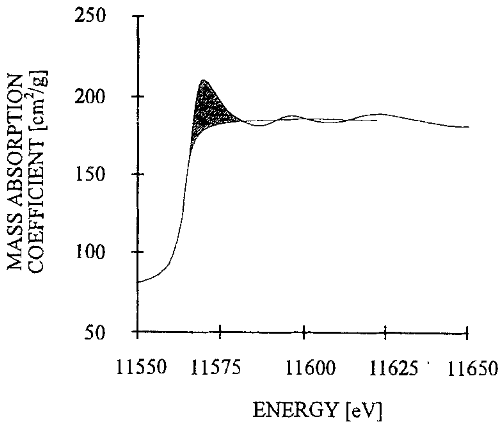

Fig. 1. Example of the simulation of the continuum step.

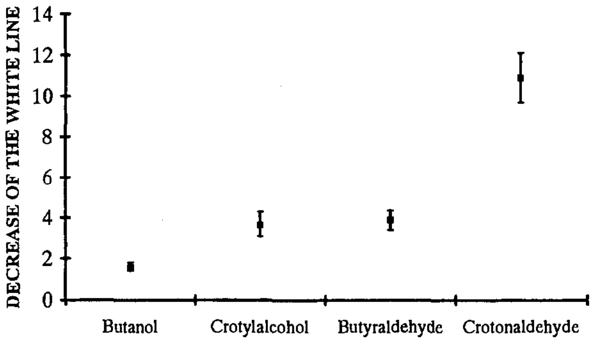

Fig. 2. Variations of the intensity of the white line after adsorption of the hydrocarbons compared to the intensity of the white line of the reduced catalyst.

hyde and 3.6% during adsorption of crotylalcohol. For butanol a decrease of about 1.5% compared to the reduced catalyst was observed.

Under the assumption that the adsorbed organic molecules do not induce changes in the band structure of the metal atoms, the decrease of the area under the peak above the edge is explained with electron transfer from the organic molecule to the absorber metal atoms, the increase of the area under the peak is explained with electron transfer from the absorber metal atoms to the organic molecule [14].

Thus, we conclude that during adsorption of crotonaldehyde, butyraldehyde and crotylalcohol the electron density of the Pt d-states in the catalyst particles increases compared to the reduced catalyst. Because the adsorption of butanol showed only a minor decrease in the intensity of the peak above the edge, the electron pair donor–acceptor interaction via the free electron pairs at the oxygen of the hydroxyl group is concluded to be significantly weaker than the interaction of the $\pi$-electrons of the double bonds. The partial oxidation of the catalyst by chemisorption of the adsorbates can be excluded, as this should lead to an increase in the peak above the absorption edge. Similarly, image charges induced by negatively charged parts of polar molecules (i.e., oxygen of the molecules investigated) lead to a local depletion in electrons and to the increase of the peak above the platinum absorption edge.

While the presented experiments do not allow to draw conclusions on specific orientations of the aldehydes adsorbed on Pt/SiO$_2$ they clearly establish a much stronger depression of the platinum white line after adsorption of a carbonyl group than of an alcohol hydroxyl group. As the electron pair donor (EPD) strength of the alcohol is equal to or higher than the EPD strength of the corresponding aldehyde, this is an unexpected result. Would it be primarily the binding of the oxygen lone pair electron, one would expect the alcohol to exert an equal or stronger depression of the white line of platinum than the aldehyde. Thus, we conclude that the interaction with the $\pi$-electrons is the dominating type of interaction in the case of butyraldehyde.

The similar decrease of the intensity of the white line observed for crotylalcohol and butyraldehyde suggests that the electron donation from the C=C and the C=O double bond to the d-states of Pt is similar under the experimental conditions. After adsorption of crotonaldehyde the intensity of the white line decreased to an extent slightly higher than the sum of the decrease observed for butyraldehyde and crotylalcohol. Thus, we conclude that during adsorption of crotonaldehyde both double bonds interact with the Pt surface. The slightly higher value compared to the additive contributions suggests that the partial delocalization of the conjugated C=C and C=O bonds in crotonaldehyde increases the overlap between the lowest unoccupied d-states in the Pt metal and the highest occupied molecular orbitals of crotonaldehyde.

It is interesting to compare the results with the selectivity in the hydrogenation of crotonaldehyde. Over Pt/$SiO_2$ crotonaldehyde is hydrogenated with almost 100% selectivity to butyraldehyde [15,16]. Previously, this was partially explained with the preferential adsorption of the carbon–carbon double bond on the Pt surface. This possibility is ruled out based on the strong decrease of intensity of the white line after adsorption of crotonaldehyde which suggests that both double bonds interact with Pt. Thus, we conclude also that the interaction via the electrons of the double bond does not suffice to catalyze the hydrogenation of the C=O bond of crotonaldehyde with an appreciable rate at low conversions. Over fully reduced Pt/$SiO_2$ the decrease of the white line after adsorption of butanol indicates that little interaction exists between the free electron pairs of oxygen (electron pair donor site [17]) and the surface Pt atoms. The lack of this interaction will cause the desorption of the molecule once the C=C bond is saturated (lower adsorption constant of butyraldehyde in comparison with crotonaldehyde).

It should be emphasized that most catalysts that catalyze hydrogenation of the C=O bond of crotonaldehyde contain accessible metal cations or positively charged metal ions at the surface. It is expected that these sites interact strongly with the electron pair donor sites of crotonaldehyde at the oxygen and might even stabilize a negative charge at the oxygen [18]. Only this electron pair donor–acceptor interaction between the oxygen and the positively charged surface entity is speculated to lead to hydrogenation of the carbonyl group. Catalysts that have a high concentration of such polar groups in proximity to Pt and the minimal concentration of Pt atoms without polar neighboring atoms should exhibit the highest selectivity for the hydrogenation of the C=O bond in multiply unsaturated molecules.

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