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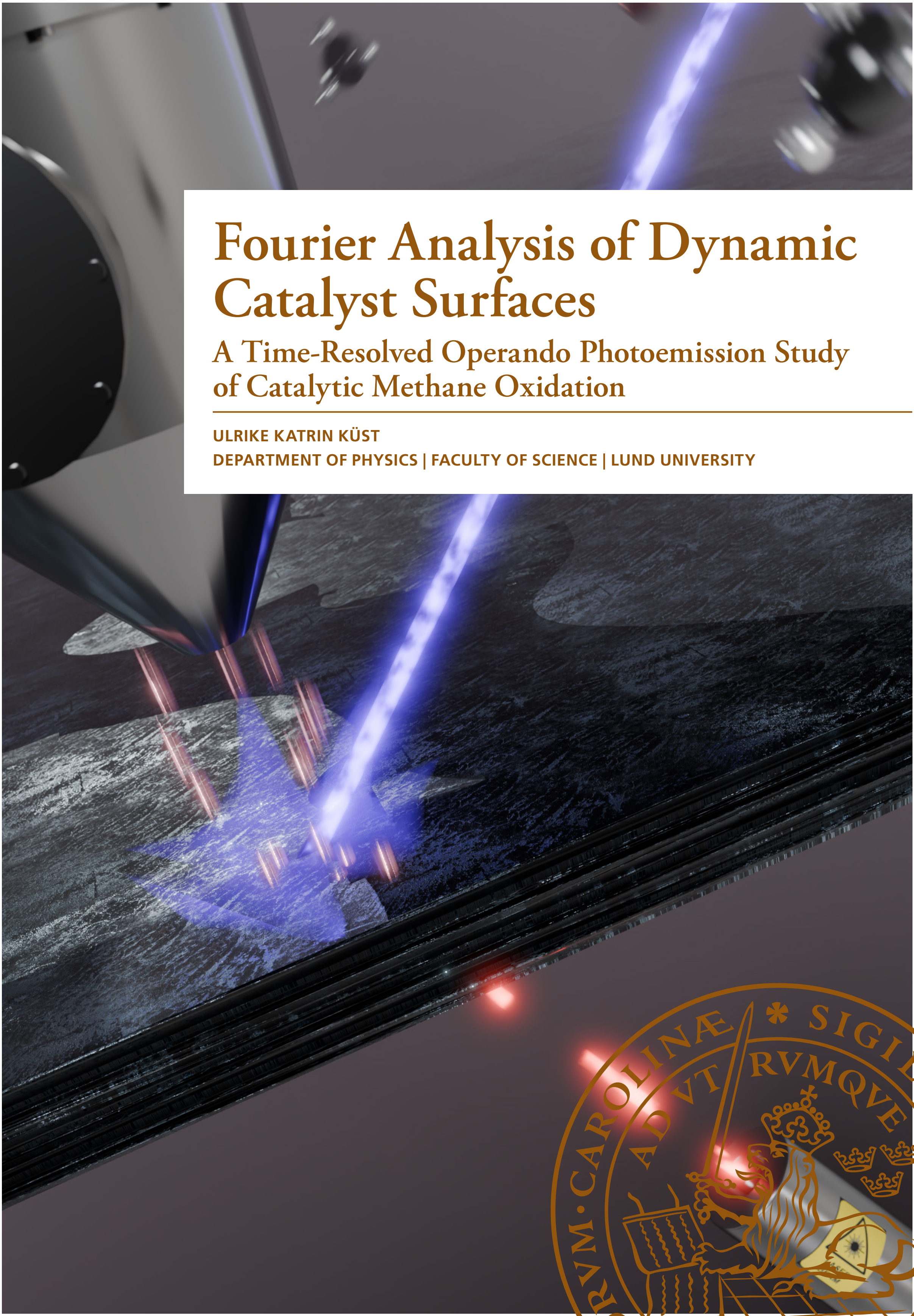

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A Time-Resolved Operando Photoemission Study of Catalytic Methane Oxidation

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LUND
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Thesis for the degree of Licentiate
Thesis advisors: Dr. Jan Knudsen, Dr. Andrey Shavorskiy, Prof. Dr. Joachim Schnadt
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Abstract

This thesis focuses on the development and application of advanced measurement and data analysis techniques for Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) to enable time-resolved operando studies of heterogeneous catalysts. A primary challenge in catalysis research is the dynamic nature of catalysts under reaction conditions, necessitating the development of new techniques capable of capturing these rapid changes with high temporal resolution.

To address this, the thesis introduces the use of Modulation Excitation Spectroscopy (MES) in conjunction with APXPS. MES involves periodic modulation of external variables such as reactant concentration or temperature, with the resulting periodic response detected by Fourier analysis. This approach enhances the signal-to-noise ratio by isolating oscillatory signals correlated with the modulation, effectively filtering out static or noisy background signals.

The methodology developed in this work enables detailed, time-resolved investigations of both the surface and subsurface regions of catalysts under realistic reaction conditions. Paper i outlines the application of the MES technique to APXPS and discusses subsequent data analysis by Phase Sensitive Detection or Fourier analysis, comparing the two analysis schemes. Paper ii demonstrates the application of Fourier analysis to MES data through a study of methane oxidation over a polycrystalline palladium catalyst, highlighting the capability to correlate dynamic changes in catalyst chemical composition with catalytic activity in real-time.

By improving the time resolution and sensitivity of operando APXPS, this thesis provides a robust framework for studying the intricate mechanisms of catalytic processes, paving the way for more informed catalyst design.

Key words

heterogeneous catalysis, Ambient Pressure X-ray Photoelectron Spectroscopy, synchrotron, palladium, methane, depth-profiling, time-resolved, Fourier transform

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by Ulrike Katrin Küst

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UNIVERSITY

A licentiate thesis at a university in Sweden takes either the form of a single, cohesive research study (monograph) or a summary of research papers (compilation thesis), which the licentiate student has written alone or together with one or several other author(s).

In the latter case the thesis consists of two parts. An introductory text puts the research work into context and summarizes the main points of the papers. Then, the research publications themselves are reproduced, together with a description of the individual contributions of the authors. The research papers may either have been already published or are manuscripts at various stages (in press, submitted, or in draft).

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MADE IN SWEDEN

Dedicated to
my family and friends

Contents

List of publications

This thesis is based on the following publications, referred to by their Roman numerals:

i **Comparing Phase Sensitive Detection and Fourier Analysis of Modulation Excitation Spectroscopy Data Exemplified by Ambient Pressure X-ray Photoelectron Spectroscopy**
U. Küst, J. Prumbs, C. Eads, W. Wang, V. Boix, A. Klyushin, M. Scardamaglia, R. Temperton, A. Shavorskiy, and J. Knudsen
Surface Science, 2025, 751, pp. 122612

I participated in developing the Fourier analysis theory and writing the Fourier analysis software. I implemented the Phase Sensitive Detection analysis software based on literature myself. I wrote the manuscript.

ii **Carbon Surface Crowding and Subsurface Traffic Jam as Drivers for Methane Oxidation Activity and Selectivity on Palladium Surfaces**
U. Küst, R. Jones, J. Prumbs, A. Namar, M. Scardamaglia, A. Shavorskiy, and J. Knudsen
In Review for Nature Communications, 2025

I participated in developing the research idea and planned the experiments. I participated in data acquisition and performed data analysis with self-written software. I wrote the manuscript.

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Publications not included in this thesis:

iii **Temperature-Dependent Selectivity and Detection of Hidden Carbon Deposition in Methane Oxidation**
U. Küst, W. Wang, C. Wang, H. Hagelin-Weaver, J. Gustafson, A. Shavorskiy, J. F. Weaver, and J. Knudsen
ACS Catalysis, 2024, 14(8), pp. 5978-5986

I participated in the data acquisition, performed the data analysis and wrote the manuscript.

iv **Time-Resolved Ambient Pressure X-ray Photoelectron Spectroscopy: Advancing the Operando Study of ALD Chemistry**
R. Jones, E. Kokkonen, C. Eads, **U. Küst**, J. Prumbs, J. Knudsen, and J. Schnadt
Surface Science, 2025, 753, pp. 122656

I helped with the Fourier transform related part of the data analysis and the respective section in the manuscript.

v **Catalysis in Frequency Space: Resolving Hidden Surface Structure and Activity Oscillations**
J. Knudsen, C. Eads, A. Klyushin, R. Temperton, **U. Küst**, V. Boix, A. Kraina, M. Scardamaglia, A. Shavorskiy, E. Kokkonen, and J. Schnadt
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I helped with the development of the method and the writing of the macros for the data analysis. I helped with the writing of the manuscript.

vi **Resolving Active and Spectator Species During the Oxidation of Carbon Monoxide over Pt(111) on the Microsecond Time Scale**
C. N. Eads, W. Wang, **U. Küst**, J. Prumbs, R. Temperton, M. Scardamaglia, J. Schnadt, J. Knudsen, and A. Shavorskiy
Nature Communications, 2025

I participated in the data acquisition and the discussion about the data analysis.

vii **Selective Catalysis Promoted by Dual-Atom Pairing in Trimetallic Alloys: Ethanol Dehydrogenation over PtCrAg Films**
J. F. Weaver, S. Xiang, J. Jamir, **U. Küst**, L. Rämisch, A. Grespi, H. Wallander, J. Zetterberg, S. Arias, E. Fornero, P. K. Routh, S. Zhang, J. A. Boscoboinik, M. M. Montemore, E. C. H. Sykes, J. Knudsen, J. Biener, L. Merte, and A. I. Frenkel
Submission planned to Science, 2025

I participated in the APXPS measurements, did the data analysis for these data and helped to write the corresponding section in the manuscript.

viii **Ambient Pressure XPS at MAX IV**

M. Scardamaglia, **U. Küst**, E. Kokkonen, A. Klyushin, J. Knudsen, R. Temperton, A. Shavorskiy
Submission planned to Beilstein Journal of Nanotechnology, 2025

I wrote a section in the manuscript about time-resolved APXPS measurements in catalysis.

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Och till sist också tack till dig min sötis för det fina gångna året och ditt stöd. ;)

Populärvetenskaplig sammanfattning på svenska

Katalysatorer används överallt för att accelerera industriella processer, producera mer gödsel eller för att avlägsna giftiga gaser från bilmotorer. Katalysatorernas design är dock baserat helt enkelt på försök vilket är väldigt ineffektivt. För att istället bygga bättre kondensatorer är det viktigt att kombinera resultaten från forskning och beräkning, likt ett pussel. Denna licentiatexamen ägnar sig åt att hitta en del av det här pusslet, speciellt åt betydelsen som kolkontaminationer har för katalysatorns beteende.

Att sitta framför ett pussel på en mysig söndagskväll, bara för skojs skull, är något som forskare får göra varje dag. Deras forskningsresultat kommer aldrig direkt att få användning i industriella sammanhang. Däremot är de en del av ett stort pussel som tusentals forskare jobbar med under årtionden. Varje litet resultat leder till framsteg i kompletteringen av pusslet och är nödvändigt för att få en fundamental förståelse av hur världen fungerar.

I denna avhandling rör vi oss dock inte i de djupaste hörnen av fundamental forskning utan samlar istället på tidigare resultat och kombinera dem med nya, mer realistiska experiment. I dessa har jag framförallt undersökt hur katalysatorer beter sig när det är varmt eller kallt, när de behöver omvandla många eller få molekyler, eller vad som händer när gasens sammansättning framför katalysatorn förändras.

Katalysatorer och deras död

Katalysatorer är metaller som beter sig likt en skola. På skolgården möts barnen mycket oftare än på gatan och på samma sätt möts gasmolekyler mycket oftare på katalysatorns yta än i gasen ovanför. Det betyder att mycket lägre temperaturer och tryck behövs för att få en effektiv reaktion vilket sparar såklart pengar.

Ett stort problem vilket orsakar höga kostnader i industrien är katalysatorernas död. En anledning för döendet är förstoppning med föroreningar. För att återkomma till skolanalogin, ibland kan barn lämna gården och gå vilse i skolbyggnaden. Något liknande kan hända för katalysatorer. Molekyler på ytan kan dyka in i katalysatorn och tas därmed bort från ytreaktionerna. Ju mer förstoppad en katalysator är, desto mer ineffiktiv blir den och kan även börja producera oönskade produkter. Någonstans i den här processen behöver katalysatorn bytas ut för att återställa effektiviteten. För att bygga hållbara katalysatorer är det därför viktigt att förstå de fundamentala processerna som omger katalysatorn.

Att lösa pusslet för metanoxidation

Att lösa problemet för alla katalysatorer på en gång är omöjligt. Det är dock en bra början att pussla i ett hörn, byggande på tidigare forskning. Mina första publikationer handlar om metanoxidation över en palladiumkatalysator. Metan, CH_4, är en liten molekyl vilken förekommer exempelvis i biogas. Eftersom den är också en farlig växthusgas, får vi inte bara släppa ut den i miljön utan behöver omvandla den till något mindre farligt, till exempel via oxidation.

Metanoxidationen med hjälp av katalysatorer sker i tre steg. Först landar metanmolekylen, vilken tididgare svävade genom gasen, på ytan. Där delas den upp i sina atomer, det vill säga kol (C) och väte (H). Samma öde väntar syremolekylerna (O_2). I nästa steg rör sig atomerna fritt på ytan tills de möter en reaktionspartner så att syre och väte blir till vatten eller kol och syre reagerar till kolmonoxid (CO) eller koldioxid (CO_2). Tredje och sista steget är att de nya produkterna lyfter och flyger iväg och i och med det skapar plats för en ny reaktion.

Dykande kolatomer

Det kan dock hända ibland att kolatomer bestämmer sig för att dyka, framförallt om de inte hittar tillräckligt många reaktionspartner på ytan. Det betyder dessvärre också att de dykande atomerna så småningom orsaker förstoppningar i katalysatorn eftersom de inte längre är tillgängliga för ytreaktionerna. Denna koldykningsprocess är en av de främsta anledningarna till katalysatorernas död.

För att förhindra döendet kan vi spela in en film som, i separata delar, fokusserar på katalysatorns olika lager. För att få en bra kvalitet på filmen använder vi en väldigt ljus ljuskälla, en synkrotron, man skulle nästan kunna kalla det för supermikroskop, för att följa och studera dessa pyttesmå molekyler och deras beteende. Första skiktet vi observerar är gasen direkt ovanför katalysatorns yta. Dess observation gör det möjligt för oss att förstå, vilka molekyler som närmar sig ytan och vilka som avlägsnar sig. Utifrån det kan vi lära oss något om katalysatorns aktivitet och vilka produkter katalysatorn förderar vid en viss tidspunkt. Andra lagret vi studerar är katalysatorns yta. Här händer det dissociationen och reaktionen till en ny produkt. Tredje lagret är lite djupare ner i katalysatorn. Observation av aktiviteten där gör det möjligt att studera kolatomernas dykning.

Kombinationen av resultaten i de olika lagren hjälper oss att förstå vilka ytprocesser hör till vilken produkt och vad effekten av kolatomernas dykning är.

Problemet med suddiga bilder

Är inte det irriterande när man verkligen vill titta på en film men tv:n visar bara brus eller suddiga bilder? Samma problem har vi här med våra filmer av katalysatorns olika lager. Ofta rör sig molekylerna alldeles för fort för att observera dem ordentligt. Om vi kunde tvinga dem att utföra samma rörelse upprepade antal gånger, skulle vi dock kunna filtrera bara molekylens rörelse medans allt som inte följer denna periodicitet, såsom brus och oviktiga molekyler, kastas bort. På så sätt kan vi få en tydlig bild som bara innehåller molekylerna som verkligen är relavanta för reaktionen!

För experimenten betyder det att vi kan tvinga fram en sådan periodisk rörelse med hjälp av temperaturförändringar, tryckanpassningar eller förändringar av molekylernas relativa koncentration. Filtern som sedan städar våra bilder heter Fouriertransformation och är en vanlig metod i, till exempel, analysen av radiosignaler.

Superkatalysatorernas design

Observationen av hur katalysatorer beter sig under olika omständigheter, hur de dör, vilka produkter de föredrar eller vad som händer på deras ytor kan hjälpa med att producera avancerade katalysatorer. Sådana 'superkatalysatorer' har sedan en ihållig bra prestation, leder till mindre kostnader och högre effektivitet.

Populärwissenschaftliche Zusammenfassung auf Deutsch

Katalysatoren werden weit und breit eingesetzt, um industrielle Prozesse zu beschleunigen, Düngerherstellung effizienter zu gestalten, oder giftige Gase aus dem Auspuff von Autos zu entfernen. Tatsächlich basiert die Gestaltung solcher Katalysatoren aber seit jeher auf einem "Ich versuch's mal, wird schon schiefgehen" Ansatz, der sehr ineffektiv ist. Um stattdessen aktiv bessere Katalysatoren zu bauen, ist es wichtig die Ergebnisse aus Forschung und Berechnungen zusammenzubringen, ähnlich der Anfertigung eines Puzzles. Diese Lizenziatsdissertation widmet sich dem Ziel einen Teil dieses Puzzles zu finden, nämlich der Bedeutung von Kohlenstoffverunreinigungen dafür wie sich der Katalysator verhält.

An einem Sonntag Abend gemütlich an einem Puzzle sitzen, einfach weil man Spaß daran hat, das ist genau das was Wissenschaftler beruflich tun. Die Ergebnisse ihrer Forschung werden nie direkt in industriellen Anwendungen verwendet werden, stattdessen sind sie Teil eines großen Puzzles an dem tausende von Wissenschaftlern über Jahrzente arbeiten. Jedes kleine neue Ergebnis sorgt schlussendlich für die Verfollständigung des Puzzles und ist notwendig, um fundamental zu verstehen wie unsere Welt funktioniert.

In dieser Dissertation begeben wir uns nicht in die tiefsten Ecken fundamentaler Forschung sondern sammeln Ergebnisse früherer, fundamentaler Forchung zusammen und verbinden sie mit neuen, realistischeren Experimenten. In diesen habe ich mir angesehen wie sich Katalysatoren verhalten wenn es heiß oder kalt ist, wenn sie viele oder wenige Moleküle umwandeln müssen oder auch was passiert wenn sich die Gaszusammensetzung vor dem Katalysator ändert.

Katalysatoren und wie sie sterben

Katalysatoren sind Metalle die sich ähnlich zu einer Schule verhalten. Auf dem Pausenhof treffen sich Kinder deutlich häufiger als auf der Straße und ebenso reagieren Moleküle deutlich häufiger miteinander wenn sie sich auf der Oberfläche eines Katalysators befinden als wenn sie im Gas herumirren. Für die Anwendung bedeutet das, dass deutlich geringere Temperaturen und Drücke nötig sind damit die Reaktion vonstatten geht was wiederum deutlich weniger Geld kostet.

Ein großes Problem und großer Kostenfaktor in der Industrie ist das Sterben von Katalysatoren. Ein Grund für dieses Sterben können Verstopfungen des Katalysators mit Verunreinigungen sein. Um auf die Schul-Analogie zurückzukommen, manchmal gehen Kinder in das Schulgebäude und dort verloren. Etwas Ähnliches kann dem Katalysator passieren. Moleküle an der Oberfläche können in den Katalysator abtauchen und werden damit unzugänglich für die Reaktionen, die an der Oberfläche passieren. Je verstopfter der Katalysator ist, desto ineffizienter wird er und manchmal fängt er sogar an, andere unerwünschte Sachen zu produzieren. An irgendeinem Punkt in diesem schleichenden Prozess muss der Katalysator ausgetauscht werden, um die ursprüngliche Leistung wiederherzustellen. Um haltbarare Katalysatoren zu bauen, ist es daher wichtig mehr über die fundamentalen Prozesse zu lernen die den Katalysator umgeben.

Das Lösen des Puzzles für Methanoxidation

Das Problem für alle Katalysatoren auf einmal zu lösen ist unmöglich. Ein Anfang ist es aber, an einer kleinen Ecke zu puzzeln, aufbauend auf früherer Forschung. Meine ersten Veröffentlichungen widmen sich daher der Oxidation von Methan über einem Palladiumkatalysator. Methan, CH_4, ist ein kleines Molekül welches beispielsweise in Biogas vorkommt. Da es aber auch ein gefährliches Treibhausgas ist, dürfen wir es nicht einfach in die Atmosphäre entlassen sondern müssen es, zum Beispiel durch Oxidation, weiterverwerten.

Um Methan mithilfe von Katalsyatoren zu oxidieren sind drei Schritte nötig. Zuerst landet das Methanmolekül was vorher im Gas herumgeschwirrt ist, auf der Katalysatoroberfläche. Dort spaltet es sich in seine Bestandteile auf, also Kohlenstoff (C) und Wasserstoff (H). Dasselbe Schicksal ereilt Sauerstoff (O_2).

Im nächsten Schritt bewegen sich die Atome frei auf der Oberfläche des Katalysators bis sie schließlich einen Reaktionspartner treffen und, beispielsweise, Sauerstoff und Wasserstoff zu Wasser werden oder Sauerstoff und Kohlenstoff zu Kohlenmonoxid (CO) oder Kohlendioxid (CO_2) reagieren.

Der dritte und letzte Schritt ist dann, dass die frisch geformten Produkte abheben und Platz für eine neue Reaktion frei machen.

Abtauchende Kohlenstoffatome

Es kann allerdings manchmal passieren, dass Kohlenstoffatome sich entscheiden, abzutauchen, insbesondere wenn nicht ausreichend Reaktionspartner an der Oberfläche zu finden sind. Das bedeutet allerdings auch, dass diese abgetauchten Atome nach und nach den Katalysator verstopfen, da sie nicht länger für Reaktionen an der Oberfläche zur Verfügung stehen. Dieser Kohlenstoff-Abtauchprozess ist einer der häufigsten Gründe für das Katalysatorensterben.

Um den Sterbeprozess zu verstehen, können wir einen Film drehen der die verschiedenen Schichten im Katalysator einzeln beleuchtet. Um eine gute Bildqualität zu erhalten, verwenden wir eine extrem starke Lichtquelle, ein sognanntes Synchrotron, sozusagen ein Supermikroskop, um uns diese winzig kleinen Moleküle und ihre Bewegung anzusehen. Die erste Schicht, die wir uns anschauen ist die Gasphase direkt über der Katalysatoroberfläche. Diese Beobachtung lässt uns verstehen, welche Moleküle sich der Oberfläche nähern und welche sich davon entfernen. Daraus können wir auf die katalytische Aktivität schließen und lernen, welche Produkte aus der Reaktion entstehen. Die zweite Schicht die wir beleuchten ist die Katalysatoroberfläche. Hier finden die Dissoziation und Reaktion zu neuen Produkten statt. Die ditte Schicht ist etwas tiefer im Katalysator. Eine Beobachtung der dortigen Aktivitäten ermöglicht es uns das Abtauchen der Kohlenstoffatome zu untersuchen.

Die Kombination der Beobachtungen aus allen diesen Schichten lässt uns dann verstehen, welche Oberflächenprozesse zu welchen Produkten führen und was für einen Effekt das Kohlenstoffabtauchen hat.

Das Problem unscharfer Bilder

Ist es nicht nervig wenn man sich wirklich gerne einen Film anschauen möchte aber der Fernseher nur Rauschen oder unscharfe Bilder zeigt? Dasselbe Problem haben wir mit unseren Filmen der unterschiedlichen Katalysatorschichten. Oft bewegen sich die Moleküle so schnell und sind so klein, dass es sehr schwer ist sie zu beobachten. Wenn wir allerdings diese Moleküle zwingen könnten, immer wieder dieselbe Bewegung auszuführen, dann könnten wir alles herausfiltern was sich nicht entsprechend wiederholt. Das bedeutet, dass alles Rauschen und alle Moleküle die für die Reaktion nicht wichtig sind einfach verschwinden und wir schließlich ein scharfes Bild erhalten welches nur die erwünschten Moleküle enthält!

Für die Experimente bedeutet das, dass wir eine solche wiederholte Bewegung durch periodische Änderungen der Temperatur, des Drucks oder der relativen Konzentration der Moleküle erzwingen können. Der Filter der dann so schön nur die gewünschten Molekülbewegungen übrig lässt nennt sich Fouriertransformation und ist beispielsweise typisch im Auslesen von Radiosignalen.

Die Gestaltung von Superkatalysatoren

Die Beobachtungen wie Katalysatoren sich unter verschiedenen Bedingungen verhalten, wie sie sterben, welche Produkte sie vorziehen oder was an ihrer Oberfläche passiert, können dabei helfen überlegene Katalysatoren zu gestalten. Diese verbesserten Katalysatoren sorgen dann für eine andauernd gute Leistung, geringeren Kosten und einer höheren Effizienz.

Popular science summary in English

Catalysts are widely used to speed up industrial processes, make fertilizer production more efficient, or remove toxic gases from the exhaust of cars. The design of such catalysts has in the past been based on a trial and error approach which is very ineffective. To design advanced catalysts, assembling pieces of knowledge is necessary, resembling the assembly of a puzzle. This licentiate thesis is dedicated to finding one piece of this puzzle, namely the influence of carbon contamination on catalyst activity and selectivity.

Sitting in front of a puzzle on a cozy Sunday night and puzzling just for the fun of it, that is exactly what fundamental scientists do for a living. The results of their research will not directly be used in an industrial application but can rather be seen as a part of a big puzzle. Every bit of research helps to complete the puzzle and is needed for a fundamental understanding of how our world works.

In this thesis, we look not in the deepest corners of fundamental research but rather assemble knowledge of previous, very fundamental studies. Together with somewhat more realistic experiments, I have then investigated how catalysts behave when it's hot or cold, when they get many molecules to catalyze or few, or also what happens when the gas composition in front of the catalyst varies.

Catalysts and their degradation

Catalysts are solid metals that behave similar to a school. In the school yard children meet and interact much more often than on the street. Similarly, when molecules adsorb on the catalyst surface they interact much more frequently with other molecules than in the gas around the catalyst, forming the desired products. In reality this means that less pressure or lower temperatures have to be used to reach a high reaction efficiency which then results in much reduced costs.

One big issue and a huge cost factor in industry is catalyst degradation. One reason for such degradation is the clogging of the material with contaminants. Relating back to the school analogy, sometimes children go into the school building and get lost there. A similar thing can happen to the molecules on the catalyst surface. They can start to dive into the catalyst material, becoming unavailable for reactions at the surface. The more the catalyst is filled with these contaminants, the less efficient for the formation of the desired product it becomes and sometimes it even starts to form new products. At some point in this process, the material has to be exchanged to maintain a sufficiently high efficiency. Therefore, finding out more about the fundamental processes that lead to this degradation can eventually help to build more degradation-resistant catalysts.

Solving the puzzle for methane oxidation

Solving the problem of catalyst degradation is a huge project, however. Thus, a natural start of this project is to start puzzling a small corner, building on all the research done previously. For my first papers, I chose the puzzle of methane oxidation on a palladium metal catalyst. Methane, CH_4, is a very small molecule that is present in biogas, for example. Since it is a dangerous greenhouse gas, it has to be removed from the exhaust after burning bio-fuels, for instance by oxidation using catalysts.

To catalyze the methane oxidation reaction, three steps are necessary. First, a methane molecule which was previously floating around as a gas sticks to the metal surface. Here, it dissociates into its constituent atoms, namely carbon (C) and hydrogen (H). The same happens for oxygen (O_2) which forms atomic oxygen after dissociation on the metal surface.

Secondly, when the atoms move around freely on this surface, an oxygen atom can meet hydrogen, and water is formed. Similarly, if carbon and oxygen meet, some toxic carbon monoxide (CO) and much carbon dioxide (CO_2) are formed.

The third step is then that these newly formed molecules fly away again and open up space on the surface for new methane and oxygen molecules to adsorb.

Scuba diving carbon atoms

Sometimes, however, if not enough oxygen is floating around on the catalyst surface the carbon atoms can "decide" to go diving into the bulk of the material. That means, however, that they are not available for the oxygen atoms anymore which cannot dive and stay at the surface. This process of carbon scuba diving is called coking and is one of the main processes for catalyst degradation since it "clogs up" the catalyst.

To understand the coking process, and thus the degradation of catalysts, we can make a movie where we watch all the molecules that are present in the different layers of the catalyst system. To make this movie, we use a very bright light source, a so-called synchrotron, a super-microscope so to say, to look at these tiny molecules and to study how they behave.

The first layer we study is the gas phase just above the catalyst surface. Monitoring this layer allows to study which molecules move towards the surface and which escape from it. This makes it possible to study how efficient the catalyst is and what the reaction products are.

The second layer to observe is the surface of the catalyst. Here, all the dissociation and reaction to new products happen.

Thirdly, observing some layers deeper in the metal enables researchers to observe the coking. Combining the observations made in all these layers then helps to understand the full coking process and what effects that has on the activity of the catalyst. It can for example be observed that carbon only dives into the catalyst when not enough oxygen is around which it could react with. This often happens at high temperatures or low initial oxygen concentrations. Thus, when designing more performative catalysts for industrial usage, these conditions need to be avoided to prevent fast catalyst degradation.

The problem of blurry movies

Isn't it annoying when you really want to watch a movie but all you can see is static noise or blurry images? We have the same problem with our movies of the different catalyst layers. Often, the molecules that move around are so fast and so tiny that we have a really hard time observing them. But then, we got a great idea! If we could force the molecules to repeatedly behave in the same way we could filter out everything that does not move with the same periodicity. That means that all the noise and all the molecules that don't play a role in our reaction simply vanish and we get a sharp movie of the molecules we do want to observe!

Experimentally that means that we can force the molecules to behave in a certain way by repeatedly changing the temperature, pressure, or relative molecular concentrations. The filter that can then so nicely filter out everything but our desired signal is called Fourier transform and is a common way to analyze for example also radio signals.

Designing super-catalysts

The findings about how catalysts behave under different conditions, how they degrade, which products they prefer, or what happens on their surface can help to design more superior catalysts. These improved catalysts then secure a continuously good performance which results in reduced costs for industry since they do not need to be exchanged as regularly and have an overall much higher efficiency.

Abbreveations

XPS	X-ray Photoelectron Spectroscopy
APXPS	Ambient Pressure X-ray Photoelectron Spectroscopy
tr	time-resolved
MES	Modulation Excitation Spectroscopy
PSD	Phase Sensitive Detection
MFP	Mean Free Path
UHV	Ultra High Vacuum
BE	Binding Energy
DLD	Delayline Detector
AFM	Atomic Force Microscopy
STM	Scanning Tunneling Microscopy
SPM	Scanning Probe Microscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
LEEM	Low Energy Electron Microscopy
(S)XRD	(Surface) X-ray Diffraction
ARPES	Angle Resolved Photoelectron Spectroscopy
XAS	X-ray Absorption Spectroscopy
PEEM	Photoemission Electron Microscopy
DFT	Density Functional Theory
STS	Scanning Tunneling Spectroscopy

Fourier Analysis of Dynamic Catalyst Surfaces - A Time-Resolved Operando Photoemission Study of Catalytic Methane Oxidation

Introduction

Heterogeneous catalysis, in which e.g. gas phase reactions are accelerated by using a solid catalyst, is used in all aspects of life. It finds application in fertilizer production, the car industry, and in batteries. The design of the catalysts used is often based on a trial and error approach which provides sufficient but maybe not optimal performance. To design catalysts that perform optimally, fundamental research on catalytic mechanisms is needed. Such fundamental research can provide an understanding of how different environmental conditions or catalyst structures influence catalytic performance which can then be used to guide the development of superior catalysts.

In recent years it has been found that, even if operated under constant environmental conditions, catalyst often behave not at all the same at all times [1,2,3,4,5]. They are rather dynamic systems whose function can be determined by metastable species [6] or self-induced, periodic concentration fluctuations [7,8,9]. These dynamic properties of the catalyst are not only fundamentally interesting. Also forcing the catalyst to behave dynamically by constantly changing environmental conditions so that the catalyst has to continuously adapt, never reaching equilibrium, yields fascinating results. On the one hand, catalyst activity can increase by doing so [10,11,12], on the other hand interesting behaviors such as programmable selectivity can be unlocked (Paper ii versus Paper iii). For these reasons, dynamic catalysis, which is highly unexplored, is a fascinating field which requires both method development to be able to improve the studies on dynamic catalysis (Paper i) as well as the studies themselves (Paper ii).

Since catalyst dynamics, e.g. activity and selectivity, can depend heavily on the chosen model catalyst and environmental conditions, these variables are carefully introduced before I discuss Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) [13,14,15], the method that is used in this thesis to study the dynamic catalyst changes. This method is used rather than other common surface-sensitive techniques such as Scanning Probe Microscopy (SPM) or Surface X-ray Diffraction (SXRD) since APXPS can probe different catalyst layers such as surface and subsurface region as well as catalytic function, all at the same time. Here, especially the surface and subsurface region of the catalyst are of interest since they are directly affected and, in turn, directly affect the catalytic function as the surface is the interface between the gas and the catalyst bulk. Separate sections are then dedicated to the special challenges of measuring time-resolved operando spectra, something that is crucial for studying the continuous changes of a catalyst. Unfortunately, the signal-to-noise ratio of acquired spectra will decrease with increasing time resolution. Together with the inherently inefficient process of core hole photoelectron generation in APXPS this decreasing signal-to-noise ratio quickly results in tr-APXP spectra not being possible to be analyzed properly anymore.

due to the low phototelectron generation cross section in XPS, the signal-to-noise ratio of acquired spectra will decrease with increasing time resolution. Hence, for studying fast dynamic processes of catalysts, methods need to be developed to face this challenge.

Modulation Excitation Spectroscopy (MES) [16,17,18] periodically modulates environmental conditions while subsequent data analysis schemes aim at isolating the spectral features that oscillate with the same frequency as the excitation, discarding noise. This, naturally, leads to a significantly improved signal-to-noise ratio with which further data processing is possible. Implementing the data acquisition with modulated environmental conditions in APXPS data acquisition together with developing the subsequent analysis tools was a major part of my PhD project so far (see Paper i). Paper ii then includes the application of this newly developed method to the study of the surface, subsurface, and catalytic function of a polycrystalline Pd catalyst during methane oxidation for which the temperature was modulated.

Heterogeneous Catalysis

A very common form of catalysis is heterogeneous catalysis, that is, the catalyst and the material that is to be catalyzed exist in two different phases. For example, the catalyst can be a solid material while the reactants come in liquid or gaseous form. The content of this chapter is based on *Heterogeneous Catalysis* by Schlögl[19] if not stated otherwise.

2.1 Surface-Adsorbate Interactions

When molecules from the liquid or gaseous phase adsorb on the surface, a redistribution of their electron density is observed which leads to weakened intra-molecular bonds. Because of these weakened bonds, the energy needed for molecules to dissociate into their constituent atoms is lowered. These atoms can then move ”freely” across the catalyst surface to meet reaction partners. Thus, moving the reaction from the gas phase to the catalyst surface not only lowers the energy necessary for the reaction to occur, it also much increases the probability of two reactants meeting which then leads to the reaction.

Not all surfaces behave the same, however. Different chemical reactions need different catalysts which can be due to the catalysts electronic properties, the available adsorption sites or also the desired reaction product since different catalysts can exhibit favoritism, so-called selectivity, in the final product.

2.2 Influences on Catalytic Activity and Selectivity

Not only the surface is relevant for determining the catalytic selectivity and overall activity, that is, which and how many product molecules are formed, respectively. Also environmental factors such as temperature and pressure or the gas composition can play a decisive role.

The influence of the catalyst temperature on the reaction rate constant k is exponential and described by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}, \tag{2.1}$$

where A is the temperature-independent pre-exponential factor, E_a the molar activation energy for the reaction, R the universal gas constant, and T the reaction temperature. Multiplying the rate constant with the reactant concentrations provides the reaction rate. For example, the rate of H_2O formation during methane oxidation can be calculated as

$$r_{\mathrm{H_2O}} = k \cdot c_{\mathrm{H}^*}^2 \cdot c_{\mathrm{O}^*} \tag{2.2}$$

where k is the respective rate constant, and c_{H^*} and c_{O^*} the concentrations of H and O atoms on the surface, respectively. The concentration of hydrogen atoms has to be taken into account two times as two H-atoms are needed for the reaction.

The influence of the catalyst on the reaction is usually assumed to be limited to the catalyst surface as this is the interaction area between the catalyst material and the gas phase it is exposed to. It has, however, become more and more recognized in the scientific community that not only the surface but also the subsurface of the catalyst can play an important role for catalytic activity and selectivity. An example for this can be found in Paper ii. The reason why the subsurface can influence catalysis is due to the modification of the surface electron distribution[20] or the adding or removing of additional reaction pathways that involve subsurface processes.

2.3 Dynamic Catalysts

Another, fortunately less and less common, simplification of catalytic systems is the assumption that they are static, i.e., they do not change under reaction conditions. It has, namely, been found in many studies that the catalyst can indeed alter its surface phase, selectivity, or activity over the course of various time scales[1,2,3]. That is, even if the catalyst is operated under constant environmental conditions, it is the dynamic nature of the catalyst that determines how it functions. This is of great interest to many fundamental researchers since an entirely new variable possibly affecting catalytic function can be explored. An especially interesting phenomenon that has been found along these lines are self-sustained oscillations during which the catalyst, affected by metastable species, periodically modulates the catalytic rate for example during methane dry reforming over Ni[6] or H_2 oxidation over supported Rh particles[21]. Another dynamic feature that has been found were the spatio-temporal waves that move across the surface of a Pt single crystal during CO oxidation[5]

But it is not only this inherently dynamic nature of catalysts that opens up a new area in catalysis research. Several studies could even find that keeping a catalyst at off-equilibrium conditions, i.e., changing environmental conditions so fast that the catalyst never reaches equilibrium, can actually enhance catalytic activity[11,12] for example during water oxidation over perovskites[10]. This possibly holds an enormous potential for industrial applications and should, thus, definitely be explored in more detail.

To study the dynamic nature of catalysts and explore these interesting new catalytic features, time-resolved studies become necessary that are able to capture the process of interest. Since these dynamic processes can happen on various time-scales it is essential to tailor the time resolution to for instance, elementary reaction steps that are expected to happen within femtoseconds (1×10^{-15} s)[22,23], molecular transport within microseconds (1×10^{-6} s)[22], and surface restructuring within milliseconds (1×10^{-3} s)[19,22,23] to seconds (1 s)[22,23]. There are, however, also processes that are expected to last even longer such as self-sustained oscillations of the catalyst on the order of minutes[9,24] or catalyst degradation on the order of minutes[7,24] to years.

The Choice of Catalyst

It is not only the chosen element in the periodic table that influences the activity and selectivity of a catalyst but also its structure. In surface science, the traditional choice of structure is a single crystal surface for the simple reason that it is much easier to control and understand than more complex structures. In industry, however, catalysts of a more complex structure are used. This discrepancy between surface science and industry is commonly referred to as the materials gap[19,25,26,27] as the findings from surface science cannot be reliably used in industry. The following sections will introduce the model catalysts that are used in the projects during this thesis and that are some of the most common model catalysts such as single crystals, alloys, polycrystals, and nanoparticles. Other model catalysts are for example curved crystals[28,29,30] or inverse model catalysts[31,32,33].

In Fig. 3.1 a sketch of a real catalyst is shown on top together with the below discussed model catalysts and which aspect of the real catalyst they are attempting to mimic. Here, the real catalyst consists of an active material of different elements (purple) deposited on a porous oxide support (grey).

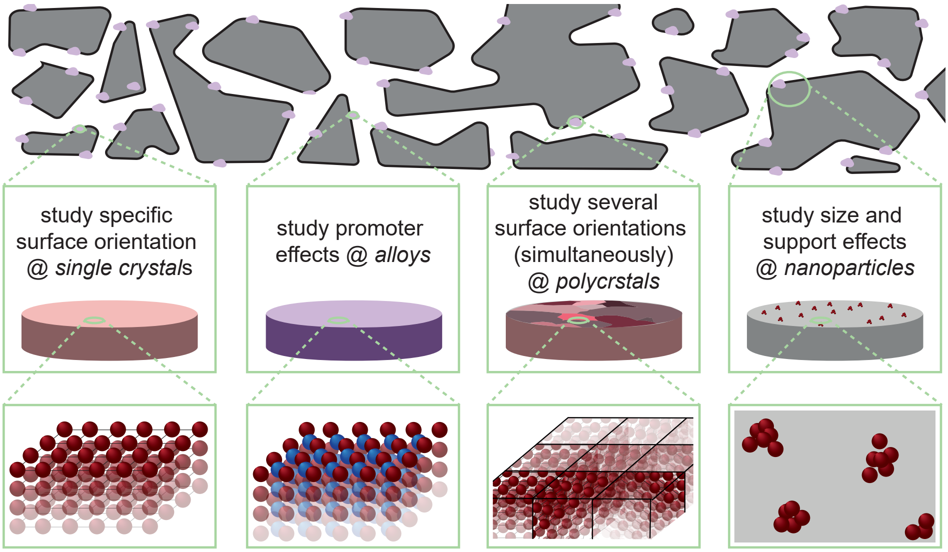

Figure 3.1: The model catalysts in this thesis and the aspect of the real catalyst they are mimicing: single crystals, alloys, polycrystals, or nanoparticles.

The development from more simplistic to more realistic model catalysts is accompanied by a development in measurement technology since different samples have different requirements as will be introduced in the following sections.

3.1 Single Crystals

The most extreme simplification of a real catalyst is that to a single crystal. A single crystal is a material with a perfectly periodic crystal structure without any grain boundaries or defects. When this crystal is cut in a certain fashion, so-called single crystal surfaces emerge that have a well-known electronic and geometric structure. Depending on how the crystal is cut, different electronic and geometric structures can be obtained leading to varying catalytic properties. To compare different catalyst surfaces a naming convention is used, so-called Miller indices, that describe the way the crystal was cut.

Single crystals are often used to understand the fundamental processes of a catalytic reaction or to understand what effect a certain element has on a given reaction. Examples of this are the study of kinetic hysteresis during methane oxidation over Pd(111)[34] or of the active phase of Pd during methane oxidation[35]. On single crystals, sometimes (ultra-)thin films are grown which can be classified as a separate catalytic system. A prominent example is the formation of oxide layers during the oxidation of reactants such as methane[34,35]. In this thesis, single crystal model catalysts were used in the Papers v and vi.

For the study of single crystals, the choice of a suitable measurement technique is mainly based on the catalyst's elemental properties. As the almost infinite surface area is assumed to behave in a uniform fashion, no requirements on measurement probing area exist. Depending on the selected measurement technique, the sample has to be conductive, however, or has to be cooled down to very low temperatures such as 30 K. As the surface is atomically flat, most microscopic measurements are possible.

3.2 Alloys

A model catalyst that is mainly focused on modeling the interaction between two or more different active elements, i.e., where two elements partake in the catalytic reaction, is the alloy. Also in real systems, catalytic function is often improved by adding so-called promoter materials. These elements can change the electronic structure, enhance or block adsorption of certain species, and, therefore, change the catalytic activity and selectivity[36]. Examples of this are voluntary alloying such as in Pt-Pd alloys that are used for hydrogen peroxide synthesis[37] or diesel oxidation[38], or involuntary alloying during the deposition of contaminants such as carbon[20,39,40,41,42] or sulfur[43,44,45]. Of course, alloys can occur in all of the available model catalysts: as single crystals (see Paper vii), polycrystals, or nanoparticles as well as many more.

3.3 Polycrystals

As the spatial resolution possible with surface-sensitive techniques improved, increasingly small structures could be studied and their individual catalytic function resolved. One model catalyst that profited from this development was the polycrystal. As the name already suggests, these model catalysts do not just include one crystallographic orientation but several. One can imagine this catalyst as many single crystals with different surface orientations glued together into one big catalyst as shown in Fig. 3.1. The advantage of this system is that the catalytic response of several different surface orientations can be studied under the same reaction conditions and at the same time. This is interesting as industrial catalysts expose many different surface orientations to the gas feed at the same time, thus, an understanding of how the different surfaces affect each other is crucial. The grain size, i.e., how much of a certain surface orientation is exposed, can vary from one polycrystal to the other. Polycrystals for surface science studies have grain sizes on the order of 2 mm by 2 mm[46,47] but the size can decrease so much until the material could be called amorphous (see Paper ii, iii) instead of crystalline. In the latter case, the term ”powder” is often used to describe the catalyst instead. Examples for studies on catalysis on polycrystals are the discussion of CO oxidation over Pd[47], electrocatalysis on Au[46] or oxidation reactions over RuO_2[48].

Naturally, the size of the grain affects the maximum possible probing size of the selected measurement technique which has to be smaller than a single grain to resolve its individual catalytic behavior.

3.4 Nanoparticles

A model catalyst that mimics a large part of real catalytic systems are nanoparticles. With them as model, both the small size of active material clusters and the metal-support-interaction can be studied. The reason why nanoparticle catalysts are so attractive for industry is because they maximize the exposed surface area while minimizing the amount of unused material by shrinking the bulk size until basically every catalytically active atom is located at the surface. Like this, the catalytic turnover per total amount of active material can be maximized.

A common problem with these model catalysts is that they are deposited on oxide supports which are non-conductive. Thus, any form of measurement technique that requires conducting samples is very challenging to apply to these catalysts.

Since nanoparticles are so small, the different exposed surface orientations affect each other intensely but also other interesting effects such as limited diffusion make this a fundamentally interesting system to study[49]. As an example, there exist reviews that focus on synergic effects over bimetallic nanoparticles[50], catalysis over Au nanoparticles[51] or the mechnanistic understanding of nanoparticle catalysis[52].

In order to study all these different model catalysts and satisfy the necessary requirements, different techniques have to be selected. The method used for the studies in this thesis is X-ray Photoelectron Spectroscopy (XPS) which requires conductive samples but provides rather small probing areas. Additional to XPS, some other techniques that can be used for the study of catalysis are introduced in the next section.

X-ray Photoelectron Spectroscopy

Directly observing catalyst surfaces, their activity, selectivity, periodicity, or stability is crucial for the understanding of catalytic reaction mechanism. X-ray Photoelectron Spectroscopy (XPS) focuses on determining the chemical composition of the catalyst surface and its near-surface-region. Details on, for example, the quantum mechanical background of XPS can be found in Hüfner[53].

4.1 The Photoelectric Effect

XPS relies on the photoelectric effect in which impinging photons of sufficiently high energy release so-called photoelectrons from the material. If X-rays are chosen for the excitation, sufficient energy is transferred to the material so that electrons from so-called core levels can be excited. With some simplifications, a direct relationship can be found between the electron kinetic energy (E_{kin}) just before exiting the material and the energy of the incoming light ($h\nu$):

$$h\nu = E_{bin} + E_{kin} \tag{4.3}$$

where E_{bin} is the binding energy of the electron. If E_{kin} is measured in an electron analyzer, sample work function and analyzer work function have to be taken into account additionally.

4.2 Electrons as Probes

Many surface-sensitive techniques use electrons as probes for the various surface properties. The reason for this is that, if they have the right kinetic energy, their mean free path (MFP) in matter is rather short. That means that all electrons that are detected must stem from the topmost surface layers. All electrons that originate from deeper catalyst layers undergo scattering and are either detected with different energies than they initially had or are absorbed within the material. Due to the short electron MFP, however, these measurements have to be done in low pressure environments ($p < 1 \times 10^{-4}$ mbar) as too many electrons would otherwise scatter with gas phase molecules.

The advantage with the short MFP is that it is universal for all metals. For this reason, the relationship between MFP and electron kinetic energy is often referred to as "universal curve" and is shown in Fig. 4.2.

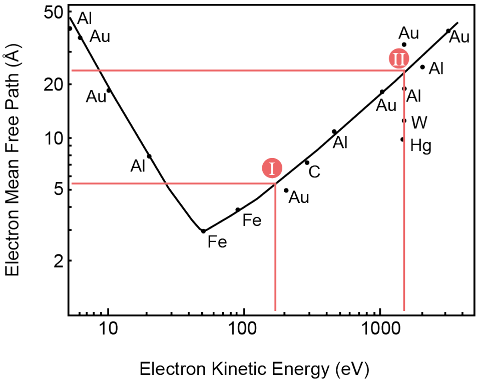

Figure 4.2: The electron mean free path in all metals as a function of the electron kinetic energy. Adapted from Hüfner[53].

This relationship can also be used to change the surface-sensitivity of the measurement, meaning that a change in electron kinetic energy, by changing the photon energy (see eq. 4.3), will lead to a change in the MFP. Hence, the measured signal will originate also from layers deeper in the crystal for a higher electron kinetic energy. The conscious choice of electron kinetic energy to probe deeper catalyst layers is called depth-profiling. This was used in Paper ii to measure the catalyst surface (chose Point I in Fig. 4.2 for measurement) and its subsurface (chose Point II).

4.3 X-rays as Signal Source

Traditionally, the X-rays necessary for XPS are generated in lab sources that utilize the elemental transitions of specific materials such as aluminum or magnesium resulting in X-ray energies of 1486.6 eV (Al Kα) and 1253.6 eV (Mg Kα). With this method, the generated X-rays have a fixed energy, which is why depth-profiling is only possible to a limited extend.

Another X-ray source is a so-called synchrotron. At the MAX IV Laboratory for instance, electrons are accelerated in two steps up to 1.5 GeV and 3 GeV, almost the speed of light. At these points, they are led onto a circular path (into a storage ring) in which their kinetic energy is preserved. For the generation of X-rays, a magnetic array is placed around a section in this circular path. Due to their charged nature, the electrons are forced onto a slalom path through the gap of the poles of the magnetic array. Accelerated, charged particles loose energy in the form of radiation, the energy of which depends on the magnitude of the acceleration. For the electron energies commonly used in these storage rings, the emitted radiation is classified as X-rays. Depending on the length and the field strength of the magnets in the array, different X-ray energies are obtained. Within a certain range, however, changing the gap between the magnetic poles of the array, and hence the strength of the magnetic field, the energy of the emitted radiation can be changed and precise selection of X-ray energy, and, thus, depth-profiling, becomes possible. The emitted radiation is, however, not of an entirely uniform wavelength. For this reason, so-called beamlines are build that focus with the help of mirrors, select a single X-ray energy with the use of monochromators, and cut the beam size while directing the X-rays from the magnetic array to the experiment. The resulting beam spot size on the sample is then at the order of $100\,\mu\mathrm{m} \times 25\,\mu\mathrm{m}$ at the HIPPIE beamline[54] located at the 3 GeV ring of the MAX IV Laboratory, where the experiments in this thesis are carried out. Photon energies between 250 eV and 2200 eV are accessible at HIPPIE. SPECIES[55], an XPS beamline at the 1.5 GeV ring has access to photon energies between 27 eV and 1500 eV.

This small beam spot size stands in contrast to the large photon emission angle of lab sources with which no spatially resolved measurements are possible. Additionally, the X-ray flux is much higher at a synchrotron (a factor 100 if not more).

4.4 The Electron Analyzer

To measure the photoelectrons that are emitted from the catalyst after being excited by an X-ray photon, an electron analyzer is needed. Different analyzer types exist, one of which is shown in Fig. 4.3, the so-called hemispherical analyzer. First, the photoelectrons are collected by a nozzle leading to the analyzer itself. In the next step, the electrons are slowed down by a so-called retardation voltage until the electrons of a desired binding energy region reach the so-called pass energy at the entrance of the analyzer. This pass energy, often 50 eV, 100 eV, or 200 eV, defines the displayable energy range at the detector (ca. 10% of the pass energy) and, as a result, the maximum energy resolution.

The analyzer itself consists of two hemispherical plates between which a voltage is applied. This voltage leads to a bending in the electron path which depends on the electron kinetic energy. Faster electrons bend less while slower electrons bend more. Finally, the electrons of the desired kinetic energy hit the center of the detector, first impinging on a Microchannel Plate (MCP). Here, they pass through small channels in the plate, being amplified with an avalanche mechanism, until they hit a phosphorescent screen, an event which is recorded by a camera. Delayline detectors (DLD), another increasingly common detector setup in XPS, consist instead of a net of orthogonal wires, also located behind a multichannel plate to increase the electron count. When an electron impinges on this net, an electrical signal travels along the wires and time-of-flight calculations reconstruct the location and exact timing of the incident.

Even though the detector records spectra as a function of the electron kinetic energy, the axis can easily be transformed to a binding energy axis via the photoelectric equation (eq. 4.3).

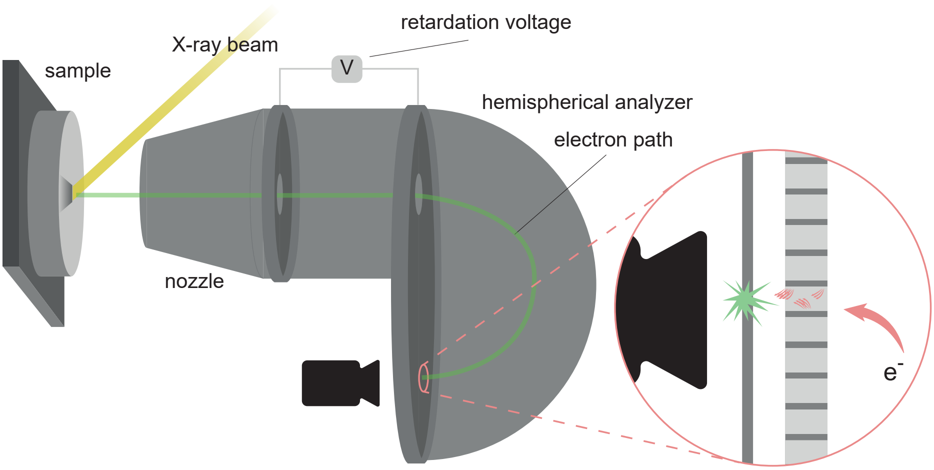

Figure 4.3: Schematic of the XPS measurement setup.

4.5 Core Levels and Chemical Sensitivity

An atom can be described by its orbitals, for instance, the electron configuration for carbon is $1s^2 2s^2 2p^2$. This means that carbon has two core electrons (1s) and 4 valence electrons (two in 2s and two in 2p). While valence electrons strongly participate in chemical bonding, core electrons remain largely unaffected by changing chemical environments. For each atom, all of the electrons in its constituent orbitals can be measured with Photoelectron Spectroscopy at the respective binding energy. Thus, for carbon one could measure the C 1s core level electrons, or the C 2s or C 2p valence electrons. The choice of measured orbital depends on several factors such as photoemission cross section, accessible photon energy, peak width, and if the desired region is crowded by peaks of other species.

The advantage with doing core-level spectroscopy is that, since core level electrons do not participate in chemical bonding, their energy levels remain largely unchanged and, thus, unique to the probed element. In XPS, if a survey scan is done, i.e., all binding energies between 0 eV and, for example, 800 eV are measured, characteristic fingerprints of all elements present at the surface can be found. An example for such a survey of a palladium surface with carbon contaminations is shown in Fig. 4.4. The fingerprints of Pd (detection of 3s, 3p, 3d, 4s, and 4p electrons) and C (1s and 2s) can be seen as well as the valence electrons. The peaks that are measured but not assigned are not an indication of an additional species but originate rather also from Pd and C and a different photoemission process (Auger effect). Another prominent effect that can be observed in Fig. 4.4 is that of secondary electron generation. Going from low to high binding energies, the background increases, especially after high peaks. The reason for this are secondary electrons, that is, electrons that originate from the excitation of the same core level as the peak but that undergo scattering events on the way to the electron analyzer and, as a result, loose a fraction of their energy. At even higher binding energies (not shown in the Figure) the number of detected secondaries increases significantly.

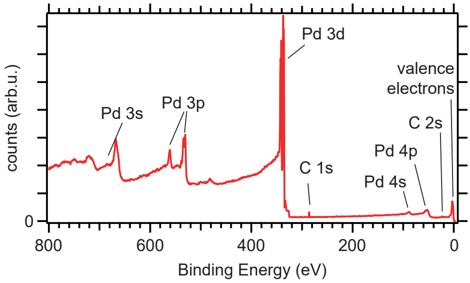

Figure 4.4: Example of a survey scan of a palladium crystal with carbon contaminations.

In valence band spectroscopy, it is much harder to assign measured peaks to certain elements since the binding energies can vary dramatically depending on the chemical environment.

Even though the core level electrons do not participate in chemical bonding, which is why their binding energies can be used as chemical fingerprints for the various elements, their binding energy is altered slightly by the changing electric potential due to the chemical environment. If this change in chemical environment is due to bond formation, the slight alteration in binding energy is termed "chemical shift" and allows us to differentiate in XP spectra between a carbon atom that sits in a CO molecule and one that sits in CO_2, for instance. Another common change in chemical environment is when a fully coordinated bulk atom turns into an under-coordinated surface atom. Then, the binding energy change due to the different chemical environment is termed ”surface shift”. This allows, for example to determine whether a C atom is located at the catalyst surface or in deeper catalyst layers.

After having discussed the binding energy of the measured peaks, one might wonder why the peaks even have a width and are not just sharp. The reason for this is manifold. One aspect is the finite lifetime of the core hole that originates from the photoelectron excitation, so-called lifetime broadening. Another is the energy profile of the photon beam used for the photoexcitation as well as the properties of the electron analyzer, so-called instrumental broadening. The peak intensity also depends on several factors. One naturally being the amount of the species probed but also the photoelectron cross section of the atom can play a (minor) role.

4.6 Ex-Situ, In-Situ, and Operando Time-Resolved Measurements

Conventionally, XPS measurements are often done in an ex-situ fashion. This means that the catalyst is exposed to a reaction environment, then extracted from it and characterized. This approach is based on the assumption that the catalyst does not change during the transfer from reaction conditions to UHV under which the measurement must be carried out.

This assumption is not always valid, however, which results in the necessity to characterize the sample under reaction conditions, leading to so-called in-situ measurements. Still, the reaction environment used here is often far from realistic conditions. Operando measurements bridge this last gap and characterize a working catalyst under (close-to) realistic conditions.

As was mentioned before in the section about dynamic catalysts, we expect continuous changes of the catalyst structure and its activity on various time scales under reaction conditions. Thus, characterizing a catalyst in its reaction environment is not enough, time-resolved measurements become necessary to capture the dynamic catalytic nature. These time-resolved measurements of the catalytic process are rather new and a special focus of this thesis’ work.

Such time-resolved in-situ or operando measurements result, however, in additional challenges for the analyzer. Especially if catalyst changes are expected on short timescales, XPS spectra need to be acquired fast. If a measurement with a phosphorescent screen and a camera is to be done in a time-resolved manner, the maximum spectrum acquisiton frequency is determined by the speed of the readout electronics of the camera and lies on the order of 8 Hz to 16 Hz. For Delayline detectors, the data acquisition is fast since it is only dependent on the travel of an electrical signal through a short wire, resulting in a maximum spectrum acquisition frequency of about 10 MHz.

4.7 Swept and Snapshot Measurements

Fundamentally, there are two different ways of using the electron analyzer to measure XPS spectra, namely swept and snapshot measurements.

Swept measurements are the more traditional way of measuring. Here, the analyzer's retarding voltage is *swept* so that all kinetic energies of interest can be measured at all points on the detector. This has the advantage that possible differences in sensitivity at different parts of the detector are averaged out. The disadvantage, however, is that this way of measuring is rather slow, sepctra are usually not measured in under 5 s. For time-resolved measurements that require a high time resolution, one, thus, often chooses snapshot measurements.

The name "snapshot" refers to the fact that the analyzer retarding voltage is kept constant while a snapshot of the analyzer is taken. This leads to a distorted spectrum since the differences in analyzer sensitivity are not accounted for. It is, however, a rather fast way to measure and the distorted spectrum can be calibrated afterwards. The calibration can be done by measuring a snapshot spectrum and a swept spectrum of the same binding energy region directly after each other and then dividing the two by each other. That results in the so-called detector transmission function which is a description of the detector sensitivity for that binding energy region. All snapshot spectra measured in that binding energy region can then later-on be divided by the detector transmission function, and, thus, intensity-calibrated. The disadvantage with this way of measuring is that, due to the fixed analyzer retardation voltage, only 10% of the pass energy can be measured on the detector. Thus, larger binding energy ranges need to be sliced up and measured in several, separate measurements.

An additional way of measuring time-resolved spectra has recently been developed and allows for the fast acquisition of swept measurements. This works only by including a pump-probe scheme, however. That means that, at a fixed analyzer retardation voltage, spectra are acquired for many pulses (of gas or the like) while always measuring a spectrum with respect to the last trigger signal that came from a beginning pulse. Thus, the spectra are internally event averaged. Then, the analyzer retardation voltage is increased slightly and the procedure is repeated, slowly building up swept measurements of the entire binding energy region. In reality, the analyzer retardation voltage is never static but slowly sweeps through the desired values. Compared to the very rapid pulses, it can however be approximated as static during one spectrum acquisition. This way of measuring requires defined pulses with a trigger signal but produces a rather good data quality.

More details on these different ways of measuring and scientific examples can be found in Paper viii.

4.8 Data Analysis and Curve Fitting

After the acquisition of spectra, the measured photoelectron kinetic energies need to be translated into binding energies (BEs) with the photoelectric equation since the BEs are independent of the photon energy used and characteristic for the elements. During this translation, small errors in the assumed photon energy can introduce errors in the BE axis that need to be corrected for[56]. This calibration is done by measuring the signal cutoff at 0 eV binding energy, the so-called Fermi edge. If this is not located at exactly that binding energy, the whole axis is offset until the Fermi edge is at 0 eV.

The next step in the pre-treatment is the removal of the intensity of secondary electrons. As explained earlier, they stem from inelastically scattered photoelectrons and belong, therefore, not to the peak that is to be analyzed. Several methods of background description exist, the two most common being the Shirely and the polynomial background.

Then, data processing can begin via curve fitting. That means a theoretical peak shape is adapted by an algorithm so that it fits the measured spectra. Several different theoretical peak shapes exist that are designed to approximate the physical curve shape. Probably the simplest approximation is done by the Gaussian function. Here, peak width, intensity, and BE are varied until the model fits the raw data. Another common curve shape is the Doniach-Sunjic model which calculates the curve shape of asymmetric metallic peaks by fitting BE, width, intensity, and asymmetry factor. A third, often used, curve shape is the so-called Voigt profile, a convolution of a Lorentzian (due to lifetime broadening) and Gaussian function (due to instrumental broadening) which is used for all fits in this thesis. Here, BE, width, intensity, Gaussian, and Lorentzian width are varied to fit the raw data. To limit the computational strain of the fit, a Pseudo Voigt is often used which analytically approximates the shape of the otherwise only numerically solvable convolution. By using two Pseudo Voigt functions with different widths that are merged at the BE, asymmetric peaks can be modeled.

For the large time-resolved data sets in this thesis that can contain up to 16000 spectra, fitting BE, Gaussian width, Lorentzian width, and intensity for every single one of the sometimes five peaks contained in one spectrum is just not feasible. Instead, many of these fit parameters, such as Gaussian and Lorentzian[57] width as well as the BE of surface peaks, are determined by using either the time average of all spectra or the first time-resolved spectrum. If vibrational splitting (e.g. CH_4) or spin-orbit splitting of components (e.g. O_2) is observed, the peak ratios are determined as well. For the fit of all other time-resolved spectra, these components are kept fixed and only the peak intensity or gas phase peak BE are adapted from spectrum to spectrum. With all these parameters fixed, the fits to a single spectrum in a time-resolved dataset might naturally not be perfect (see Fig. 4.5) but good enough considering the compromise with computational effort.

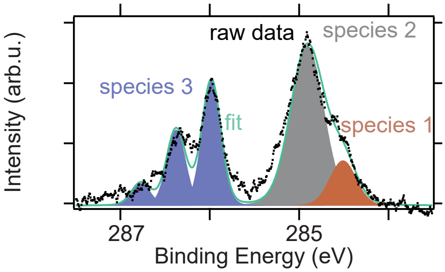

Figure 4.5: Examples of curve fitting to C 1s data within a time-resolved measurement. The figure is adapted from Paper ii.

After the fit of time-resolved data, often the intensity evolution over time of a certain species is further analyzed and discussed.

4.9 Other Techniques for the Study of Catalysis

XPS is a rather inefficient technique due to the low photelectron generation cross section and the large fraction of secondary electron generated as compared to unscattered core-hole electrons. Additionally, XPS, as any other technique, can only provide limited information about the studied system. Thus, often a combination of different techniques is used to obtain a full understanding of the catalyst and its function, as for instance done by Zaera et al.[58].

Microscopy techniques such as Atomic Force Microscopy (AFM)[59,60], Scanning Tunneling Microscopy (STM)[59,60], Scanning Electron Microscopy (SEM)[61,62], Transmission Electron Microscopy (TEM)[59,63], or Low Energy Electron Microscopy (LEEM)[64,65] are used to image the electronic or geometrical surface structure of the catalyst, often even with atomic resolution. Due to the high signal strength, images of the surface can be acquired fast (ca. 20 Hz[23]) and dynamic changes can be followed. Unfortunately, some of these microscopy techniques (e.g. AFM and STM) require atomically flat surfaces. Thus, only very specific model catalysts can be studied. Additionally, few of the techniques allow for elevated pressures or sample temperatures that are often necessary for operando catalysis studies.

Information about the surface or bulk periodicity can be obtained by Surface X-ray Diffraction (SXRD)[66,67] or X-ray diffraction (XRD)[61], respectively. The acquisition of a full dataset is, however, rather slow for these methods which is why it becomes difficult to follow fast structural changes of the catalyst. These diffraction methods require a periodic crystal or surface structure, thus, only single crystal[66,67] or polycrystal catalysts with large grains[68] are feasible models.

Angle-resolved Photoemission Spectroscopy (ARPES) can provide further information on the electronic band structure which is especially interesting for understanding how surface reactions affect the electronic structure of the catalyst[69,70]. Spectra acquisition in ARPES can be rather fast so that catalyst surface restructuring can be followed. However, since this method is based on the photoelectric effect, just as XPS, inefficient signal generation can be an issue. A requirement for ARPES studies is that the studied sample is conductive or a semiconductor which excludes many thick oxides.

Often, the chemical composition of the surface is of interest, something that can be studied with X-ray Absorption Spectroscopy (XAS) which is especially sensitive to chemical bonds between species[71,72] and their geometrical proximity but does require conductive samples. Even though spectra acquisition has become faster in the last decade, scanning across the entire absorption edge is a rather slow process and it is, therefore, only possible to follow slow surface restructuring. Another method that can determine the chemical composition of the surface is Photoemission Electron Microscopy (PEEM)[64].

All of these experimental techniques can be complemented by theoretical modeling, e.g. Density Functional Theory (DFT)[20,70].

Ambient Pressure X-ray Photoelectron Spectroscopy

It is not only the choice of catalyst structure and material that differs between surface science and industrial applications. Also the pressure to which the catalyst is exposed can be different by a factor of up to 10^{14}, from UHV (1×10^{-9} mbar) in surface science to 100 bar in industry, a discrepancy often titled pressure gap[19,25,27,73]. Naturally, the reaction mechanism observed at UHV conditions can differ significantly from that observed at high pressures and it is, therefore, crucial that we try to bridge the gap.

Simply increasing the pressure of the reaction studied with XPS is no solution, however. As gases are introduced in front of the sample and the pressure rises, more and more photoelectrons scatter and never reach the analyzer. For example, already at 1 mbar the mean free path decreases down to 1 mm which is much shorter than the sample-to-detector distance of about 1 m. Additionally, the detector needs to be remain in a low pressure environment ($p < 1 \times 10^{-5}$ mbar) due to the high voltages that are applied there. Developments of the past two decades have, however, made it possible to measure X-ray Photoelectron spectra at pressures up to several mbar, in one special setup even at 1 bar[74], almost reaching industrial conditions.

The most important technical advances that made such high pressure measurements possible are described in the following sections. Further details can be found in the works of Hüfner, Ogletree, Cai, Edwards, and Bluhm[14,53,75,76,77]. More details on time-resolved measurements can be found in the works of Shavorskiy *et al.*[78,79,80].

5.1 Differential Pumping and Electrostatic Lenses

The fact that XPS measurements at high pressures became possible is mainly thanks to differential pumping in the pre-lens. This means that several stages with powerful pumps are passed by the electrons on their way from the sample to the hemisphere (see Fig. 5.6). During each of these pumping stages, the pressure is reduced by roughly a factor 1000, especially in the first stage from the sample into the nozzle, so that the electrons can reach the detector before undergoing a scattering event. Still, many electrons are lost due to scattering in the gas, decreasing the measured signal drastically. To enhance the signal quality, electrostatic lenses are added to each differential pumping stage. These focus the electrons onto the apertures between the pumping stages reducing the number of electrons lost in the pre-lens and, therefore, increasing the analyzer acceptance angle[14].

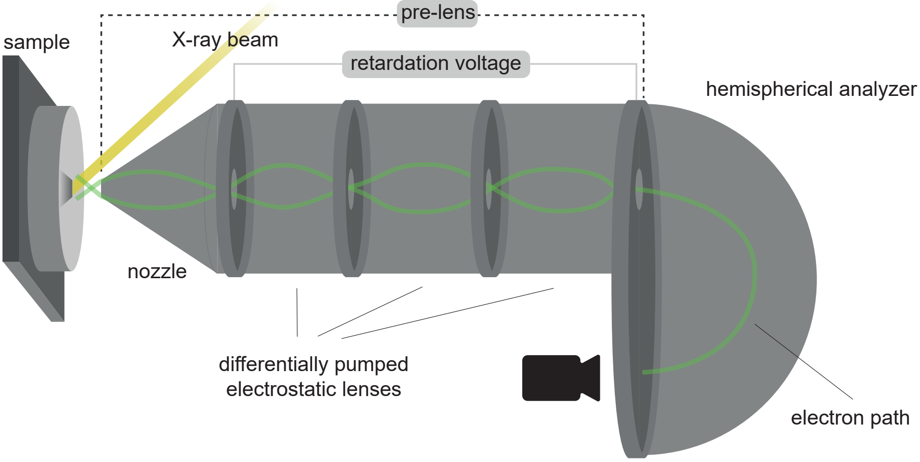

Figure 5.6: The differential pumping of the electrostatic lenses focusing the electrons on their way from the sample to the analyzer.

Due to the large pressure gradient between the differential pumping stages, a lot of gas (several ml per minute) is ”sucked” through the holes between two neighboring stages. That also applies to the first pumping stage, i.e., between the sample and the first electorstatic lens. To minimize the amount of gas that is sucked into the pre-lens and away from the sample, several measures can be taken. First, the nozzle opening should be kept small though this is a compromise between electron transmission and gas transfer, nozzle openings of around 300 µm are common. Second, the pressure gradient between both sides of the aperture should not be too high, i.e., the first pumping stage cannot be equipped with too powerful pumps. Then, to maintain an almost homogeneous pressure landscape across the sample the nozzle is typically positioned at a distance of two times its opening from the sample. For a common nozzle opening diameter of 300 µm that leads to a sample-nozzle distance of 600 µm.

Not only the analyzer needs to be modified to adjust to the increased pressures, also the sample environment needs control. This control can be realized by so-called cells, little chambers in which the sample and its controlled environment are located.

5.2 Ambient Pressure Cells

Depending on the requirements on the sample environment different cell designs are chosen to accommodate these. For example, the HIPPIE and SPECIES beamlines at the MAX IV Laboratory in Lund use the cell-in-cell approach during which a small ambient pressure cell is placed inside a larger UHV cell enabling the researcher to do both ambient pressure and UHV measurements. Other setups can be to place the sample in a large chamber (an example is the electrochemistry branch at HIPPIE), or to use many small, exchangable cells[15].

During the experiments in this thesis, we rely heavily on quick gas exchange times in front of the sample as well as quick temperature adaptations on the order of milliseconds to seconds. To achieve the first requirement, a small ambient pressure cell of approximately 0.5 L in volume is chosen while the gases are introduced into the cell by two gas pipes next to the nozzle, pointing towards the sample (HIPPIE beamline at MAX IV[54], Fig. 5.7 (A)). Another possibility is a double-cone design in which the gases are pre-mixed and blown towards the sample within the cone (SPECIES beamline at MAX IV[55], Fig. 5.7 (B)). To achieve highly controlled gas changes with these setups, the gas lines can be equipped with piezoelectrically controlled valves that are placed behind the usual mass flow controls (MFCs), gas cleaners, and gas bottles. Relying on the MFCs alone, gas exchanges are on the order of several seconds while piezo valves can reach gas exchanges within 10 ms.

To achieve quick temperature adaptations, the HIPPIE beamline uses an infrared laser which hits the back of the sample (Fig. 5.7 (A)). With this method a heating rate of larger than $10\,^{\circ}\mathrm{C\,s^{-1}}$ can be achieved. SPECIES, on the other hand, is equipped with resistive heating, i.e., the resistive heat that electrons generate in a wire heats the back of the sample (Fig. 5.7 (B)). This type of heating is usually slow in the beginning of the heating process and increases then in heating rate.

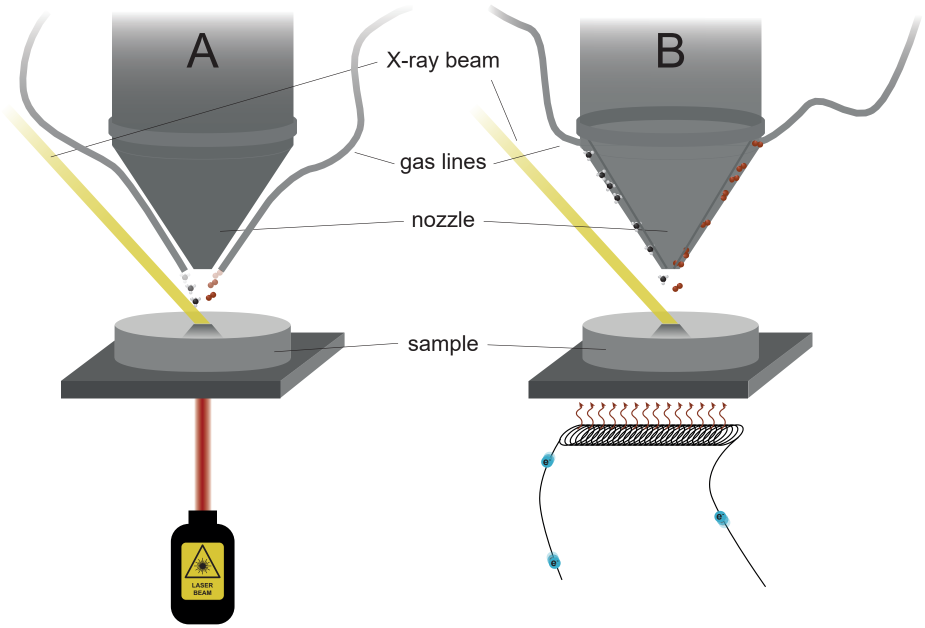

Figure 5.7: The different gas dosing and heating techniques used at the HIPPIE (A) and the SPECIES (B) beamline at the MAX IV Laboratory.

5.3 Measurements of the Catalyst Surface, Subsurface, Catalytic Activity, and Selectivity

To relate the catalyst chemical structure to its activity and selectivity the time evolution of the catalyst subsurface, its surface, and the gas phase just above the surface need to be measured. Commonly in catalysis research, only the relationship between the catalyst surface and the catalytic function is discussed. As shown in Paper ii, however, even the subsurface can play an important role and should, therefore, not be neglected here.

As discussed earlier, the optimum sample position is at a distance of 600 µm from the analyzer nozzle. For SCIENTA analyzer systems, the focus of the electrostatic lenses is placed here, leading to a maximum electron transmission. For this reason, that point is also selected as the volume in which the X-ray beam and the analyzer acceptance volume intersect. With this sample position relative to the analyzer, a maximum surface signal is measured together with small contributions of the gas phase just above it (see Fig. 5.8 (A)). Depending on the chosen photon energy, as discussed earlier, the measurement can include either only the topmost surface layers or probe deeper into the bulk. An example of a surface snapshot spectrum measured in the O 1s region is shown in Fig. 5.8 (B) including a large background of secondary electrons that result from scattering events in the crystal. In such cases, polynomial background models can be subtracted from the data to make it analyzable (see Fig. 5.8 (C)).

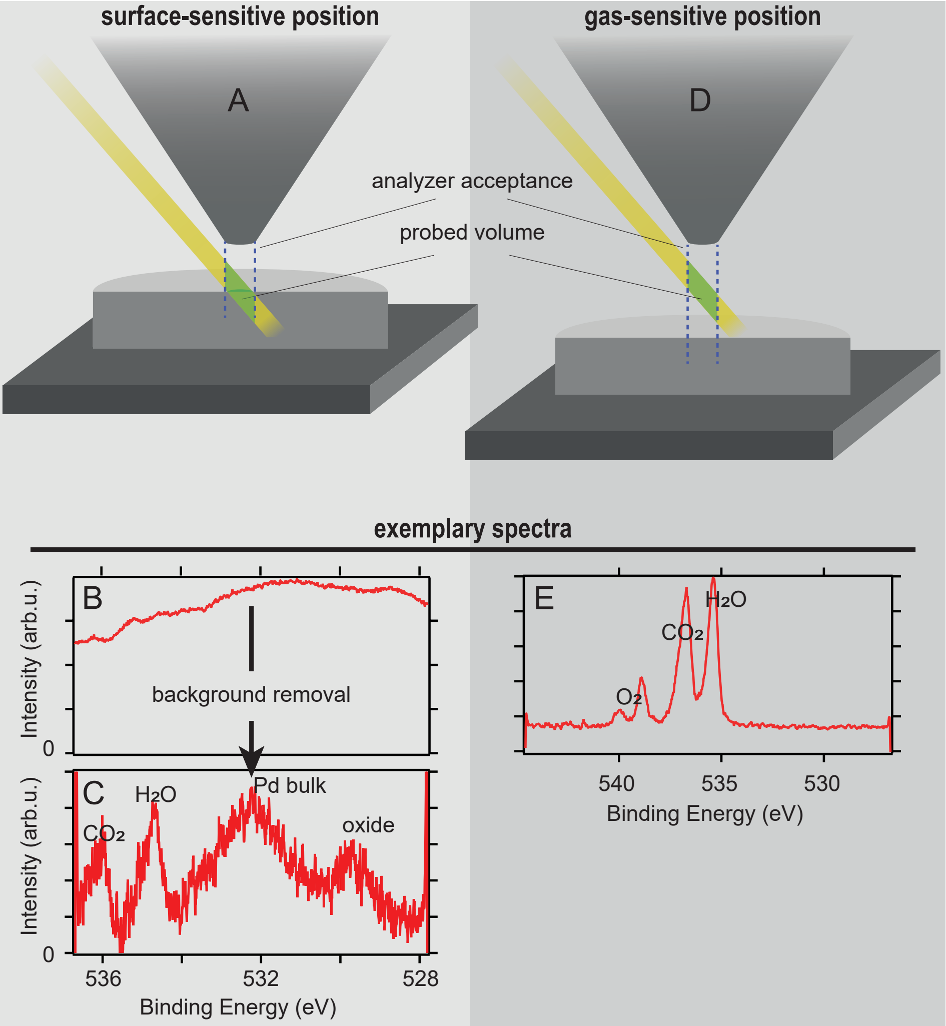

Figure 5.8: The different sample-to-analyzer distances with the respective probing volume for surface-sensitive (A) and gas-sensitive (D) measurements and corresponding exemplary spectra.

If, then, the sample-to-analyzer distance is increased by additionally 300 µm the sample moves out of the X-ray beam and the gas phase is measured instead (see Panel (D,E)). In this position, the weak gas phase signal (see CO_2 and H_2O in Panel (B) and (C)) picked up in the surface sensitive measurements is maximized (see Panel

(E)). Sometimes, secondary electrons still contribute to a constant background and should be removed. Since the gas phase is measured just above the sample surface, the probed gas molecules are affected by the electrical potential landscape between the surface work function and the analyzer work function. Thus, if two different surface patches with two different work functions co-exist in the measurement region, the measured photoelectrons from the same gas molecules travel along different potentials and are measured with different apparent binding energies. Hence, gas phase spectra can provide information about work function differences at the catalyst surface (see Paper v).

Then, to compare the gas phase time-resolved measurements with the time evolution of the surface and subsurface, the different measurements first have to be time-aligned. If the time-resolved spectra were measured with internal triggering, i.e., all spectra were measured with respect to the latest trigger signal, the spectra are automatically time-aligned. If this is not the case, the time-alignment has to be done manually. This can either be done by aligning the time evolution of components that are picked up in all spectra, e.g. strong gas phase signals. Another possibility is to modulate environmental conditions as described in the next chapter and to use the changing electron transmission through the gas phase as an artificial synchronization signal. When this is done, the comparison of the catalyst and its function yields conclusions about the relationship between different surface phases and the catalytic activity and selectivity. This is a special focus of Papers ii and iii.

Modulation Excitation Spectroscopy and Fourier Analysis

As described earlier, XPS is a rather inefficient technique due to the low photoelectron cross section which is why the measured spectra can often become quite noisy with increasing time resolution and, thus, shorter measurement time. Other reasons for a low signal-to-noise ratio can be intense scattering of electrons in the gas phase due to high pressures or a small molecule concentration. In those cases, Modulation Excitation Spectroscopy (MES) can be employed to strengthen the signal-to-noise ratio [16,17,81,82]. The method aims at modulating environmental parameters and measuring a spectroscopic response to this excitation. The idea is that only the catalytically active species will respond to the modulation while the noise and other, inactive species remain unaffected. An example of the resulting modulated response in a 1D wave is shown in Fig. 6.9 (A). Event averaging, a common analysis method, makes use of the periodicity in the modulation and averages over all periodic sections in the time-resolved data (see Panel (B)), resulting in the time-resolved data during one such section with much improved signal-to noise ratio (see Panel (C)) [23]. Analysis methods such as Phase Sensitive Detection (PSD) [83,84,85], which is discussed in detail in Paper i, or Fourier analysis (Papers i, ii, iv, v) take advantage of the fact that only the catalytically active species is affected by the periodic excitation and isolate the modulation in the spectra (the so-called harmonics in Panel (D)), discarding noise and observer species that do not actively partake in catalysis. Here, one can either choose to only focus on the changing species (see Panel (E)) or to include also the static components (see Panel (F)), including background from secondary electrons. In this example, the only difference between Panels (E) and (F) is the offset, however, if the oscillation is small compared to a large background, visualizing the data without the background can reveal the small oscillations that would otherwise be hidden. The sections below give a short introduction to the most important aspects of MES and Fourier analysis while a more detailed discussion, also of PSD analysis, is left to Paper i.

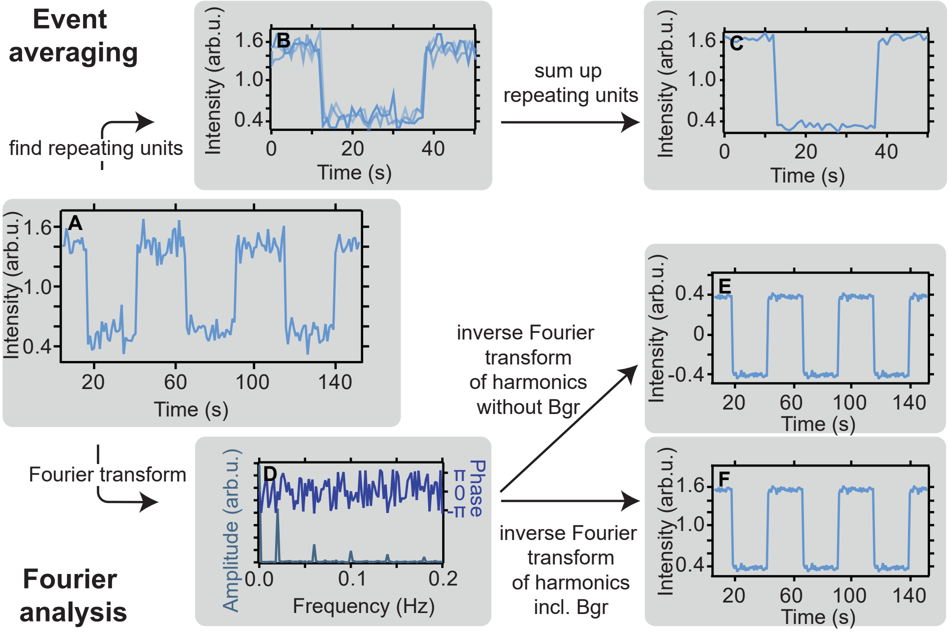

Figure 6.9: Example of event averaging (B,C) and Fourier analysis (D,E,F) to a modulated 1D dataset (A).

6.1 Modulation Excitation Spectroscopy

During MES, parameters such as temperature, gas pressure, or gas composition can be varied. When choosing a time scale of the modulation, the time scale of the process that is to be observed has to be kept in mind. For instance, if surface restructuring is to be observed the modulation has to be applied on a similar time scale. If the modulation is too fast or slow, the system might not react to the modulation.

When choosing the spectra acquisition frequency, the Nyquist-Shannon sampling theorem has to be taken into account, i.e., during one period of the modulated excitation at least two spectra have to be measured to avoid signal distortion. After spectra acquisition and as long as the excitation was periodic, methods such as event averaging, PSD, and Fourier analysis can be used for the spectra analysis. However, before the analysis is done, the acquired spectra need to be normalized for varying signal intensity in time due to the applied modulation. For example, when gas pulses are introduced in front of the catalyst, the electron transmission from the surface through the gas phase to the analyzer is varied depending on the gas pressure and its scattering coefficient. The varying surface signal intensity that is measured is then not a real variation of the surface but rather an artifact that needs to be corrected.

6.2 Fourier Analysis

Fourier analysis is used in many areas of physics as a lock-in amplifier, e.g. in Scanning Tunneling Spectroscopy (STS). An increasing number of research fields discover, however, new applications of Fourier transforms such as recently done for APXPS. The advantage of Fourier transforms is that they can de-convolute a signal into a sum of sine waves of increasing frequencies. If one now Fourier transforms an XP spectrum measured over time (see Fig. 6.10 (A) being transformed to Amplitude A and Phase Φ (B)), such a de-convolution is done for each binding energy. Since we know the frequency of the MES modulation, we can simply take this as the fundamental frequency and extract this and its higher harmonics while discarding all other frequencies from the Fourier transform (see Fig. 6.10 (C)). Then, one can make the choice to include the 0 Hz signal, i.e., the static signal, in the inverse Fourier transform (see Fig. 6.10 (D)). This is done if only the noise should be removed from the spectra. If one chooses not to include the static components, the resulting image after inverse Fourier transform is corresponding to just the oscillating components in the spectra (see Fig. 6.10 (E)). This is often done if small spectroscopic changes within a large background of static species should be measured, for example if the catalytically active species is a minority species.

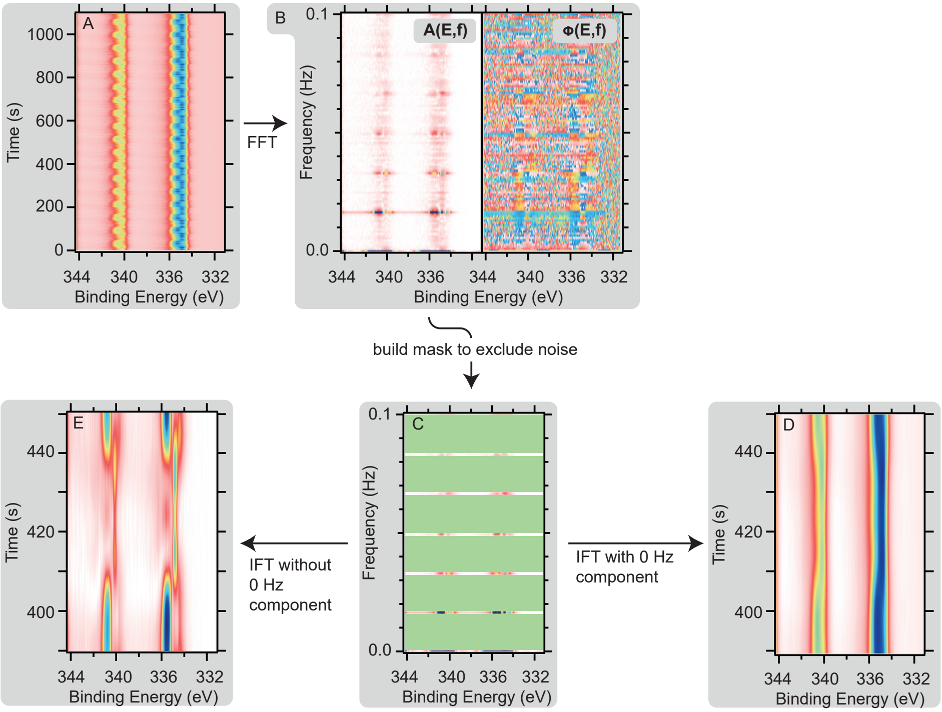

Figure 6.10: Example of Fourier analysis of raw data (A). The Fourier transform leads to the amplitude A and phase Φ for all binding energies and frequencies (B). Masking everything but the modulation frequency and its higher harmonics (C) can then, via inverse Fourier transform, lead to a de-noised spectrum either with (D), or without (E) the static species. The figure is adapted from Paper i.

The method has its limitations, though. Since Fourier analysis is based on modeling the original signal as a sum of sine waves, very sudden changes in a species concentration are difficult to display. Furthermore, it is difficult to estimate the error that Fourier analysis introduces into the spectra. A more detailed discussion of this can be found in Paper i.

Summary of Papers

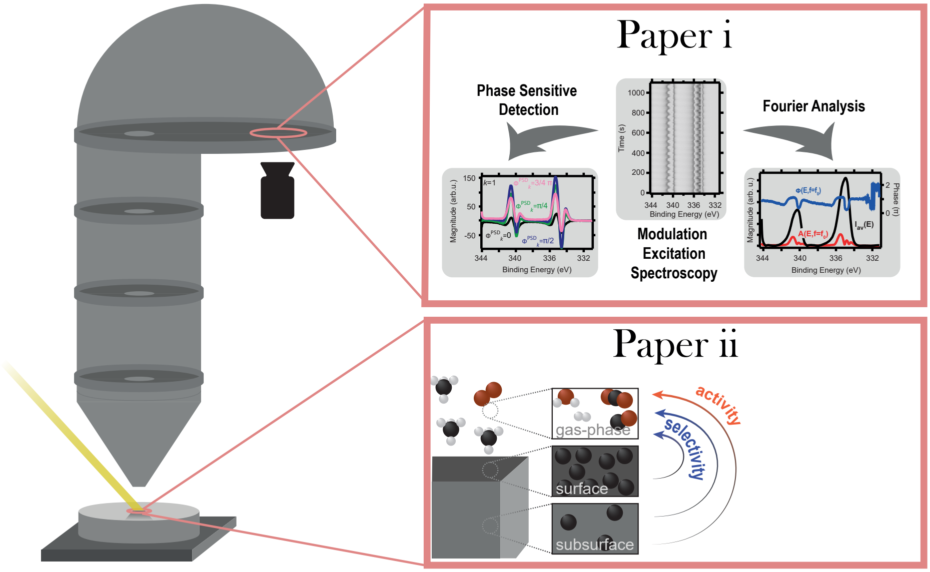

Figure 7.11: Schematic of the papers' content. Paper i discusses two different analysis approaches to MES data while Paper ii applies one of those approaches, Fourier analysis, to a methane oxidation study. Here, the influences of surface and subsurface on the catalytic function are discussed. The graphical abstracts are adapted from Papers i and ii, respectively.

Paper i: Comparing Phase Sensitive Detection and Fourier Analysis of Modulation Excitation Spectroscopy Data Exemplified by Ambient Pressure X-ray Photoelectron Spectroscopy

This paper presents the technical details of Fourier analysis and compares that new analysis method with conventional Phase Sensitive Detection (PSD) analysis of MES data. After giving a short introduction to the MES method, a thorough analysis of an exemplary dataset with PSD is presented alongside the relevant math. To compare, the same dataset is analyzed with Fourier analysis, again together with presenting the necessary math. Advantages and disadvantages of both methods are presented in direct comparison. Finally, we discuss more details of Fourier analysis due to the novelty of the method.

As time-resolved measurements with high time resolution are gaining increasing popularity new techniques evolve to improve data analysis. This paper aims at creating an understandable methodology review that can be used by other researchers that want to enter into this newly emerging and exciting field of transient catalysis.

Paper ii: Carbon Surface Crowding and Subsurface Traffic Jam as Drivers for Methane Oxidation Activity and Selectivity on Palladium Surfaces

In this paper we focus on investigating the influence of the subsurface on the catalytic reaction. In particular, we observe that carbon in the subsurface of a palladium catalyst influences the catalytic activity towards methane oxidation and alters the selectivity of the reaction. We reach these findings by doing depth profiling studies by altering the X-ray photon energy used as described in sec. 4.2. In the most surface sensitive measurements we probe ca. $0.6\,\mathrm{nm}$ into the catalyst while we probe $1.5\,\mathrm{nm}$ deep after increasing the photon energy, that corresponds to 3 and 8 atomic layers, respectively. Fourier analysis then makes it possible to compare the rather surface-sensitive and rather subsurface-sensitive measurements and we find evidence for the dissolution of carbon in the catalyst and the slow filling of subsurface layers with the contaminant. Comparing these observations with the measured changes in the gas phase, correlations between the surface carbon coverage and the amount of produced gaseous CO can be found. Additionally, the more carbon can be transported away from the surface by subsurface diffusion, the more carbon is deposited. Thus, the subsurface behavior influences the measured methane turnover. But not only the activity is influenced, also the selectivity reacts to subsurface dynamics. We conclude this from the fact that, when the subsurface is entirely filled with carbon, the catalytic selectivity shifts from methane decomposition to C and $2H_2$ towards the production of C and $2H_2O$.

The main takeaway messages from this paper are on the method-side, that measuring and correlating subsurface, surface, and catalytic function are possible within one measurement technique, and, scientifically, that the subsurface plays an important role in catalytic processes.

Outlook

These main findings, especially from the second paper directly lead to the short-term goals for the other half of my PhD studies. First of all, the journey towards more realistic catalytic systems will be continued. While experiments with nanoparticles are planned, studies including powder catalysts or alloys have happened and will hopefully continue to happen in collaboration with other researchers.

The second goal that I will hopefully reach before my PhD defense is to check for carbon dissolution in other catalysts or other catalytic structures. That is, I want to investigate whether doping palladium with another metal, e.g. Pt, prevents carbon dissolution and what effect dissolved carbon has on nanoparticle catalysis.

Finally, the biggest project we plan for during my PhD will be to apply the discovered carbon diffusion to more relevant systems. Our hope is that carbon diffusion is not entirely bad but can, with membrane catalysis, be used as a precursor for another reaction.

In the long run I hope that the methods investigated here will help to suppress catalytic deactivation by finding suitable catalytic systems. Furthermore, I also hope that the methods can help to dope catalysts in a controlled fashion and directly study the effect of this doping within one method.

Scientifically, I hope that these investigations will lead to a sustainable and efficient use of catalysts since they can be operated at exactly the right conditions without risking de-activation due to carbon deposits.

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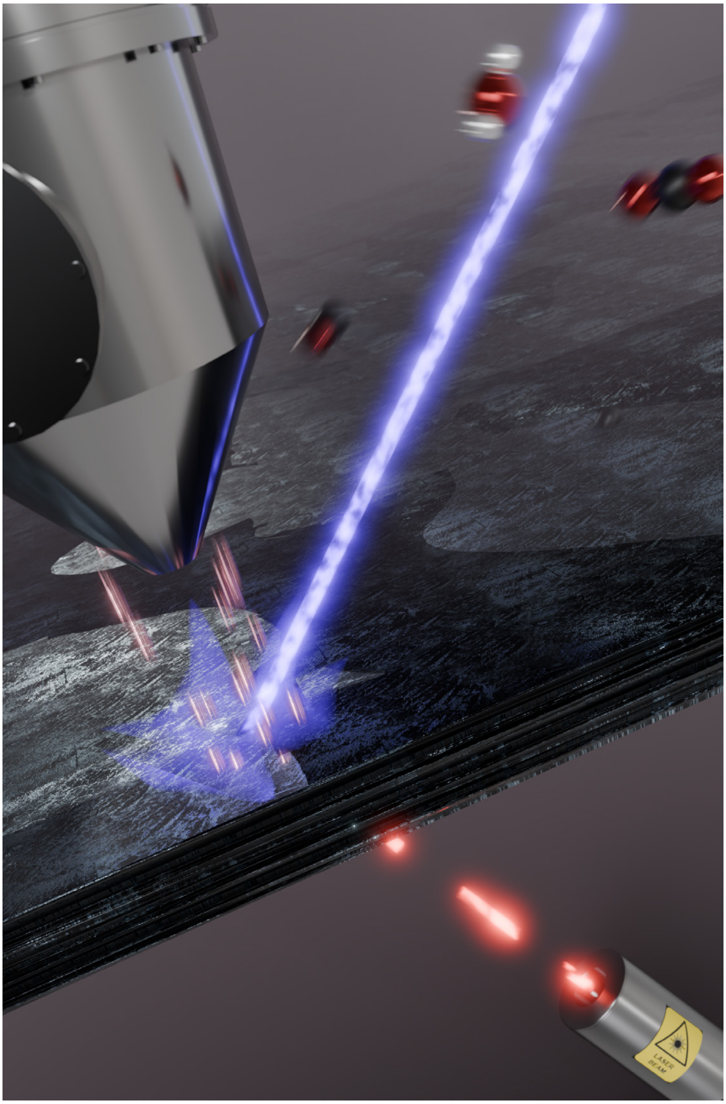

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