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Search for new catalysts from a fundamental basis

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Abstract

In this overview, we present some of our more fundamental approaches for making new and/or improved catalysts. First, the effect of mono atomic steps is discussed both in relation to the mechanism of the ammonia synthesis, and in terms of relevance for other reactions, such as the steam reforming and methanization processes. The possibility for utilizing steps to improve selectivity is also discussed. It is shown how micro kinetic modelling can be used to predict how the catalyst for the WGS reaction could be improved. Furthermore, an experimental technique is demonstrated, where alloys consisting of up to four metals can be tested under realistic conditions without loosing the ability to study the catalysts with surface science techniques both prior to and after they have been subjected to reaction conditions. Finally, the importance of in situ measurements will be demonstrated for some preliminary investigations of systems of relevance to fuel cell technology.

Keywords: Reactivity; Screening; In situ PM-IRRAS; Alloy; Micro kinetic modelling

1. Introduction

In this overview, we shall describe a number of approaches for finding new and improving existing catalyst systems for use in large-scale industrial production of chemicals and energy. Our approach relies to a large extent on gaining a fundamental understanding of the catalyst material on the molecular level and to utilize this knowledge in the catalyst formulation. We also rely heavily on DFT calculations and enjoy a close collaboration with a very strong theory group that is supplying us with valuable information on details on reaction steps and trends in reactivity for different metals and alloys. In the following, we shall demonstrate how the philosophy illustrated in Fig. 1 is applied to catalyst development in our laboratory.

2. Reactivity of mono atomic step sites

The insight that mono atomic steps may have an extremely strong impact on surface reactivity has had a profound impact on our research [1]. Atomic steps and defects were suggested by Taylor [2] to be more active than atoms on terraces even before surface science was capable of elucidating this phenomenon. The terms structure sensitive and structure insensitive reactions have been used by, for example, Boudart [3]. An interesting example is the technologically important steam reforming process [4] see Eq. (1), where the forward rate is known to be structure sensitive [5], while the reverse reaction—the methanization reaction has been deemed structure insensitive in a pioneering work by Goodman [6].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (1)$$

The result that the ability of a ruthenium surface to dissociate molecular nitrogen relies solely on the presence of mono atomic steps [1], and that these steps are more than nine orders of magnitude more reactive than the atoms on the terraces started a number of both experimental and theoretical studies aimed at investigating how general this effect was. Theoretical studies revealed that the effect consisted of two contributions: First, there is the effect of under-co-ordinated sites sitting at the edge of the mono atomic steps. Their increased reactivity can easily be

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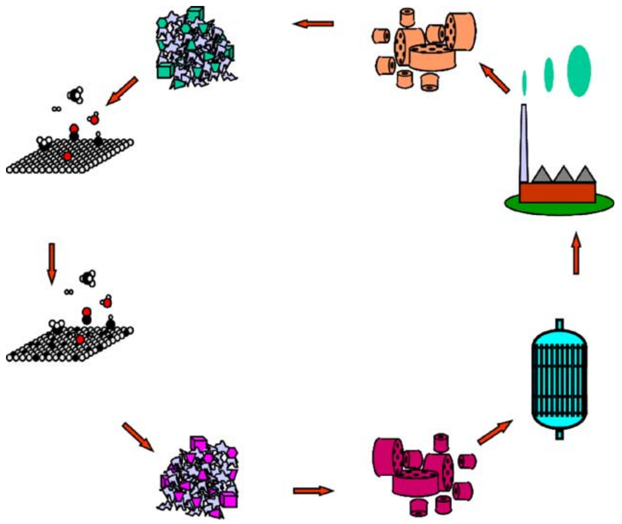

Fig. 1. An illustration of the interdisciplinary approach. To the left, the fundamental investigations rely heavily on the surface science approach. But there is not much perspective in surface reactivity if it is not realized by synthesis of real catalysts, as illustrated by the middle section. Finally, the ultimate test of a useful catalyst is that it can actually catalyse a reaction and that it can be produced and handled in a reactor. Testing here may, however, give feedback to the fundamental studies for further improvements realized when meeting realities completing the cycle.

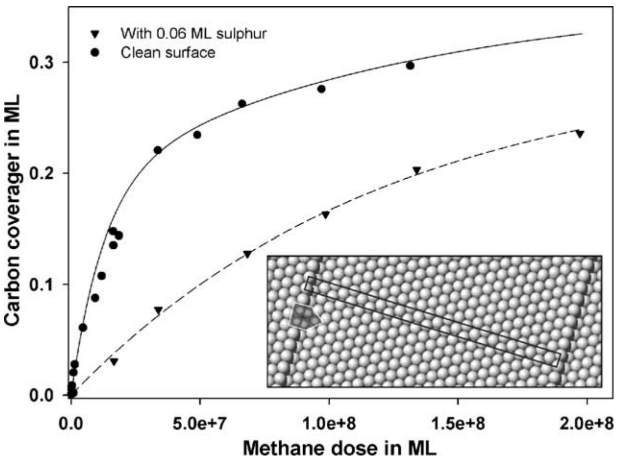

Fig. 2. Carbon uptake curves measured when exposing the Ni(1 1 1) surface with (1 1 0) steps to increasing doses of methane. The upper curve shows the uptake for the clean crystal, while the lower curve shows the uptake for a situation where all the mono atomic steps are covered with sulphur. The insert shows a model of the Ni(14 13 13) surface with indication of the unit cell and a so called B5 site.

explained in terms of the d-band model proposed by Hammer and Nørskov [7]. This model also nicely explains the structure sensitivity and trends in reactivity when going from the close packed surface towards the more open structure. The stepped surfaces can, naturally, be considered to be the ultimate open surface. The second contribution stems from the fact that a new ensemble can take part in the reaction dissociating the molecule. On the plane surface, the ensemble reacting with nitrogen consists of four ruthenium atoms, whereas on the mono atomic steps five atoms can be involved—a so-called B5 site. In this way, none of the ruthenium atoms has to be shared by two nitrogen atoms. This leads to a substantial reduction of the activation barrier for the dissociation by two-thirds, and is thus, the major source of the enhancement seen. Density functional calculations by Nørskov et al. [8] have predicted that this is a general phenomenon for a number of, especially, di-atomic molecules, but that the principle also applies to, for example, the important class of C–C bond scission. In the following, we shall discuss some of our recent experimental investigations to reveal what effect the presence of steps may have in relation to the steam reforming process discussed above and how this may be utilized, for example, for selectivity control in the future design of catalysts.

Fig. 2 shows the uptake of carbon on a stepped Ni(14 13 13) single crystal measured as a function of methane dose [9]. The structure of the Ni(14 13 13) crystal is shown as an insert and is basically a Ni(1 1 1) crystal with lines of mono atomic steps for every 27 terrace atoms exposing the B5 sites discussed above. The upper curve shows the carbon uptake on the clean crystal, while the lower displays the effect of adding 0.06 Ml of sulphur to the surface. The sulphur is known to block the steps just as gold does on ruthenium, and it therefore, specifically blocks all the step sites. (Gold also works on Ni, but the situation is somewhat more complex due to the fact that gold also forms a surface alloy here [10].) Thus, it is possible to reveal the effect of the steps on methane dissociation and it is found that the steps are roughly a factor of 150 more reactive than the terrace atoms. This reactivity is primarily due to a localized transition state of the methane molecule reacting on a single atom on the step. Therefore, the reaction is only influenced by the electronic effect of the under co-ordinated atom sitting here [9]. This is in good agreement with the theoretical calculation made by Beengard et al [11]. Now, turning to the reverse process the situation is much more pronounced. Here, the amount of carbon increases continuously for the clean surface, while basically no carbon can be observed under the same conditions when the step sites of the Ni(14 13 13) crystal has been poisoned. This is in good agreement with other measurements and in reasonable agreement with calculations [11]. Thus, we agree with the earlier observations that the forward rate of the steam reforming is structure sensitive, but certainly not to the interpretation of earlier data where the reverse rate should be structure insensitive. Instead, our data suggest that the backward reaction is extremely structure sensitive and that the reactivity seen for different vicinal surfaces Ni(1 1 1) and Ni(1 0 0) [6] is merely a result of the fact that any such surface will always contain mono atomic steps. Since, the latter are extremely reactive, especially towards di-atomic species, such as CO, they can completely dominate the overall reactivity due to the fact that both the electronic and the geometric effect can come into play.

Thus, there are two ways of utilizing this strong effect of the mono atomic steps or the so called B5 sites: For some

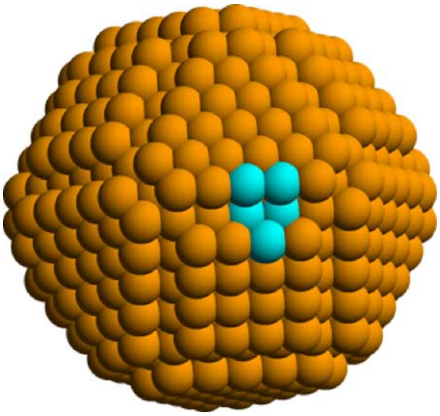

Fig. 3. A schematically shown nanoparticle exposing the simple basal planes and a B5 site.

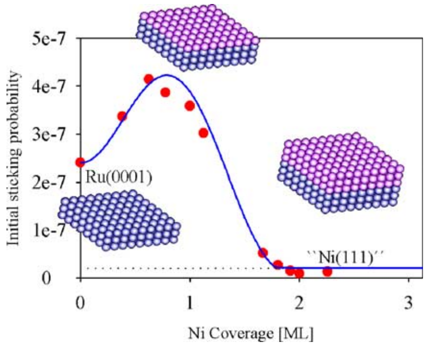

Fig. 4. The reactivity for dissociation of methane on pseudomorfic overlayers of nickel on ruthenium.

reactions, like, for example, for the ammonia synthesis and the steam reforming, we would like to have as many steps as possible. It is thus, not just a matter of getting the smallest possible particles in the catalyst in order to gain the highest possible area, but much more important to get the particles of such shape and morphology that they can accommodate the B5 sites. Such a particle is illustrated in Fig. 3. An example of this has been illustrated for the ammonia synthesis on Ru supported on a Al_2MgO_4 spinel [12].

The second area where the realization of this strong enhancement by steps may play an important role is in controlling selectivity. For example, in hydro- or dehydrogenation reactions it is mandatory to avoid scission of other bonds than the X–H bonds. Here, the knowledge on what controls the presence of steps and, in particular, how to block them under reaction conditions could be very valuable for gaining higher selectivity, i.e., converting alkanes into alkenes by dehydrogenation avoiding C–C bond braking. Thus, the presence of steps and their reactivity is an area of particular interest for our laboratory.

3. Trends in reactivity

The recent insight provided by the d-band model [7] and the effect of strained and compressed metal overlayers [13,14] have given much inspiration concerning the trends in reactivity and especially on how to modify existing system into, hopefully, better catalysts. An example of how this works is demonstrated in the following [15]: as we have seen, methane dissociation works well on nickel and it is actually even better on ruthenium. But what happens if we grow a layer of nickel, one atom thick, on ruthenium? Using the models, nickel should be strained if it is growing pseudomorphically on ruthenium, since the latter has a larger lattice constant. The theory, therefore, predicts that the overlayer should be more reactive than pure nickel. This is indeed what is seen experimentally in Fig. 4. The overlayer is not only more reactive than nickel, but it is even more reactive than ruthenium. Thus, taking a less reactive metal and growing it pseudomorphically on a more reactive metal can make the overlayer more reactive than the pure metals. Another similar and also, we think, counter intuitive effect has been observed for cobalt on copper for the same reaction [16]. Cobalt is reactive towards methane dissociation, whereas copper is not at temperatures below 600 K. Nevertheless, taking the more reactive cobalt and growing it on the unreactive copper makes an overlayer that is more reactive than cobalt [16]. Thus, although quite academic, the cobalt copper results clearly show that a new and well-understood playground for increasing/decreasing reactivity is available.

It is naturally necessary to know whether the reactivity for a particular reaction needs to be enhanced or decreased. This depends critically upon the overall reactivity of the surface. Sometimes, the surface is basically empty of reactants and intermediates and it is essential to decrease the barrier for the rate-limiting step in order to enhance the overall reactivity. Thus, in this case, the surface should be made more reactive. In other situations, the surface is covered to such an extent that basically no free sites are available where the, still, rate limiting step can take place. In such cases it is more important to decrease the overall reactivity of the surface in order to free active sites. This is the well-known principle of Sabatier [17], which leads to the volcano curves in catalysis. Through the Principle of Universality in Catalysis which states that the activation energies and the bonding energies are strongly correlated through the Brøndsted–Evans–Polanyi relation, one can actually find that the most suited catalysts are those with a specific bonding energy for some of the intermediates. Here, it is shown that the trends in reactivity can conveniently be described by a single descriptor, such as, for example, the nitrogen bonding energy, as shown for the ammonia synthesis [18]. We have recently tried to apply this idea to a more complicated system, namely, the Water Gas Shift reaction (WGS) where most of the DFT data are available. By using existing models [19] and data bases for bonding and activation energies calculated with DFT it was possible to show that many bonding energies are actually correlated. Since, the activation energies for the presumed rate limiting steps are correlated through the Brøndsted–

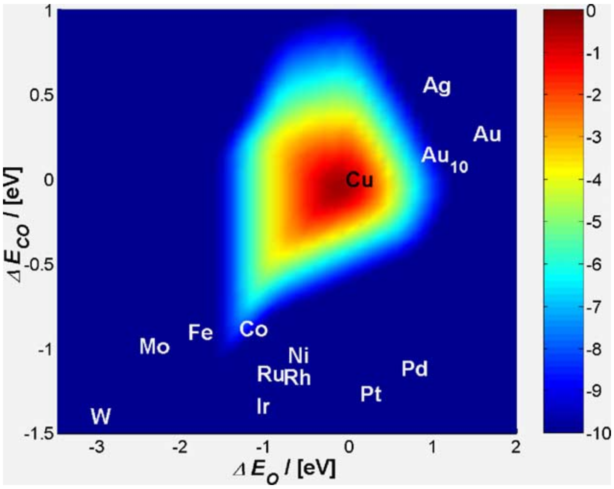

Fig. 5. A close up of the maximum turnover frequency (TOF) at p = 30 bar, T = 225 °C, and a feed gas composition of 2.5% CO, 12.5% CO_2, 37.5% H_2, 25%, H_2O, and balance N_2. Based on chemisorption energies from Nørskov and co-workers [18]. Adapted from [20].

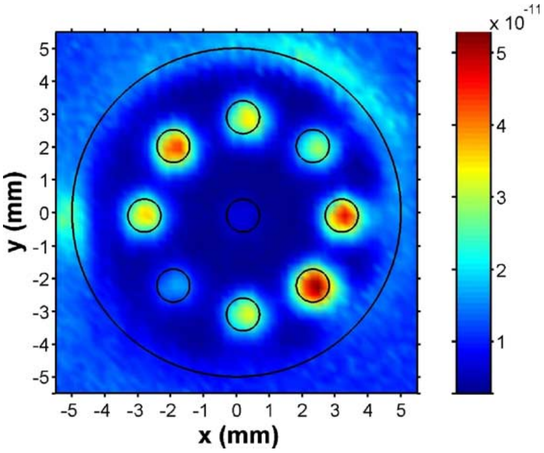

Fig. 6. The H–D signal measured over an oxidized Al sample with 9 Pd/Ni spots. The gas mixture consisted of 1.4% H_2 and 1.4% D_2 in Ar at a total pressure of 1 bar. The temperature was 250 °C. Usually, the local H–D signal over the centre of each spot is taken as a measure of their activity, and a complete catalytic map, as the one above, is not measured.

Evans–Polanyi relations it was possible to reduce ten different parameters to two so called descriptors which proved to be the oxygen and CO bonding energies [20]. In this manner, the micro kinetic model can predict the rate for the reaction as a function of the bonding energies. The result is shown in Fig. 5 as a three-dimensional plot. Different metals are superimposed on the plot for reference. It is immediately clear that although the model describes the reactivity of different metals qualitatively it completely fails to describe them quantitatively. This has to do with the fact that the coverage dependence of the binding energies is neglected in the micro kinetic model.

Thus, the calculation shows clearly that, for example, platinum is a very poor catalyst because it is completely poisoned by CO, while in fact, it is quite a reasonable WGS catalyst. Thus, the important outcome of this exercise is not the overall trends but merely the results that copper is quite close to the maximum and that the way to improve the existing catalyst, which is copper based, is to improve its reactivity slightly towards CO and oxygen. This could for instance be done by the method of forming strained overlayers of copper on other substrates, as described above, provided that the overlayers can be made stable under realistic reaction conditions. The latter is naturally the great challenge when applying these theoretically principles to real catalysts.

In order to investigate and test different ideas for catalyst design, we have recently constructed an apparatus that can perform screening of model alloy catalysts [21] consisting of up to four different metals. The alloys are synthesized in situ by electron beam evaporation of spots, 1 mm in diameter, on a support material, e.g., graphite. The sample can then be transferred to a high-pressure cell where the reactivity of each individual spot can be tested by flowing reactants over the spot of interest, while probing for the relevant products with a gas sampling device, see [21] for details. By scanning the sampling device over the surface, the local reactivity can be monitored, as shown in Fig. 6. In the figure, the locations of the support and the spots are indicated by black circles.

The reaction studied here is the exchange of hydrogen and deuterium into H–D over increasing amounts of platinum deposited on nickel. The objective of investigating this relatively simple reaction is to find new alloys and metal overlayer systems that can replace platinum in the low temperature Proton Exchange Fuel Cells (PEMFC), a field that has received much interest lately [22]. A simple estimate reveals that even with the lowest loadings of platinum used today, the use of these fuel cells for automotive applications would require roughly 20 g platinum per automobile. The annual production of platinum only amounts to some 190 tonnes a year [23], which corresponds to the requirement for constructing 10 mio. automobiles. When this is compared to the 750 mio. vehicles in the world today, one immediately sees the requirement for a cheaper, less scarce material than platinum. The exchange reaction is a convenient way to measure the ability of different alloys to dissociate hydrogen, and thus, their ability to act as the anode material in the fuel cell. The result as a function of temperature is shown for the individual spots in Fig. 7. It is easily seen that platinum is superior to any of the platinum overlayers deposited on nickel. The reason is that platinum and nickel easily alloys in the surface and nickel simply bonds hydrogen too strongly. The alloying is easily seen by taking the samples back into the UHV chamber where we can use standard surface sensitive methods like Auger electron spectroscopy (AES), X-ray electron spectroscopy (XPS), low energy ion spectroscopy (LEIS), and temperature programmed desorption (TPD) for characterization. Thus, we can get full information of the composition of the individual alloy spots both before and after the reactivity test and in this manner not only get information on which ones that are working, but also why. The post mortem

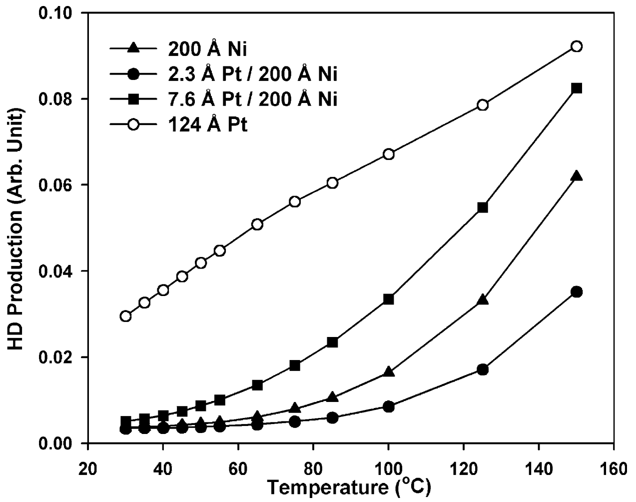

Fig. 7. The H–D exchange rate on Pt overlayers on Ni. Ni spots (200 Å) are evaporated, and, on top of those, varying amounts of Pt are evaporated. The activity is measured in a flow of 3.3% H_2 and 3.3% D_2 in Ar at a total pressure of 1 bar. Pure Pt is observed to be a far superior catalyst, showing high activity even at room temperature.

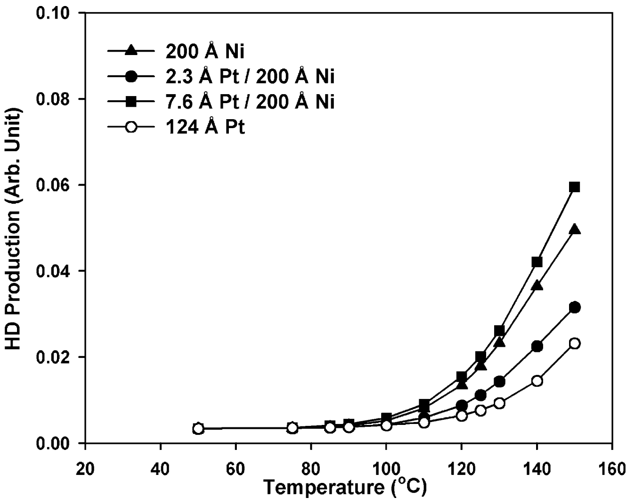

Fig. 8. The H–D exchange rate on Pt overlayers on Ni in the presence of CO. The activity is measured in a flow of 3.3% H_2, 3.3% D_2 and 0.9 ppm CO in Ar at a total pressure of 1 bar. In the presence of only 0.9 ppm CO the situation is reversed completely from that in Fig. 7; Pt now exhibit the worst activity. Although none of these spots exhibit a measurable activity at temperatures interesting for the use in a PEM fuel cell (<80 °C), it is interesting that, whereas the activity first drops with increasing Pt overlayer thickness, it suddenly increases and becomes more active than both pure Pt and pure Ni.

analysis is particularly important because it also give us detailed information on changes in the alloy composition induced by the chemical potential in the high-pressure cell. Needless to say, this also provides full control of the cleanliness of the system, which is always a major problem when performing measurements at or above atmospheric pressure. The finding of replacement materials for platinum is not the only issue. It is also highly desirable to find materials that are less prone to be poisoned by impurities present in the hydrogen. One particular problem is posed by CO, which will be a common impurity as long as the hydrogen is produced from fossil fuels according to Eq. (1). The effect of CO can easily be elucidated by adding just 0.5 ppm of CO to the hydrogen/deuterium mixture and again measure the exchange rates as shown in Fig. 8. The trend in exchange rate is now completely changed as the pure platinum appears to be the least active catalyst, while the nickel spots with an overlayer of platinum appears the best, although there is an overall reduction in the rate of all the catalysts. This effect can easily be understood in the framework of the d-band model: The platinum deposited on, or alloyed into, the nickel will be compressed due to the smaller lattice constant of the latter. Its reactivity will, therefore, decrease and it will bond CO less strongly than the pure platinum, and therefore, not be blocked/poisoned to the same extent. Exactly the same mechanism can also explain why the platinum/ruthenium catalyst is much more effective than the conventional Pt catalyst in fuel cells. It should be mentioned that this is an area of some disagreement. The experiments shown here are performed without water or any electrical fields present, in contrast to the situation in a real fuel cell. In electrochemical investigations, another mechanism is also possible for reducing the blocking effect of CO, namely, oxidation of the adsorbed CO by water. This can only occur at a considerable overpotential, but the overpotential can be lowered by adding, for example, ruthenium to the surface. We have also performed similar experiments on real fuel cell catalysts and seen that the CO bonding energy is crucial for the poisoning effect and that lowering the bonding energy would decrease the poisoning effect at reasonable overpotentials [24]. Nevertheless, this is still an area of ongoing discussion and various schemes for adding water to the high-pressure cell experiments are now being tried out. Having added water it is also possible to start searching for new alloy compositions that may improve the WGS reaction, since we now have a general idea based on the volcano plot where to look for better catalysts. Also here, the stability of the overlayers and alloys is essential.

4. In situ measurements

Improving catalysts requires a detailed understanding of the rate limiting step and information on what kind of species that are present on the surface under reaction conditions. In the case of CO present in the hydrogen gas fed to a fuel cell, it is quite easily recognized that the CO bonding energy constitutes a problem, but for more complicated reactions identifying the parameters that control reactivity may be a considerable problem. For example, by combining experimental effort and micro kinetic modelling, we have earlier shown that the rather stable formate is an important intermediate in the methanol synthesis over copper [25], and that formate, at higher pressure, may also be a spectator in the WGS reaction blocking sites [26]. However, the best way to judge whether a species is present is naturally to be able to detect its presence during reaction conditions or at least under some conditions approaching the real conditions. We have, therefore, converted existing equipment for high-pressure experiments on well-defined single crystal surfaces, so that it is also possible to monitor surface species under reaction conditions with the help of IR spectroscopy.

Infrared spectroscopy is a method that can be used successfully under ambient conditions and for in situ measurements. However, the gas phase will often absorb IR light at the same frequencies as the surface species, and therefore, special precautions must be undertaken in order to study species adsorbed on a surface. Molecules adsorbed on a metallic surface can only absorb infrared radiation if the species has an active dipole standing normal to the surface. This means that the surface species are only observed if the incoming light is p-polarized. The gas phase, however, is insensitive to this selection rule and will absorb both s- and p-polarized light if the gas molecules possess the necessary dipole moment. Thus, if one measures first with p-polarized light and then subtracts the result obtained with s-polarized light, and normalize with the sum of s-polarized and p-polarized light, a spectrum with contributions solely from adsorbed species is achieved. This technique is called PM-IRRAS and is performed by switching between the two polarizations with 100 kHz in order to eliminate time variations in the cell. Such an experimental set up has recently provided very nice results on the reaction of CO and NO at elevated pressure and temperatures in the group of Goodmann and co-workers [27] and we shall here present some initial experiment performed with our set up.

In a previous work, where we investigated the effect of CO poisoning on fuel cell catalysts, an exchange method of labeled CO was utilized to extract the desorption rate as a function of coverage for a fixed temperature [24]. The desorption rates extracted proved to be much higher than those predicted from the oxidation mechanism both for the pure platinum, and for the platinum/ruthenium catalysts [28]. Now, having this new set up, it was tempting to see how a well-defined single crystal behaved under such conditions. The exchange rate can easily be found by measuring the absorption line around 2052 cm^{-1} due to the internal CO vibration of CO molecules in the on-top position. Also, the bridge bonded CO is easily observed although considerably weaker at 1809 cm^{-1}. By placing the crystal saturated with $C^{18}O$ in the high-pressure cell and letting in normal CO the exchange process can be followed in time. In Fig. 9, this exchange process is followed by taking spectra as fast as possible with reasonable statistics. It is clearly shown that the above-mentioned features are vanishing, while new features belonging to the normal CO at 1852 and 2094 cm^{-1} grows in. What was much more surprising was that the pressure needed for this exchange was much smaller than what was expected from the measurements on the real catalyst. This is probably due to a profound difference in the nature of adsorption of CO on extended single crystals as compared to the small nanoparticles present in the real catalyst. This difference will be the issue of a forthcoming publication [29], where the influence on the adsorption of CO of a hydrogen pressure of 1 bar is also being investigated. This kind of investigation has mainly been performed by using second harmonic generation [30], but they can equally well be done by this somewhat simpler and cheaper method. Our long-term objective is to use PM-IRRAS to investigate whether there are strong interactions between the adsorbed reactants and intermediates present under reaction conditions that has not or could not be revealed with the usual surface science methods. Such information may have a strong impact on our understanding of how a specific chemical reaction proceeds. One reaction of particular interest is the methanol reforming process, which is of great importance for the direct methanol fuel cell. According to the literature, there are several mechanisms influencing the rate of this reaction [31,32]. By performing experiments on the more well-defined single crystal, it is our hope to identify the most important steps and by the principles described above devise methods to improve on these by, for instance, alloying or step management.

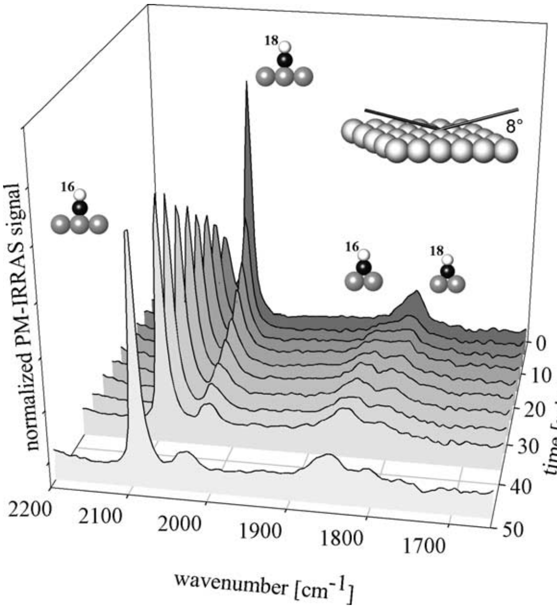

Fig. 9. The subsequent PM-IRRAS spectra of the CO stretch region, while the $C^{18}O$ is being exchanged by normal CO. The experiment was performed at room temperature in a background of $p_{CO} = 1.2 \times 10^{-6}$ mbar.

5. Summary

Our approach for developing new and better catalysts is based on fundamental investigations of the basic mechanisms, relying on interplay with theoretical predictions. Realizing the importance of mono atomic steps for some reactions, has prompted a number of researchers to investigate to what extent this is a general phenomenon.

The influence of steps may be further explored in order to improve overall selectivity by enhancing activity under some conditions, while reducing it under other conditions. We have discussed the possibility of combining micro kinetic modelling with screening measurements for optimization of catalysts by alloying. It is also demonstrated how these experiments can be performed in a semi-parallel form without loosing the possibility to determine the exact surface composition before and after the high-pressure experiments. Finally, we have demonstrated the importance of being able to perform in situ experiments in order to reveal important reaction steps.

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