

3 Introduction

Surfaces and interfaces have for many decades been the subject of intense physical and chemical investigations. Their properties are interesting and quite often even surprising. Several surfaces and interfaces have proven to possess special “functionalities”. An example of such is the special “functionality” of iron oxide surfaces in the synthesis of ammonia from its elements, which has been explored by Fritz Haber, who was awarded the Nobel prize in Chemistry for his research in 1918[1]. This special surface with its functionality has not only found its way into applications – it has also preceded an area of research, which is enormously wide and active – the research on heterogeneous catalysis[2–4].

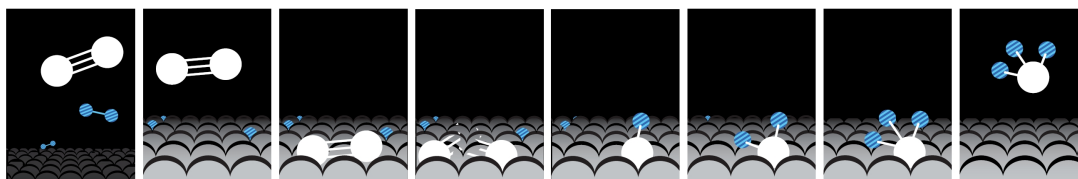


Figure 3.1: Schematic representation of the Haber-Bosch-Method for ammonia synthesis with its different steps: N_2 and H_2 molecules in the gas phase; adsorption of both molecules; bond cleavage into single N and H atoms; successive combination of N and three H . A detailed description can be found elsewhere[4]. – Figure reproduced from [5].

To understand or even tailor surface functionalities is a very interesting and challenging task. There are several possibilities to accomplish this. One very promising approach is the use of adsorbed molecules[6, 7]. For atoms within a crystal, their properties in the ensemble are totally different than from the single atoms. For molecular ensembles instead, the molecular properties are preserved or only slightly altered, but the primary functionalities of the molecules are not changed. This makes them very interesting for surface manipulation, especially as chemical synthesis allows for a direct control of the molecular properties by the insertion of functional groups.

The adsorption of molecules on surfaces is determined by the properties of the surface. However, to a large extent the interaction between substrate and adsorbate is determined by the chemical properties of the molecules. These properties depend on the structure of the molecule, which is altered upon adsorption. These chemical properties again are in close relation to the molecule’s electronical properties, which are influenced by the

electronic properties of the surface. Understanding this triangle of chemical, structural and electronic properties, mutually influencing each other, is a key to understanding and tailoring the function of adsorbate surfaces.

For small molecules, the above mentioned properties and their mutual dependencies are nowadays well understood. This can e.g. be seen in this year's Nobel prize in Chemistry awarded to Gerhard Ertl[5]. Still countless challenging questions remain. I will try to provide first answers to a few of these questions in the next chapters.

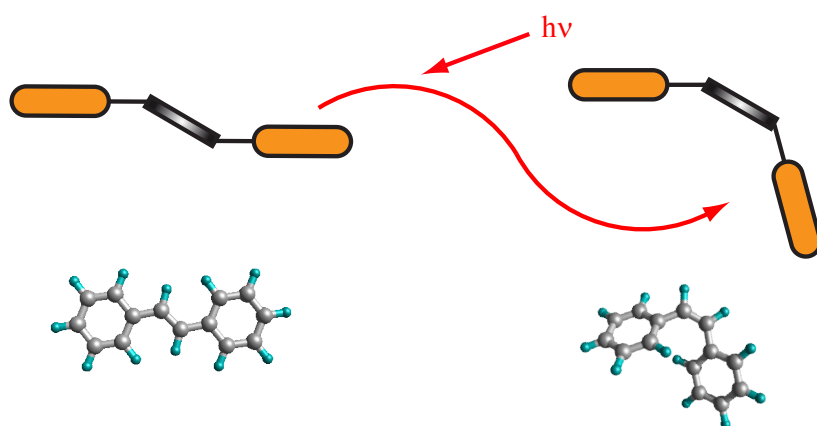


Figure 3.2: Idealized molecular switch (top). The orange lobes represent conductive π -systems, while the black bar may be a double-bond-entity. Such molecules can change their shape upon photoillumination as indicated. At the bottom the stilbene molecule, a prototype molecular switch, is shown with its two isomers.

An intriguingly interesting class of molecules are the ones bearing double bonds, e.g. C=C or N=N bonds. The substituents at either end of these double bonds may acquire an arrangement where they are on the same side of the bridge (called the cis-isomer) or on opposite sides (the trans-isomer). A transition between both isomers can be induced by the excitation with light. If these bridges are substituted with conducting entities that can change their orientation toward each other, a “molecular switch” has been created[8]. Aromatic entities with π -orbitals have been shown to exhibit conductive properties. Overlap between π -orbitals takes place only along the direction of the π -orbitals, leading to an anisotropy in physical properties, i.e. charge carrier mobility or optical absorption[9, 10]. For large molecules with extended π -systems, even the formation of bands has been observed [11] suggesting the occurrence of high carrier mobility due to band transport.

The stilbene molecule, two phenyl-groups connected by a C=C bridge, is an example for such a “molecular switch” (see figure 7.1.3). Indeed, the photoinduced isomerisation of stilbene is known and well investigated[12–15]. However, up to now isomerisation has only been performed in gas phase and in solution. In this work I will investigate the adsorption of stilbene. Special focus will lie on the manifestation of the two isomers in the adsorbed phase. An unambiguous and ideally straightforward identification of, and

differentiation between, the two isomers by spectroscopic means is of special interest. X-ray absorption spectroscopy (NEXAFS) provides not only exactly this but also a lot of information on the orientation of the molecules on the surface and the interactions between substrate and adsorbate. Here, stilbene has been adsorbed on two surfaces – Si(100) and Cu(110). Si(100) is the prototypical semiconductor surface. With its directed bonds strong interaction between molecules and single substrate atoms are possible. In metals like Cu bonds are more diffuse, and thus a weaker, delocalized bonding may occur. How strong the impact of this different bonding interaction upon the stilbene isomerisation is, can be seen in a later chapter.

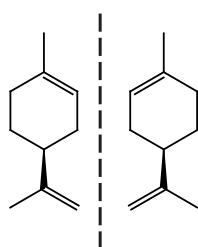


Figure 3.3: *Limonene is a molecule where the S-enantiomer (left) has the smell of lemons, while its R-enantiomer (right) smells of orange. Each of the chiral receptors in our nose reacts only to one of the forms.*

Surface functionalities can also point into a totally different direction. While the synthesis of ammonia on a catalyst is comparably simple (and still it took decades to fully understand this process), the synthesis of modern chemicals is much more complicated. Especially biologically active molecules, e.g. medicine or food additives, possess a property that complicates their synthesis. Many of these molecules contain a carbon atom that is surrounded by four different ligands. These four ligands can arrange in two different ways, the resulting isomers behave like mirror images to each other – like a left and a right hand. Indeed, this property is called handedness or chirality. The molecule limonene shown in figure 3.3, for example, has the smell of either oranges or lemons, depending on its handedness. This different smell can only be sensed because the human receptors are also handed and only entities of the same handedness can interact. For chiral molecules to fulfill their function in biological systems as the human body, only one handedness alone is required. In the worst case, the opposite isomer may even have harmful effects. One example therefore is the molecule known in Germany as “Contergan”¹. Contergan was widely used as sleeping pill for pregnant women. Thalidomide, Contergan’s active agent, reacted as pacifier in the right handed R-form, while the left handed S-enantiomer caused genetic changes leading to crippled limbs of the newborns.

Using standard wet chemical synthesis, both enantiomers are always produced in the same amount. This is called a racemic mixture. Separation is expensive, difficult and leads only to very low yields. New recently proposed approaches for the enantiopurification of racemic mixtures through the enhancement of handed properties are up to now without any practical realisation[17, 18]. Thus this problem has to be approached directly at the beginning – by the synthesis of only one enantiomer. One approach is the use of

¹More information on this topic can be found elsewhere[16].

homogeneous chiral catalysts[19] such as the ones developed by Sharpless[20], Knowles[21] or Noyori[22]. On the other hand heterogeneous catalysts[1, 2, 4, 5] may also be used. These have a great advantage over homogeneous ones as they can be easily separated from the reaction mixture and are usually reused (after reactivation if needed). Tartaric acid adsorbed on Raney nickel is currently one of the three most important asymmetric heterogeneous catalysts[3, 23], effective for β -functionalized ketones with an enantiomeric excess (i.e. the amount of the desired enantiomer as product compared to the non desired one) up to 98.6%.

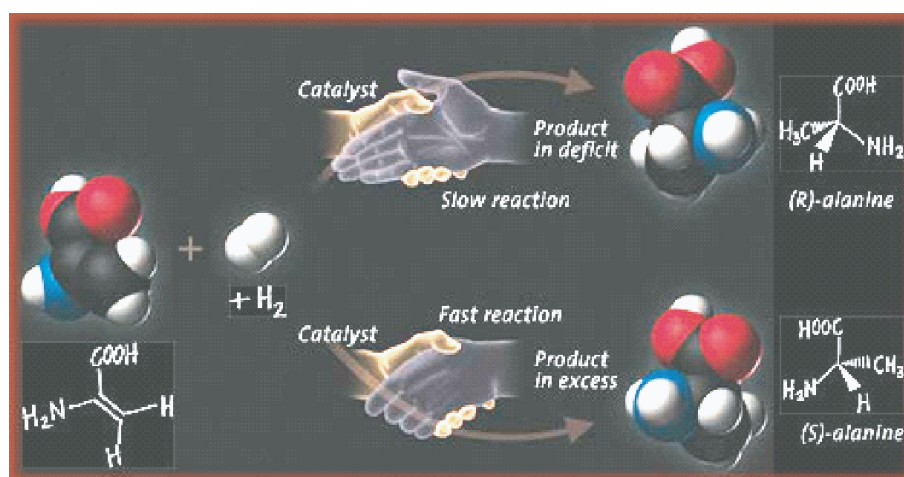


Figure 3.4: In heterogeneously catalysed asymmetric synthesis, the product with the same handedness as the catalyst is formed in vast excess as they fit geometrically better to each other. This is a comparable situation as a shake-hands, where only the same side hands fit well to each other. – Figure reproduced from [19].

Handed surfaces can be prepared in different ways. An exciting method is, of course, the use of molecules, because molecules can be shaped in a way that they adsorb in a handed fashion on the surface. Molecules with a “kink”, like the C=C bridge in stilbene, can adsorb with the kink oriented to the left or to the right. Although the molecules themselves are achiral, because of the two possible orientations in the adsorbed phase, the covered surface is chiral.

With the “correct” substituents attached, the ordering of the molecules on the surface can be influenced as the responsible intermolecular interactions depend on exactly these substituents. A stilbene molecule with two carboxylic endgroups at either side, as I will show in a later chapter, can form two different networks – assuming a herringbone or a parquet pattern. With other substituents the formation of different networks, like squares, trigonal or hexagonal tilings, or just simple rows are possible[6]. With the two adsorption enantiomers – C=C bond oriented left or right – another phenomenon can be observed. Phases can be formed that contain either only left or right handed molecules. Also Phases exist that contain an equal amount of both isomers, i.e. racemic phases. As it is well known for mixtures of enantiomers in the gas phase and in solution, upon thermal activation

the two separate phases vanish in favor of the racemic one. All this can be investigated by taking a look at the surface, by imaging the molecules, with a scanning tunneling microscope (STM).

It is of course much easier to form a chiral surface with molecules that are intrinsically chiral; tartaric acid is an example of those. Surely these molecules can also adsorb in a chiral fashion. But also achiral adsorption geometries have been observed, which perfectly disguise the chiral nature of the adsorbate. So how is it possible to detect the molecular chirality? And what influence does the chiral or achiral adsorption geometry have? This will be topic of the last part of my thesis.

The common method to detect handedness is optical rotation, i.e. the rotation of the polarisation plane of linear polarised light. Unfortunately not all right handed molecules rotate the polarisation plane to the right, and not all left handed molecules to the left. Therefore the use of optical rotation requires prior knowledge about the molecule under investigation. Thus a spectroscopic method would be needed that directly tells us whether a molecule is left or right handed, and ideally in a separate way for every carbon atom. C1s core level photoemission spectroscopy is just that tool. An emission signal from every C atom can be detected and assigned. Using circular polarized light, the absorption for both polarisations is different for left and right handed C atoms. Monitoring the angular dependence of this dichroism provides a spectrum that directly tells the handedness of every carbon atom in an adsorbed molecule. I will show that indications are strong that a quantitative description might also be possible.

