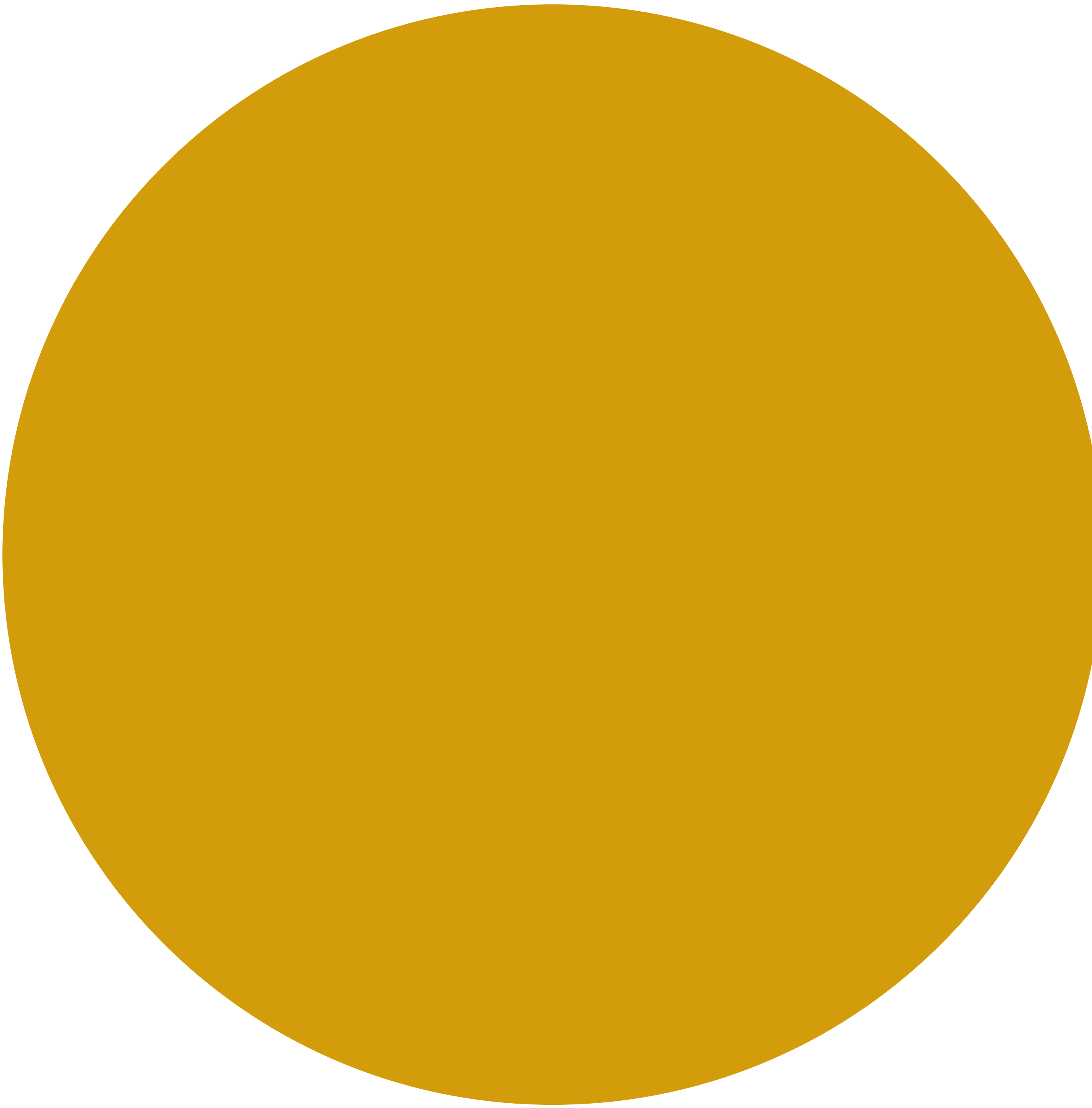
Small in Size, **Big in Impact**

If you take a well-known material – gold for example – and reduce it to the size of just a few atoms, it suddenly becomes something quite different. This inert precious metal is now a catalyst which reacts with other molecules, thus accelerating chemical reactions. Prof. Ulrich Heiz builds nanocatalysts like this atom by atom. His objective is to produce customized catalysts for the widest range of applications.



Graphics: ediundsepp

Gold has long been considered totally unsuitable for catalytic reactions because it is chemically inert in the solid state and therefore highly inactive.

Birgit Fenzel

Winzlinge mit Potential

Auf den zweiten Blick sehen Dinge gelegentlich ganz anders aus. Der Chemiker Ulrich Heiz, Lehrstuhlinhaber für Physikalische Chemie der TUM, ist so einer, der genauer hinsieht. Sein Forschungsgebiet liegt im Nano- und Subnanobereich. Mit eigens dafür entwickelten Techniken und Messmethoden zerlegt er dazu mit seinen Mitarbeitern ausgewählte Elemente in ihre Einzelbausteine, um sie dann wieder Atom für Atom zusammenzusetzen und zu untersuchen. Sein Ziel ist es, maßgeschneiderte Katalysatoren für chemische Reaktionen zu entwickeln, um diese schneller, günstiger oder überhaupt erst möglich zu machen.

Von seinen Expeditionen ins Reich der Zwerge verspricht er sich, an alten Bekannten neue Materialeigenschaften zu entdecken. Denn wie er inzwischen vielfach beobachtet hat, halten sich die Zwerge nicht unbedingt an die Regeln der Makrowelt. Zum Beispiel gilt das Paradigma der Größenunabhängigkeit bestimmter Reaktionen dort nur bis zu einem gewissen Punkt. Je kleiner die Oberfläche, desto geringer ist chemische Reaktivität – dieser eigentlich logische Lehrsatz der Chemie wird ab einer Anzahl von Clustern unter 100 Atomen zu Makulatur. Darunter beginnt der nicht skalierbare Bereich, in dem sich Eigenschaften eines Materials und Größe nicht mehr in einer linearen Funktion befinden und auch nicht mehr vom Festkörper abzuleiten sind. Zum Beispiel zeigt Gold, das lange Zeit wegen seiner chemisch inerten Materialeigenschaften als denkbar ungeeigneter Katalysator-Kandidat galt, in diesem Bereich plötzlich glänzende Katalysatoreigenschaften.

Inzwischen hat Heiz mit seinem Team verschiedene Verfahren entwickelt, um die kleinen Cluster auf unterschiedlichen Trägermaterialien fixieren und untersuchen zu können. Denn wie sie bei ihren Experimenten auch herausgefunden haben, gibt es elektronische Wechselwirkungen zwischen Trägermaterial und Cluster, die die Katalyse beeinflussen können. Zusammen mit der Größe haben sie damit ein weiteres Instrument für das Design ihrer maßgeschneiderten Clusterkatalysatoren gefunden, an dessen Verfeinerung sie derzeit arbeiten.

Ab Mai dieses Jahres wird Heiz seine Arbeit in dem neuen Katalysezentrum am TUM-Campus in Garching fortsetzen, dessen akademischer Direktor er auch ist. „Zentrales Ziel ist dabei die Entwicklung von Clusterkatalysatoren, mit denen wir Kohlendioxid reduzieren oder idealerweise in etwas Sinnvolles umwandeln können“, beschreibt er den Fokus seiner künftigen Forschung, von deren Erfolg für ihn viel abhängt. „Da müssen wir in den nächsten Jahren den Durchbruch schaffen, sonst wird es kritisch.“ □

„Wir wollen die neuen Eigenschaften der Materie, die im Nano- und Subnanobereich auftreten, aufzeigen und neue Katalysatoren finden.“

Ulrich Heiz

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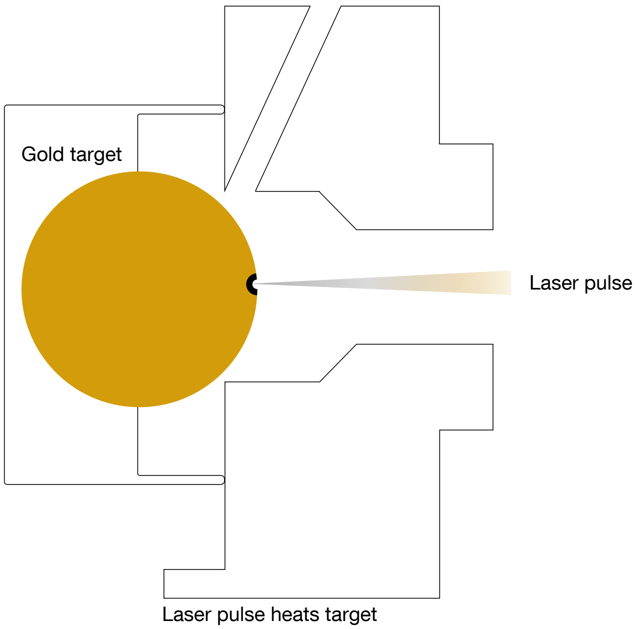
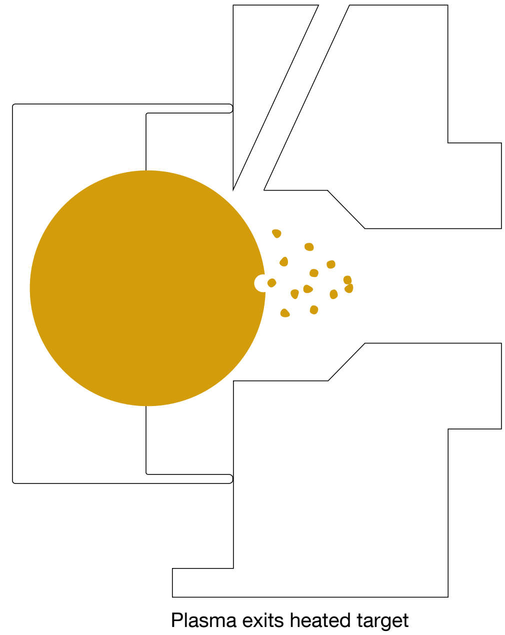
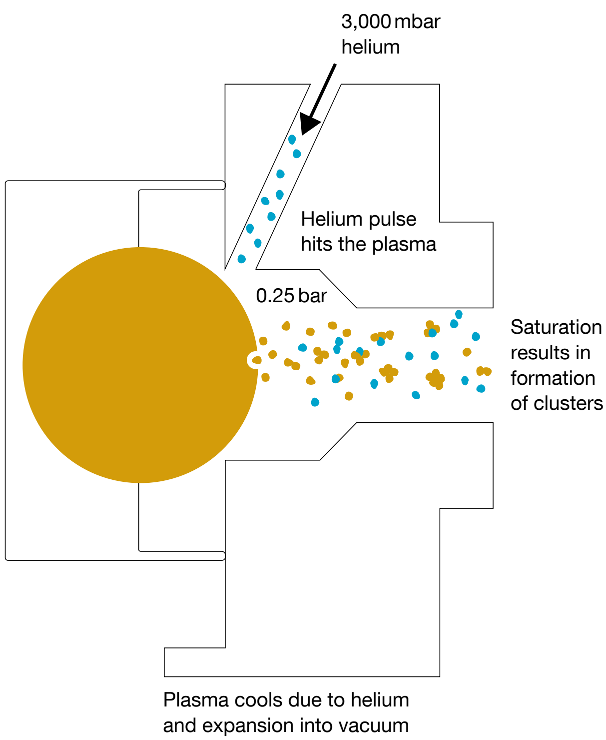
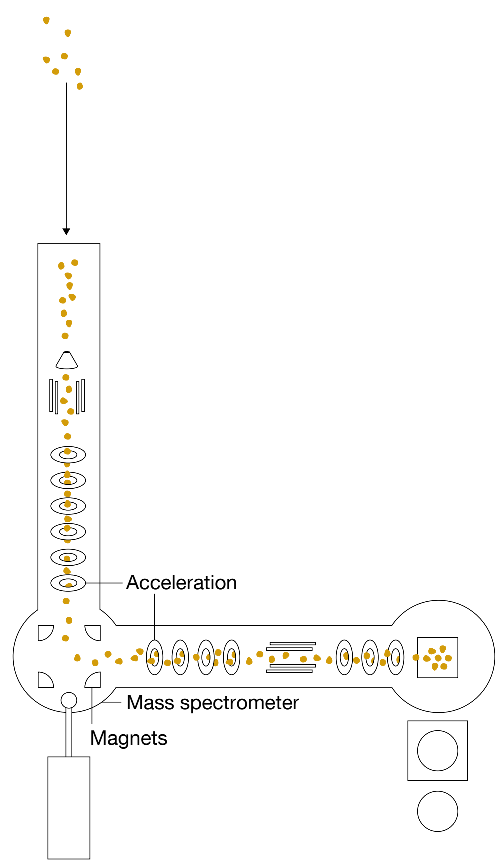
In a size range of
eight to 20 atoms,
gold exhibits excellent
catalytic properties.

Graphics: ediundsepp









How to produce nanoclusters: A laser pulse heats a target and vaporizes some nanograms of material. The resulting plasma is cooled through both a helium gas pulse and expansion into the vacuum of a thermolization chamber. The atoms aggregate into clusters; the size distribution can be varied by setting different parameters. A mass spectrometer is used to select a cluster of a precise number of atoms from the distribution generated by the cluster source.

In times past, alchemists attempted to turn base metals like lead or mercury into gold and other precious metals. Today, scientists at TUM are taking a different approach. For over two decades, Ulrich Heiz and his staff at the Chair of Physical Chemistry have been experimenting with metal clusters. Unlike the earlier alchemists, however, they are not looking to transmutate matter, but rather to nanostructure metals so that their physical and chemical properties can be controlled. So instead of transforming one chemical element into another by changing its atoms, Heiz controls the material properties of his clusters specifically by changing their size. Unreactive metals can suddenly become catalysts and trigger specific chemical transformation processes.

Heiz specializes in heterogeneous catalysis, in other words, catalysis in different chemical phases, on the nano and subnano scale. That is where he sees the "philosopher's stone". When asked what inspires and drives his work, he says: "Our aim is to demonstrate the new material properties that emerge on this scale and use those insights to discover new catalysts". It's a bit like putting Lego bricks together.

Through his basic research, the chemical scientist is thus shedding light on an area that was previously more or less in the dark due to the lack of suitable methods. When it comes to applications, too, his research into the nano universe holds huge potential. Catalytic processes are of major importance in nearly all branches of industry. "More than 90 percent of all industrially manufactured compounds undergo at least one, and sometimes several, catalytic reactions during their synthesis," he explains. His work may also help provide much-needed answers to the main challenges facing modern society – the need to conserve resources and use them efficiently, protect our climate and store energy.

Size matters

Heiz and his colleagues focus on just one element at a time when they venture into the nano and sub-nano realm. "Basically, you get a big cluster of a precious metal and make it smaller and smaller," is how he describes his method. This increases the ratio between the number of atoms on the surface and the atoms within the metal. "This is important, because the surface atoms are the ones that catalyze the reactions," he explains. "The smaller we make the clusters, the more precious metal atoms we have to trigger the catalysis. Initially, however, no new effects can be observed relative to the large cluster. Activity initially scales with size. But this no longer necessarily applies once you get to very small clusters with fewer than a hundred atoms. And it is this non-scalable dimension in matter that interests us. We build clusters using a specific number of atoms – 2, 4, 6, anything up to 100 in fact – and see what happens."

The atoms which the team under Ulrich Heiz in Garching uses to build their clusters are around 300 picometers in diameter – one picometer equals one trillionth of a meter. By comparison, nanotechnology is like playing with large Duplo building blocks. In other words, they are more than one order of magnitude larger. "We are doing pioneering work in this field," declares Heiz. The controlled creation of nanocatalysts with a precisely defined number of atoms required new methods and techniques, and the further development and understanding of these techniques also form part of his research. "It's not like you can hop out to the DIY store to pick up the equipment you need to make clusters," comments his colleague Florian Schweinberger, research coordinator at the TUM Catalysis Research Center.

How do you build a cluster with just a few atoms?

A self-built cluster machine is positioned just a few steps from Heiz's office. It includes a pulsed laser vaporization source, a system of electrostatically and radio frequency-driven ion optics, an analysis chamber for examining the properties of the clusters, various controls and sliders for changing the parameters, as well as a tangle of connecting cables and hoses. "With this machine, we can create clusters of a precise size and deposit them on a surface from the gas phase or else store them in a trap in the gas phase. We can then look at the properties of these size-specific clusters and measure them," he explains. "That is what we specialize in."

With each pulse of the laser, a few nanograms of the material are vaporized. This creates a plasma, a mixture of atoms, ions and electrons, which is cooled in the thermalization chamber through a helium gas pulse on the one hand and through expansion into the vacuum on the other. The atoms aggregate into clusters, the size distribution of which can be varied by changing the nozzle size, for example, or the pressure in the vacuum. Finally, the scientists use a mass spectrometer to select a cluster of a precise number of atoms from the distribution formed in the cluster source. ▷

Graphics: ediundsepp (source: TUM)

"Our aim is to demonstrate the new material properties that emerge on the nano and sub-nano scale and use those insights to discover new catalysts."

Ulrich Heiz

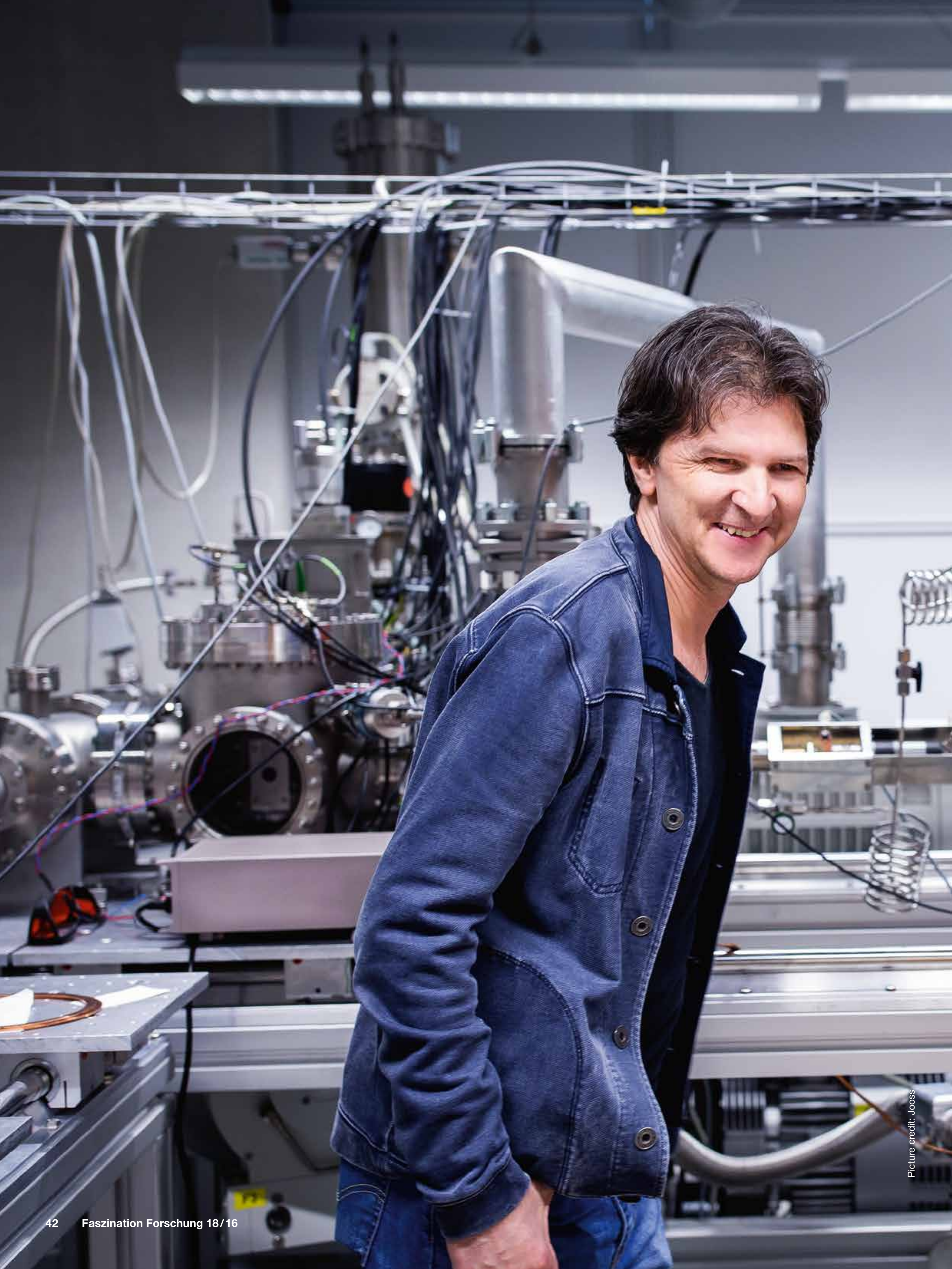
These experiments have shown that different rules apply in the nano realm than in the macro world of solids. Because of its specific properties, gold has long been considered totally unsuitable for catalytic reactions because it is chemically inert in the solid state and therefore highly inactive. In a size range of eight to 20 atoms, however, the normally highly inert precious metal suddenly revealed excellent catalytic properties. With this discovery, the Munich-based chemical scientists had found the smallest known active gold cluster comprising just eight atoms.

Platinum clusters challenge long-established assumptions

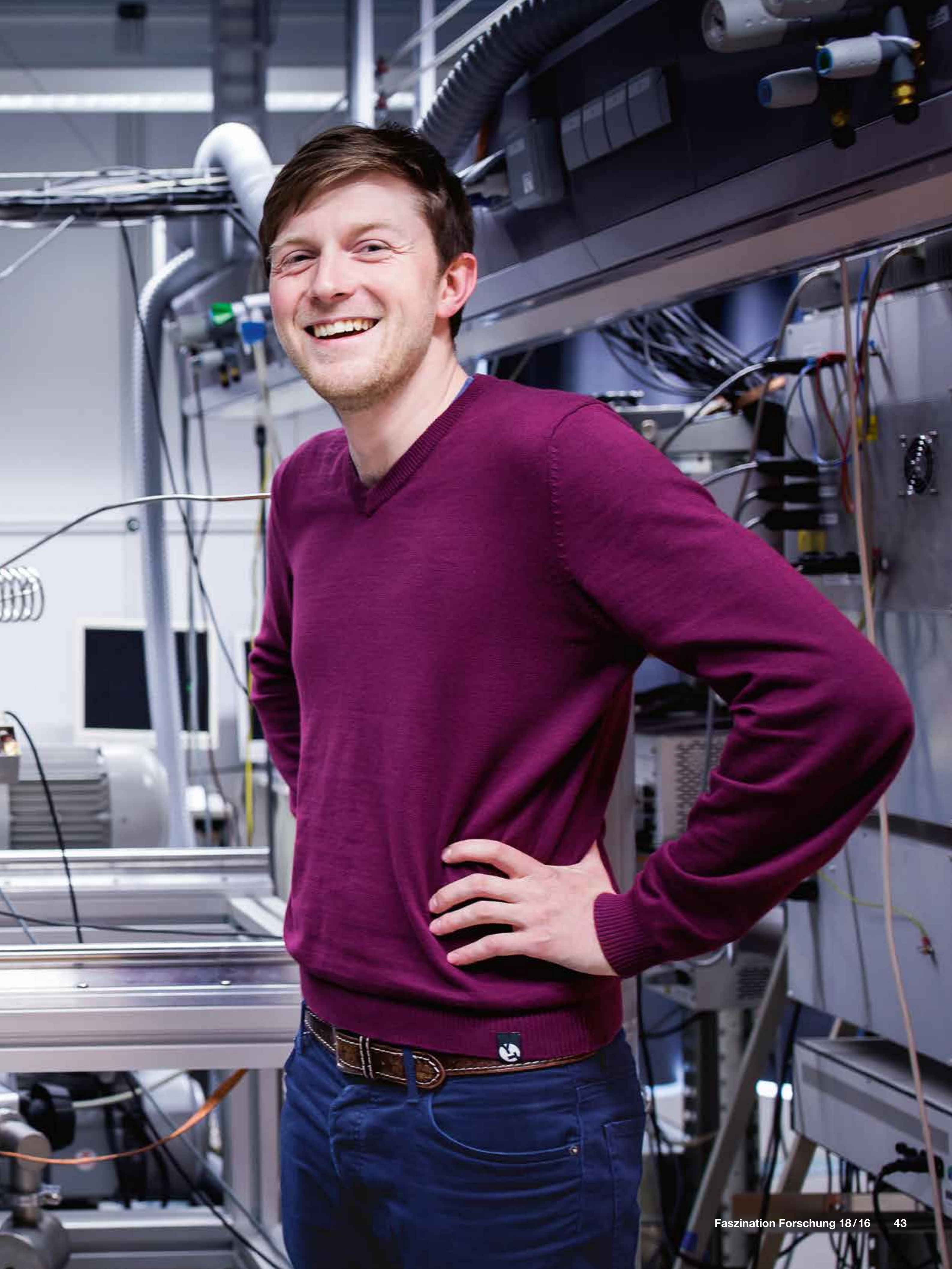
Experiments with platinum have recently shaken up long-established assumptions among scientists working in this field. "For a century or so, there has been an accepted differentiation between reactions that are influenced by the structure and size of the catalyst, and reactions where these two parameters play no role," relates Heiz. "We suspected, however, that this differentiation does not apply to catalyst particles at sub-nanometer scale." In order to find out for sure, he and his team have spent the past two years carrying out further experiments with ethene. This hydrocarbon was chosen because of its ability to react with hydrogen, known as hydrogenation; this reaction is regarded as a typical example of a size-independent reaction. For their experiments, the researchers used platinum catalysts with sizes ranging from one to 80 atoms. Their suspicions were confirmed when they allowed these particles to react with ethene and hydrogen. Clusters with fewer than ten atoms were barely active. Catalytic activity then increased in the presence of more than ten atoms, with maximum activity reached in clusters of 13 atoms. "We have thus provided further clear proof that decade-old theories claiming that size does not matter in this reaction are simply unfounded," maintains Heiz. His assumption now is that all kinds of materials have a turning point somewhere in the nano or sub-nano range from which a linear relationship no longer applies between size and physico-chemical properties. Because quantum size effects then come into play, the properties can no longer be predicted at this scale. "This shift from the scalable to the non-scalable range brings many new opportunities for basic research, but also for applied research," Heiz is convinced.

Theoretical proof of the experimental observations from the recent platinum studies has been provided by the team under physicist Uzi Landman at Georgia Institute of Technology in Atlanta. Landman is one of the world's foremost theorists in the field of nanoscience and a long-time collaborator of Ulrich Heiz in the search for new ways to control chemical reactions. "The fact that our systems are so precisely defined and transparent means that the theorists can accurately calculate and model our results," he comments. In their calculations and computer simulations, they were able to precisely demonstrate which atom is responsible for which activity and why. ▷

Picture credit: Jooss



Picture credit: Jooss



For the hydrogenation reaction of ethene in the presence of platinum, all of the negative charge from the oxide surface is stored in a single atom. All the other atoms keep their original charge. “It is clear that the arrangement of the atoms in the structure of the cluster also plays a role,” concludes Heiz. This is a highly interesting finding for the development of customized catalysts. “It means that we can change a property by adding an atom.”

Stabilizing the nanoclusters

However, the development of catalysts based on nanoclusters reveals a fundamental challenge, explain the Munich-based chemical scientists; it is specific to the process of nano-scaling itself. Tiny particles are unstable because the atoms on their surface are weaker bonded. And because they are only bonded to the substrate over a small area, they are prone to wander off and bond with the next-biggest particle. This phenomenon can be noticed in the corners of many a room. The dust bunnies that gather there are simply conglomerations of tiny dust particles that keep on gathering more dust. It’s the same idea at the nano scale, says chemical scientist Friedrich Esch, one of whose tasks as part of Heiz’s team is to find out how the particles can be stabilized. “It’s not just cluster migration that leads to a change in size distribution: the small clusters can also disintegrate through exchange processes. The smaller they are, the greater the likelihood of atoms vaporizing and exchanging between the clusters. This leads to ever bigger particles,” he explains. This process is known as Ostwald ripening, which was discovered at the beginning of the 20th century by the polymath and winner of the Nobel Prize in Chemistry Wilhelm Ostwald. “So for us, the big question was how can we prevent this process and keep our nanoparticles stable for longer,” Esch explains.

Along with Swedish colleagues from Chalmers University of Technology in Gothenburg, the scientists studied various methods to get their tiny particles under control. “This effect can be pretty well suppressed in clusters with exactly the same number of atoms even at high temperatures,” says Esch. So the scientists overcame the Ostwald ripening challenge by ensuring same-size clusters.

Meanwhile, the Munich team has developed various processes for attaching the small clusters to substrate materials so that they remain stable at high temperatures, are kept at a distance from each other and in each case have the same bonding location with specific properties. The choice of substrate ▷

Prof. Ulrich Heiz

Academic Director of the TUM Catalysis Research Center

Ulrich Heiz, born in 1960, studies the physical and chemical properties of matter at the nano and sub-nano scales. In this size range, the properties of particles are determined by the exact number of atoms they contain and are no longer scaled from the solid state. He considers his work to be a combination of basic and applied research. His discoveries so far lead him to believe that tiny particles hold the key to solving major challenges in the areas of environmental protection and clean sources of energy.

Chemistry did not figure at all in Heiz’s early career plans. In fact, the choice was between physics or medicine. He would most likely have made a good doctor – and even started down that road. After completing his school-leaving exam at Gymnasium Bern Neufeld, he stayed in his home city in Switzerland to study medicine at the University of Bern. After just a few semesters, however, Heiz realized that he was more attracted to the natural sciences. “It so happened that the medicinal chemistry lectures were the ones I enjoyed most,” he recalls. He quickly took up his new calling. In 1987, he completed his chemistry degree at the University of Bern and his doctorate in physical chemistry four years later. He quickly discovered his interest in the nano world of atoms. Even his Ph. D. supervisor Ernst Schumacher had previously conducted experiments with small clusters in the gas phase.

After his doctorate, Heiz spent time as a researcher at the laboratory of the Exxon Research and Engineering Company and at the University of Pittsburgh. In 1998, he completed his postdoctoral lecturing qualification at the University of Lausanne. After taking up various posts in Japan, Berlin and Ulm, he accepted the position of Chair of Physical Chemistry I at TUM in 2004. Ulrich Heiz is also Academic Director of the newly opened TUM Catalysis Research Center. He is married to a French teacher and the couple have one daughter. He likes to listen to jazz in his free time.

Picture credit: Jooss

material plays a decisive role here. It must have a suitable, highly ordered surface structure offering neither overly strong nor overly weak bonding. “Fine, corrugated carbon films – graphene sheets in Moiré patterns – fit the bill. They provide traps for the clusters at precise distances while largely preventing the exchange of atoms between these traps,” is how Esch described the method they used to inhibit the Oswald ripening effect.

The influence of the substrate material

As part of their search for new nanocatalysts, the TUM chemistry researchers experimented with different substrate materials. Stability was not their only concern, either. “Similar to the cluster size, substrate material is a vehicle that we can use to customize the properties for a specific reaction,” declares Heiz. As they also discovered in their series of experiments, these substrates are themselves capable of influencing the catalytic reaction. They had already made use of this effect in a project funded to the tune of EUR 2.3 million by the European Research Council, the objective of which was to create chiral gold clusters. Chiral substances consist of two compounds called enantiomers, which while having the same structure are actually mirror images of each other, like our left and right hands. The researchers wanted to use chiral catalysts to selectively create only one of the two enantiomers. “For this, we created a surface onto which we vaporized single-chirality molecules,” explains Heiz. “When we then deposited gold clusters on the surface, they followed the same pattern. If the substrate is of one chirality, so too will the deposited molecules be.” They observed similar interactions with the substrate material atoms when hydrogenating ethene with platinum as the catalyst.
“These asymmetric catalysts are an important discovery for the pharmaceutical industry in particular,” according to Heiz. In the manufacture of pharmaceutical active ingredients, only one of the two enantiomers can be used as a rule. “The other one can actually be dangerous in some cases,” he points out, referring to the drug penicillamine by way of example. Its active agent is a chiral compound. One enantiomer, D-penicillamine, acts as an antibiotic, whereas its mirror enantiomer, L-penicillamine, is toxic. If both products are created, the undesirable enantiomer has to be detached. This complex process is performed millions of times in industry. In the future, the gold clusters created by the Munich team could save costs and reduce waste in that only one enantiomer would selectively be created.

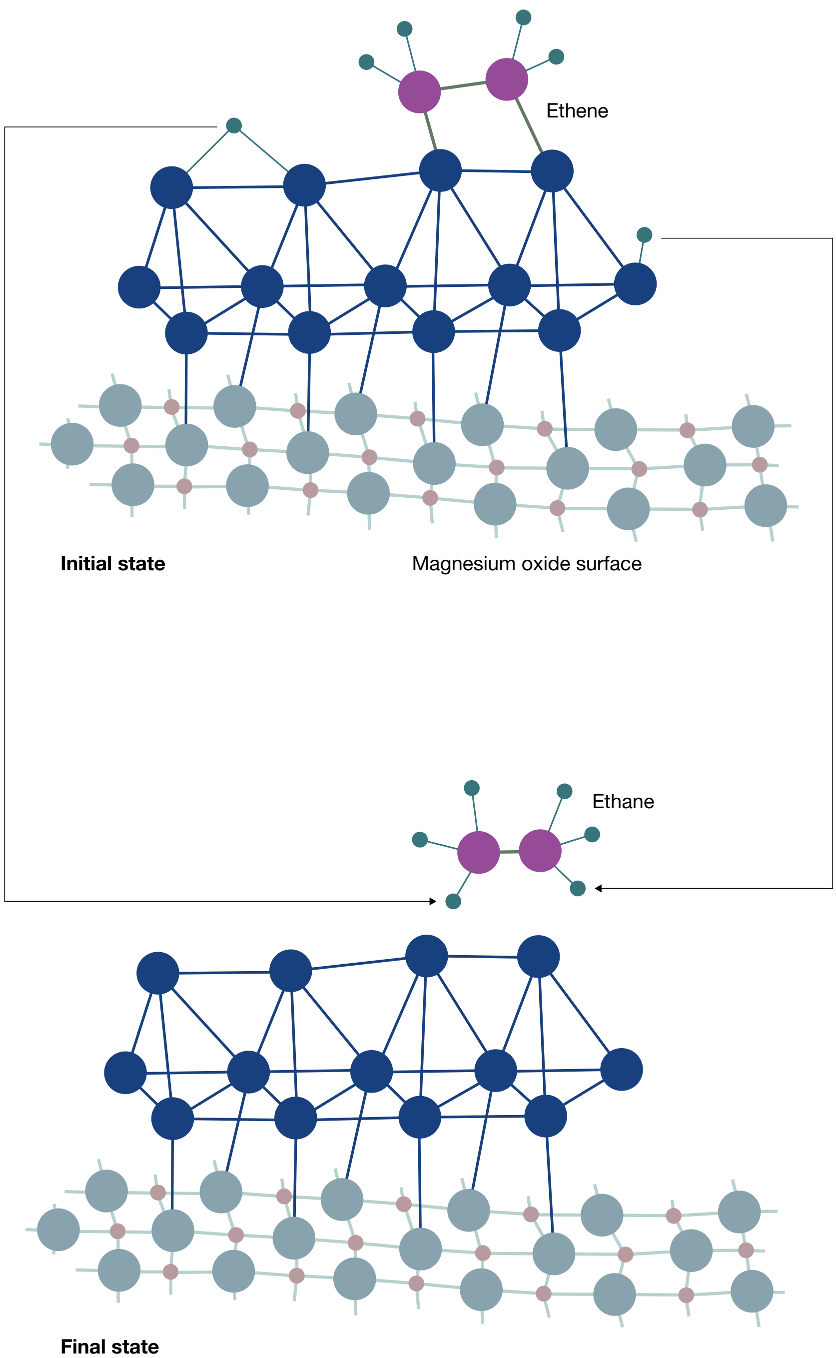
The next step is to replace the expensive precious metals with cheaper materials. Metals like iron or nickel have not come into the equation until now because they are either too reactive or not reactive enough in solid state. “But when we reduce them to nanoscale, there is a possibility that we can transform them into very useful catalysts – also by tuning the substrate materials.”

Research alliance with industry

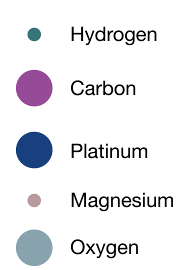
The study and application of innovative catalyst systems is also the focus of the research alliance in place since November 2010 between TUM and chemicals manufacturer Clariant. TUM scientists have been focusing on chemical catalysis with Clariant researchers at the new TUM Catalysis Research Center on the Garching campus since November last year. Clariant is providing funding of up to EUR 2 million per year to support this basic and applied research work. Heiz is the Center’s Academic Director.
One of the research center’s core objectives is to develop catalysts for the efficient transformation of carbon dioxide. “We aim to develop clusters that mitigate carbon dioxide and ideally transform it into something useful,” says Heiz of his plans for upcoming collaborations with colleagues at the research center. Carbon dioxide is after all more than just ▷

“In the new TUM Catalysis Research Center, we aim to develop clusters that mitigate carbon dioxide and ideally transform it into something useful.”

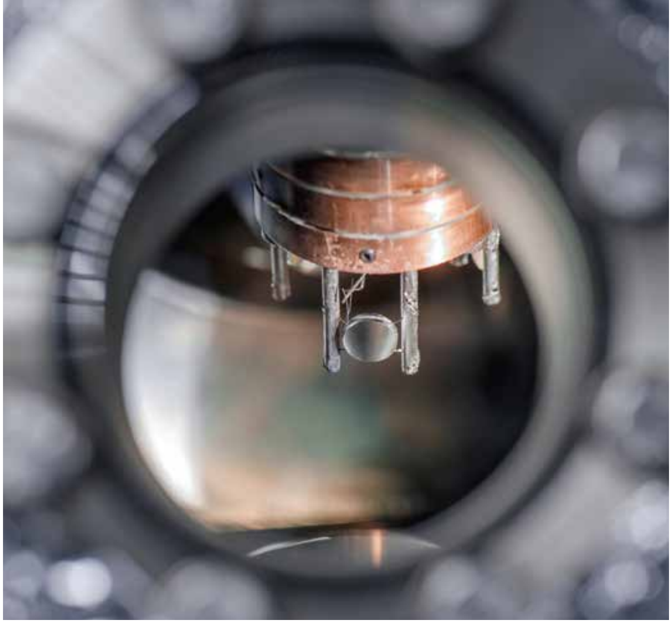
Ulrich Heiz



Ulrich Heiz's working group produced platinum particles with only a small number of atoms.They found that clusters with 13 atoms show maximum reactivity. Shown here is the platinum catalyzed reaction converting ethene to ethane.

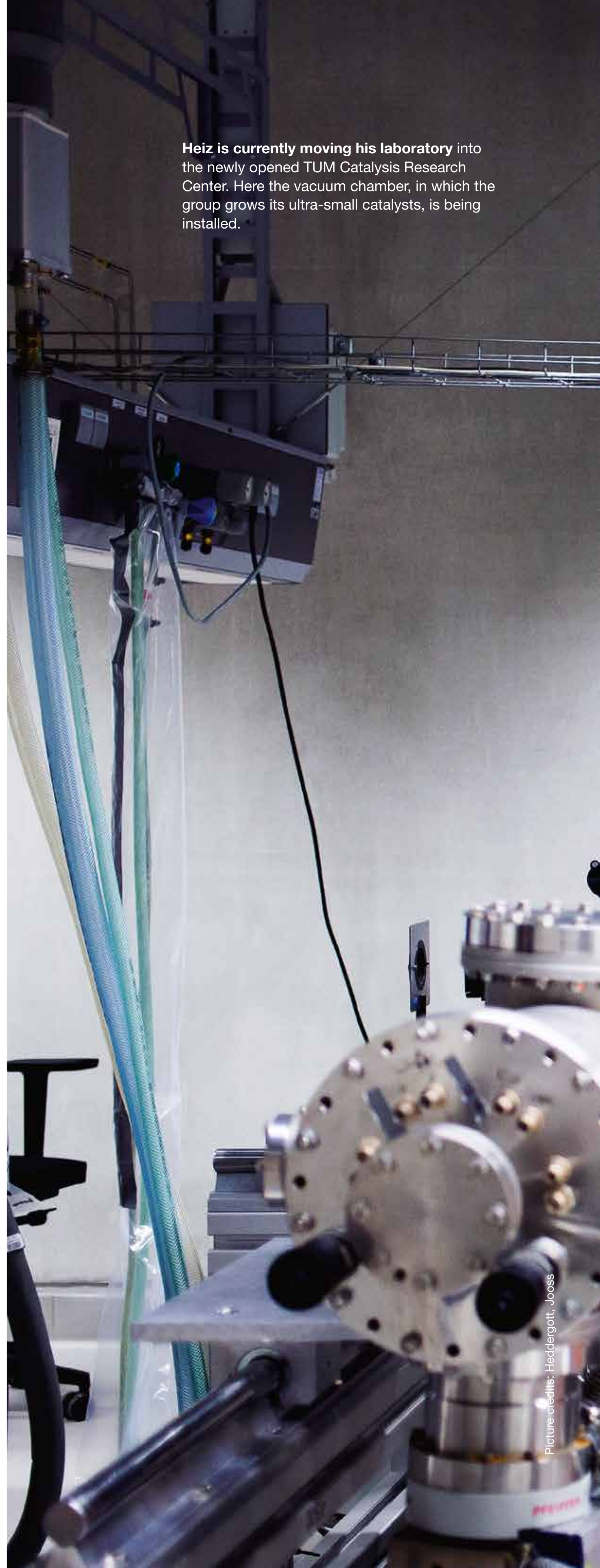


Graphics: ediundsepp (source: TUM)



Sample holder with three single crystals on which the catalyst particles are deposited.

an exhaust gas and a contributor to global warming. It is also a raw material that can be profitably used by industry to make many products. This greenhouse gas may even play an important role in the transition to cleaner forms of energy. When transformed into methane or methanol, it could in the future store surplus electricity from wind and solar farms. Up to now, the awkward properties of this actually quite simple compound have impeded these visions. “We have to make the breakthrough in the next few years, otherwise the need will become critical,” asserts Heiz, who in his roles as scientist and academic director of the new facility has chosen a hard nut to crack. Carbon dioxide is an essentially inert gas with very tightly bonded carbon and oxygen molecules. But it is totally conceivably that a solution will again be found in the nanoscale world. After all, countless experiments with different materials have proven that interesting surprises await on the non-scalable nano level. Not least the transformation of an inert metal like gold into a shining example of a promising catalyst. *Birgit Fenzel*



Heiz is currently moving his laboratory into the newly opened TUM Catalysis Research Center. Here the vacuum chamber, in which the group grows its ultra-small catalysts, is being installed.

Picture credits: Heddergott, Jooss