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Decomposition Mechanism of Lignin Models on Pt(111) : Insights from Single Crystal Experiments and First Principle Calculations.

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PURPOSE OF THE ABSTRACT

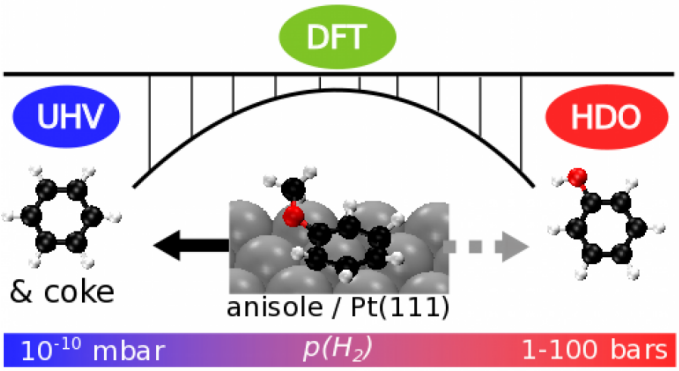
Lignin is Nature's most abundant aromatic polymer [1]. It therefore represents an extraordinary renewable source of aromatic compounds. To be valorised into BTX (benzene, toluene and xylene), it is necessary to develop heterogeneous catalysts that can remove, under a hydrogen pressure, the oxygenated functions of the lignin fragments, while keeping the aromatic moiety intact. This hydrodeoxygenation (HDO) reaction can be catalysed using CoMoS and NiMoS or noble metals (Ru, Pd, Pt) for example. Among them, Pt shows the highest conversions but unfortunately affords mainly phenolics [2-4]. To gain insight into the performances of the later catalyst, we examined, combining first principle calculations and single crystal experiments, the decomposition mechanism of both anisole and 2-phenoxyethanol, which are models of lignin fragments.

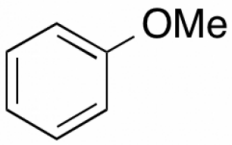
Our Ultra-High Vacuum (UHV) experiments (10^-10 mbar) shows that anisole gives benzene, carbon monoxide and coke as the main products of decomposition. Surprisingly enough, we cannot to detect phenol, which is the main product of decomposition under catalytic conditions (1-100 bars). To address this pressure gap, we performed a mechanistic investigation using Density Functional Theory (DFT). We show that anisole readily decomposes (barrier of 100 kJ/mol) intro phenoxy (PhO) and methylidene (CH). In UHV conditions, methylidene can further decompose into atomic carbon. The later species is responsible for the oxygen removal of phenoxy (PhO) into phenyl (Ph), which explains the production of both benzene and carbon monoxide. This very mechanism is not possible under catalytic conditions since methylidene is more likely to be hydrogenated rather than dehydrogenated. Similarly, we show that PhO can undergo dehydrogenation. That happens at higher temperatures (> 450 K under UHV conditions) but leads to a full decomposition into carbon monoxide and carbonaceous species. All these mechanistic features obtained from DFT are in full agreement with the experiments (Temperature Programmed Desorption and X-ray Photoelectron Spectroscopy). [5]

The same experiments on 2-phenoxyethanol (PhOCH2CH2OH) confirm that PhO is the key intermediate of the decomposition on Pt(111). However, the decomposition of the C2-substituent gives more carbonaceous species. It drastically increases the coverage of the surface and affects the selectivity of the reaction: benzene is still the major product (95%) but phenol and anisole are also detected (5%) when the coverage gets close to one monolayer.

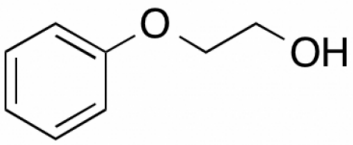
This study reveals the protecting role of hydrogen towards aromatic decomposition; the need of a reductant (here atomic carbon) to deoxygenate the key intermediate PhO; and the effect of coverage. It opens the door to a rational design of noble metal based catalysts within the context of lignin valorisation.

FIGURES





anisole



2-phenoxyethanol

FIGURE 1

Opposite selectivity of Anisole decomposition under UHV and catalytic conditions. The mechanism elucidation provided by DFT helps reconcile the two and highlights guidelines for the design of better catalysts.

UHV: ultra high vacuum

HDO: hydrodeoxygenation (catalysis)

DFT: Density Functional Theory

FIGURE 2

Lignin models studied in this work

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KEYWORDS

lignin models | deoxygenation | DFT | UHV

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