

Editor Choice paper

# Adsorption modes of aromatic ketones on platinum and their reactivity towards hydrogenation

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## Abstract

Heterogeneous catalytic hydrogenation of ketones is an important synthetic route to alcohols, but the detailed reaction pathway of this common reaction is still unknown. In particular, different opinions exist concerning the nature of the surface intermediates that eventually react with the activated surface hydrogen:  $\eta^1(\text{O})$  and  $\eta^2(\text{C},\text{O})$  adsorbed intermediates have been postulated by different authors, leading to different surface reaction pathways. Here we studied the hydrogenation of aromatic ketones activated by an ester group in  $\alpha$ -position. Ethyl benzoylformate (**1**) was hydrogenated on Pt/Al<sub>2</sub>O<sub>3</sub> under mild conditions, but insertion of one or two *o*-substituents into the aromatic ring diminished or completely eliminated the reactivity of the ketone. The dramatic difference between the reactivities of **1** and ethyl mesityl glyoxylate (**5**) prompted us to investigate the adsorption geometries and energies of the two ketones by electronic structure calculations on a model platinum (1 1 1) surface. The calculations revealed that the presence or absence of *o*-substitution on the phenyl ring strongly affects the interaction mode of the C=O moiety with the metal surface. In particular, *o*-substitution suppresses adsorption modes where the keto-carbonyl group is bound to the metal in  $\eta^2(\text{C},\text{O})$  mode. Following such observations the reactivity of aromatic ketones is discussed, and a correlation between adsorption mode and reactivity of the ketone towards hydrogenation is proposed that could be critical for the further investigation of a complete reaction mechanism.

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## 1. Introduction

The adsorption of ketones on transition metals has been the topic of many studies employing surface science techniques [1–5] typically in ultrahigh vacuum and consequently under *ex situ* conditions. Such experimental studies are often combined with density functional theory (DFT) calculations of the ketones on model surfaces aiming to unravel their interaction with the metal. This is often critical for the interpretation of the rate and the chemo- and enantioselectivity of hydrogenation reactions [6–8]. Previous to surface science techniques such topic had been addressed mainly by means of isotopic exchange and by studying the kinetic effects due to substitution [9,10]. In general, ketones adsorb on transition metal surfaces *via* two alternative bonding configurations: as  $\eta^1(\text{O})$  in an end-on adsorption

configuration in which the oxygen atom is bonded by its lone pair orbital to the metal surface, or as  $\eta^2(\text{C},\text{O})$ , with both the carbon and the oxygen atoms of the keto-group  $\sigma$ -bonded to the metal and the C=O moiety lying parallel to the surface. Thermal desorption spectra (TDS) and high-resolution electron energy loss vibrational spectroscopic (HREELS) studies of acetone on a Pt foil have shown evidence of both adsorption geometries [4]. On the basis of DFT electronic structure calculations and comparative studies on the rate of hydrogenation of acetone (non-activated ketone) and 1,1,1-trifluoroacetone (activated ketone), it was proposed that the  $\eta^2(\text{C},\text{O})$  adsorption mode could be the reactive intermediate for the hydrogenation of carbonyl compounds on platinum group metals [5]. The basic idea behind this proposal emerged from the following observations: (i) while acetone hardly reacted on platinum, 1,1,1-trifluoroacetone was quickly hydrogenated under the same reaction conditions, and (ii) acetone prefers an  $\eta^1(\text{O})$  adsorption mode while 1,1,1-trifluoroacetone assumes a more stable  $\eta^2(\text{C},\text{O})$  adsorption mode. On the contrary, other authors pro-

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posed that the hydrogenation of acetone occurs via an  $\eta^1(\text{O})$  intermediate [7], in a similar fashion to what had been proposed for the hydrogenation of formaldehyde on Pt(1 1 1) [11]. Since the two proposals other studies have appeared, which are more consistent with the critical role of an  $\eta^2(\text{C},\text{O})$  intermediate [12,13], but nonetheless a clear picture of the reaction pathway has not yet been obtained.

The preceding models are largely based on the comparison between catalytic data and DFT calculations, as well as high vacuum investigations. Adsorption geometries may be affected also by the reaction conditions including temperature, pressure, solvent, and concentrations [14], which are still difficult to model at a sufficiently accurate level of theory for real systems [15]. For the heterogeneous enantioselective hydrogenation of  $\alpha$ -ketoesters over cinchona-modified Pt/Al<sub>2</sub>O<sub>3</sub> it has been shown that depending on the modifier concentration various adsorption geometries of cinchonidine (*via* the quinoline ring) on Pt are feasible and the adsorption mode of the modifiers determines the outcome of enantioselective hydrogenation of the ketone [16]. Recently, it has been suggested for the enantioselective hydrogenation of ethyl pyruvate that the role of the modifier is to interact with the  $\eta^1(\text{O})$  adsorption mode of the substrate and tilt the substrate plane toward the surface to an  $\eta^2(\text{C},\text{O})$  adsorption mode, in which hydrogenation of the keto-carbonyl group is possible [7]. Due to the fact that hydrogenation is also possible in the absence of chiral modifier, this flip from  $\eta^1(\text{O})$  to  $\eta^2(\text{C},\text{O})$  should be ascribed as a property of the substrate itself. The adsorption behavior of methyl and ethyl pyruvate has already been investigated by many surface sensitive techniques such as XPS and UPS [17], XANES [18], STM [19], and NEXAFS [20].

Herein we report an intriguing new experimental observation in the hydrogenation of activated aromatic ketones, which suggests that there is an important steric requirement a ketone has to fulfill to be hydrogenated on Pt. DFT calculations on a model surface support the experimental results, thus providing interesting insight concerning the possible correlation between the adsorption mode of the ketones and their reactivity towards hydrogenation on platinum.

## 2. Experimental

### 2.1. Materials

Ethyl benzoylformate (**1**, 95%, Aldrich) and ethyl mesityl glyoxylate (97%, Alfa Aesar) **5** were carefully distilled in vacuum before use. Ethyl 3,5-dimethylbenzoylformate (**2**), ethyl naphthylglyoxylate (**3**) and ethyl anthracenylglyoxylate (**4**) were prepared by the reaction of the corresponding Grignard reagents with diethyl oxalate or ethyl chlorooxoacetate according to known methods in the literature [21,22]. All synthesized substrates were carefully purified using flash chromatography and their structure and purity were checked by GC, GC-MS, HPLC, and NMR. Acetic acid (AcOH, 99.8%, Fluka) was used as received and toluene (99.5%, J. T. Baker) was dried and stored over activated molecular sieve. The 5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> (E-4759) catalyst was purchased from Engelhard.

### 2.2. Catalytic hydrogenations

The hydrogenation reactions were carried out in a mechanically stirred eight parallel pressure reactor system (Argonaut Technologies) or in a magnetically stirred stainless steel autoclave controlled by a computerized constant-volume constant-pressure equipment (Büchi BPC 9901). The 5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was pre-reduced before use in a fixed-bed reactor by flushing with N<sub>2</sub> at 400 °C for 30 min, followed by reductive treatment in H<sub>2</sub> for 60 min at the same temperature. After cooling to room temperature in H<sub>2</sub> (30 min), the catalyst was transferred to the hydrogenation reactor. According to standard conditions, 42 mg catalyst, 1.84 mmol substrate, and 5 ml solvent were stirred (1000 rpm) at 10 bar and room temperature (23–25 °C) for 2 h.

According to TEM measurements, the average particle size of Pt after the reductive heat treatment was 3.7 nm [23].

### 2.3. Analytics

Conversion was determined by a HP-6890 gas chromatograph equipped with a HP-5 (30 m × 0.32 mm × 0.25 μm) capillary column as well as by HPLC using a MERCK LaChrom system with a CHIRACEL OD column (4.6 mm i.d., 240 mm length, 10 μm particle size). The HPLC measurements were carried out at 10 °C with a liquid flow of 0.5 ml/min. The UV detector was set to 210 nm. For all substrates a mixture of *n*-hexane/isopropanol (9/1) was used as eluent. Products were identified by GC/MS (HP-6890 coupled with a HP-5973 mass spectrometer) and by <sup>1</sup>H and <sup>13</sup>C NMR. All NMR data were recorded on a Bruker Avance 500 with TMS as internal standard.

### 2.4. Computational methods

Adsorption studies have been performed using the Amsterdam Density Functional (ADF) program package [24] using a Pt 31 cluster to simulate the metal surface. A detailed description of the application of such cluster for adsorption studies has been published elsewhere [8,13,25,26] and we here give only some basic information on the model chemistry used. A frozen core approximation was used for the description of the inner core of the atoms. Orbitals up to 1s were kept frozen for the second row elements, while orbitals up to 4f were kept frozen for platinum. The core was modeled using a relativistically corrected core potential created with the DIRAC utility of the ADF program. Furthermore the relativistic scalar approximation (mass–velocity and Darwin corrections) was used for the Hamiltonian, with the zero order regular approximation (ZORA) formalism, where spin-orbit coupling is included already in zero order [27–31]. The ZORA formalism requires a special basis set, to include much steeper core-like functions, implemented in the code. Within this basis set the double- $\zeta$  (DZ) basis functions were used for platinum. For second row elements and hydrogen double- $\zeta$  polarized (DZP) basis functions were used. The local part of the exchange and correlation functional was modeled using a Vosko, Wilk, Nuisar parametrization of the electron gas

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