T H E C H E M I C A L R E C O R D

Cluster, Facets, and Edges: Site-Dependent Selective Chemistry on Model Catalysts

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ABSTRACT: More than activity, selectivity of catalytic reactions is the focus of research in the 21st century. We review studies on model systems that address the issue of directing a catalytic reaction on disperse metal catalysts by controlling the specific surface site. Three examples are explored: methanol dehydrogenation over Pd/alumina, NO dissociation on Pd/alumina, and reaction studies for molecules relevant in a Fischer-Tropsch scenario on a bimetallic Pd/Co/alumina model catalyst. We show how surface science can be used by combining a variety of experimental techniques to study the chemistry of model catalysts at the atomic level. © 2003 The Japan Chemical Journal Forum and Wiley Periodicals, Inc., Chem Rec 3: 181–200; 2003: Published online in Wiley InterScience (www.interscience.wiley.com) DOI 10.1002/tcr.10060

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Introduction

The catalytic cycle is the basis for catalytic action.¹ A catalyst is, according to Michel Boudart² (see also chapter 1.1 in ref. 1), a substance that transforms reactants into products, through an uninterrupted repeated cycle of elementary steps in which the catalyst participates while being regenerated in its original form at the end of each cycle. The catalyst's activity represents the number of revolutions of the cycle per unit time (turnover rate). On real catalysts there are different active sites exposed, and also "the amount of surface which is catalytically active is determined by the reaction catalyzed", as Taylor stated in his groundbreaking article in 1925.3 In other words, if a reaction can proceed along different pathways, being a branching reaction, a consecutive reaction, or a combination of such reactions, specific regions or sites on the surface may be responsible for a specific reaction path. Thus, understanding the relation between surface heterogeneity, morphology, and chemical reactivity will provide us with key insight into what researchers

in catalysis call "selectivity".² The latter quantity is defined as the amount of a desired product obtained per amount of consumed reactant. In other words, if a reactant can undergo a variety of reactions it is quite likely that different specific surface sites are responsible for different reaction channels. Thus, by understanding the interrelation, we may be in a position to manipulate the selectivity on an atomic basis. If we achieve this, we have reached an important goal in catalysis, which is as important as optimizing catalyst activity. It appears that reaching 100% selectivity is one of the key tasks for present and future research in catalysis.

In the present article we would like to address the atomic approach to selectivity in heterogeneous catalysis by studying chemical reactivity of model catalysts that have been prepared

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under ultrahigh vacuum conditions and fully structurally characterized. In this way structure-reactivity relations can be established. As examples we have chosen methanol dehydrogenation,⁴ NO-dissociation on Pd nanoclusters,⁵ and reaction studies on molecules relevant in a Fischer-Tropsch scenario on bimetallic (Pd-Co) deposited particles.⁶ In all cases the metal particles are deposited on an alumina thin film model support.^{7–18}

Model Catalysts

In a technical catalyst, a catalytically active component such as a transition metal is dispersed over a suitable support material —usually¹⁹ an oxide like alumina or silica. In the first place, this is done in order to achieve the highest possible surface area of the active phase. There is still only very limited fundamental knowledge about the relationship and the interplay between structure, adsorption behavior, and chemical or catalytic activity of small deposited metal aggregates. Because the complex structure of real catalysts often hampers the attempt to connect macroscopic effects with the microscopic processes taking place on the surface, an increasing number of model studies have been conducted so far to tackle these questions.

Recently, a number of reviews concerning the "surface science approach" have been published taking a critical look at the different strategies to compose and explore model catalysts.^{10,16,18,20–24} *Advances in Catalysis* has dedicated an entire



Hans-Joachim Freund (born 1951) studied physics and chemistry at the University of Cologne and received his Ph.D. in 1978 with a thesis on quantum chemical calculations and spectroscopic studies on transition metal carbonyl compounds in comparison with carbon monoxide adsorbates. Between 1979 and 1981 he worked in the Physics Department at the University of Pennsylvania as a postdoctoral fellow on synchrotron studies of the electronic structure of adsorbates. After having returned to Cologne he finished his habilitation in 1983 and accepted in the same year a position as Associated Professor at the University Erlangen-Nürnberg. In 1987 he moved to a position as full Professor for Physical Chemistry at the Ruhr-Universität Bochum. In 1995 he accepted a position as Scientific Member and Director at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, where he is head of the Department of Chemical Physics. He serves as Adjunct Professor of the Ruhr-Universität in Bochum, and of the Freie Universität, Technische Universität, and Humboldt Universität in Berlin. In 1995 he received the Gottfried Wilhelm Leibniz Award of the German Science Foundation (DFG) and since 1996 he has been an ordinary member of the Chemical Sciences Section of the Academia Europea as well as of the Berlin-Brandenburgische Akademie der Wissenschaften since 1998. He has been Fellow of the American Physical Society since 2001. He is a member of several scientific societies and of several advisory boards of scientific journals and has published more than 350 scientific papers.



▶ Jörg Libuda is Staff Scientist at the Department of Chemical Physics of the Fritz-Haber-Institut der Max-Planck-Gesellschaft (Berlin, Germany). Born in 1968 in Bochum (Germany), he received his Ph.D. in 1996 from the Ruhr-Universität Bochum. In 1996, he set up a workgroup performing molecular beam experiments on model catalysts in the department of Professor Freund at the Fritz-Haber-Institut (Berlin). From 1998 to 1999 he joined Professor Giacinto Scoles' group at Princeton University (Princeton, USA) as a postdoctoral fellow. He received a grant of the Studienstiftung des Deutschen Volkes, was awarded the Otto-Hahn-Medal of the Max-Planck-Society, and is author or coauthor of more than 50 publications in international journals. As the head of the molecular beam group in the Department of Chemical Physics (Fritz-Haber-Institut), his research interests include the kinetics and dynamics of chemical reactions at complex surfaces. His recent work has focused on an understanding of reaction kinetics on heterogeneous catalysts at the molecular level. ■ issue to this area recently.²⁵ The spectrum ranges from studies based on polycrystalline or amorphous oxide substrates²⁰ to investigations on oxide single crystals or well-ordered films.^{10,16,21-24} Also with respect to the preparation of the par-

ticles, different concepts have been proposed. One approach is to apply techniques that come as close as possible to industrial catalyst manufacture, like wet impregnation or exchange in solution.²⁰ Unfortunately, this often involves the disadvantage



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▶ Thomas Risse was born in Cologne, Germany, in 1967. He received his doctorate in Physical Chemistry from Ruhr-University Bochum under the Supervision of Professor Freund. Since 1997 he has been a group leader in the Department of Chemical Physics at the Fritz-Haber-Institute. From 1999 to 2000 he spent year at the University of California in Los Angeles working with Wayne Hubbell. His research interest is focused on the application of electron spin resonance spectroscopy to well-defined single crystal surfaces. The systems investigated range from magnetic properties of small metal particles and paramagnetic centers in solids, such as color centers, to site-directed spin labeling of adsorbed proteins. ■



▶ Anders Carlsson was born in 1975 in Sweden. He studied Chemical Engineering at the University of Minnesota from 1993 to 1997. He received a Master's degree in Chemical Engineering at Stanford University in 1998 and a Ph.D. in the same field also from Stanford University in 2001. In the same year he was awarded a National Science Foundation fellowship for research at national Taiwan University. From 2001 to 2003 he performed research at the Fritz-Haber Institute of the Max-Planck Society in the Department of Chemical Physics in Berlin, Germany, on the basis of a fellowship awarded by the Alexander-von-Humboldt Foundation.



Fig. 1. Scanning tunneling images $(1000 \times 1000 \text{ Å})$ of: (a) clean alumina film on NiAl(110); (b) 0.2 Å Pd deposited at 90 K; (C) 2 Å Pd deposited at 300 K; (d) 0.2 Å Pd deposited on the prehydroxylated film at 300 K.

that structure and morphology of the deposits are rather difficult to control. Thus, vapor deposition of metals^{10,16,18,21-24} or deposition of metal clusters from the gas phase²⁶ under UHV conditions have been preferred in experiments keyed to more fundamental questions about the correlation between structure and properties of small metal particles.

In this context, ultra-thin oxide films grown on a metallic substrate are an excellent choice in order to circumvent problems^{10,16,18,21-24} connected with the insulating nature of some bulk oxides. It has been shown that even films with a thickness of just a few angstroms can exhibit physical properties characteristic of the bulk material.^{27,28} This idea was expressed by authors early on²⁹ and seems to have been accepted now²⁸ after a long controversial discussion. Various groups have extensively explored preparation techniques based on the evaporation of a metal (or nonmetal) onto a host crystal—mostly a refractory metal—in an ambient oxygen atmosphere.^{23,24,30–32} Another promising possibility is the oxidation of a suitable alloy sample containing the metal that should be oxidized. A well-known example of that kind is the formation of well-ordered thin alumina films on the low index surfaces of certain Al alloys,^{7,8,33–37} but it is not unlikely that this approach also works in other cases.³⁸ An overview of some well-ordered thin oxide films described in the literature can be found in ref. 15.

In Figure 1 we show results on an alumina-based model system that has been prepared by oxidation of an NiAl(110) surface and studied via STM in our laboratory.¹⁵ The upper left panel (a) shows the clean alumina surface as imaged by a scanning tunneling microscope.⁸ The surface is well ordered and there are several kinds of defects present. One type consists of reflection domain boundaries between the two growth

directions of Al₂O₃(0001) on the NiAl(110) surface.⁷ There are antiphase domain boundaries within the reflection domains, and, in addition, there are point defects that are not resolved in the images. The morphology does not change dramatically after hydroxylating the film.³⁹ The additional panels show STM images of palladium deposits on the clean surface at low temperature (b), and at room temperature (c), 15,40 as well as an image after deposition of Pd at room temperature on a hydroxylated substrate (d).41 The amount (given as an average uniform layer thickness in Angstrom as determined via a quartz-balance) deposited onto the hydroxylated surface is equivalent to the amount deposited onto the clean alumina surface at room temperature. Upon vapor deposition of Pd at low temperature small particles (the protrusions shown in Fig. 1b) nucleate on the point defects of the substrate and a narrow distribution of sizes of particles is generated. If the deposition of Pd is performed at 300 K, the mobility of Pd atoms is considerably higher so that nucleation at the line defects of the substrate becomes dominant (features line up with the bright lines in Fig. 1c). Consequently, all the material nucleates on steps, reflection domain, and antiphase domain boundaries. The particles have a relatively uniform size, in turn depending on the amount of material deposited. If the same amount of material is deposited onto a hydroxylated surface, the particles (the protrusions shown in Fig. 1d) are considerably smaller and distributed across the entire surface, that is, a much higher metal dispersion is obtained that is very similar to the dispersion found at 90 K.39

The sintering process is an interesting subject. Research on this process is just beginning.¹⁵ A more basic process is metal atom diffusion on oxide substrates. Diffusion studies⁴² could profit from atomic resolution, once it is obtained for deposited aggregates on oxide surfaces. While for clean TiO₂ surfaces and a few other oxide substrates atomic resolution may be obtained routinely, there are few studies on deposited metal particles where atomic resolution has been reported.⁴³ A joint effort between Fleming Besenbacher and our group⁴⁴ has lead to atomically resolved images of Pd aggregates deposited on the thin alumina film. Figure 2a shows such an image of an aggregate of about 50 Å in width. The particle is crystalline and exposes on its top a (111) facet. Also, on the side, (111) facets, typical for a cubooctahedral particle, can be discerned.

The cluster on the oxide support is schematically represented in Figure 2b. Terrace sites and edge, corner, and interface sites are differently shaded in order to make their specificity obvious. These "extra sites" in combination with the finite size of the facets render the situation on a cluster different from the one encountered on a single-crystal metal surface.⁴⁵

It is obvious that progress has been made towards a controlled preparation of simple model catalysts, however, the question remains how model systems for more complex



Fig. 2. (a) Scanning tunneling images of a room temperature Pd deposit on $Al_2O_3/NiAl(110)$. The inset shows an individual deposit in atomic resolution.⁴⁴ (b) Schematic representation of a cubooctahedral metal cluster on a substrate.

systems can be prepared in a defined and reproducible manner.⁴⁶ Bimetallic catalysts, for example, represent a highly interesting class of catalysts. This is due to the fact that one metal can tune and/or modify the catalytic properties of the other metal as the result of both ligand (electronic) and ensemble (structural) effects.⁴⁷ Bimetallic clusters of Pd and Co, for example, have shown improved selectivity over pure Co in Fischer-Tropsch reactions.⁴⁸⁻⁵² Because the conversion of



Fig. 3. STM images $(100 \times 100 \text{ nm})$ taken after depositing 2Å Pd and 2Å Co alone (top panels) and together (bottom panels) onto a thin alumina film at 300 K. In the latter case the metals have either been deposited subsequently (left: 1st Pd, 2nd Co; right: 1st Co, 2nd Pd).

natural resources into syngas $(CO + H_2)$ and then to clean fuels through the Fischer-Tropsch reaction will likely become evermore important with changing supplies and environmental concerns,⁵³ a detailed understanding of such effects by means of suitable model systems is urgently needed. As in the case of pure Pd particles the preparation of the bimetallic particles is based on metal vapor deposition onto a thin alumina film. On this film, nanometer-sized Pd-Co particles are generated by *sequentially* depositing the two constituents onto this support. Inspired by earlier work by Henry and coworkers relying on codeposition techniques,^{54,55} different structures and compositions were obtained in a controllable way by taking advantage of the different nucleation and growth properties of the two metals. This is demonstrated in Figure 3 by STM images taken after depositing Pd and Co alone and together on this film.⁴⁶ In the case of pure Pd, the data show that the majority of Pd particles nucleate and grow at line defects of the support. These line defects, appearing as protruding lines in the differentiated part of the image (upper left corner), are antiphase and reflection domain boundaries of the alumina film.⁵⁶ Another point to note is the regular shape of the aggregates, suggesting that they have a crystalline structure. Closer inspection has shown the sides and top to be mainly formed by (111) faces.⁴⁴ In contrast, pure Co preferentially nucleates at point defects on the alumina film.^{57,58} As can be inferred from the corresponding STM image, this results in both a higher particle density and a more homogeneous particle distribution

on the surface. Unlike Pd, there are no indications of crystalline order.

Let us now assume that Pd is deposited on a surface already covered by Co particles. Due to the higher mobility of Pd on the surface, it will be trapped at Co particles before reaching the line defects. The STM image presented in Figure 3 essentially corroborates this expectation. The arrangement of particles found for this sequence strongly resembles the situation for pure Co, thus suggesting particles with a Co core and a Pd shell. If, on the other hand, Pd is deposited first, the less mobile Co atoms should partly cover the Pd crystallites and partly nucleate between them. The STM image (Fig. 3) indeed shows triangular and hexagonal crystallites as well as a number of new small clusters in between.

Site Specific Reactivity

Herein we present evidence for the specific activity of coexisting sites on a well-defined supported nanoparticle system.⁴ As a model reaction we choose the decomposition of methanol on well-ordered Pd crystallites.⁴ For this reaction system two competing decomposition pathways exist: whereas dehydrogenation to CO represents the dominating reaction channel,^{59,60} slow carbon-oxygen bond breakage leads to formation of adsorbed carbon and CH_x species.⁶⁰⁻⁶²

We show that on ordered Pd crystallites these carbon and hydrocarbon species preferentially block defect sites on the particles such as particle edges and steps (see Fig. 4). With increasing carbon coverage, the rate of carbon-oxygen bond breakage drops rapidly, whereas the kinetics of dehydrogenation is hardly affected. From this, we conclude that activity for carbon-oxygen bond breakage is drastically enhanced at the particle defect sites, whereas this is not the case for the dehydrogenation pathway.

Kinetic measurements were made on these model surfaces. Here, we employ *molecular beam techniques* (e.g., refs. 21, 63–65), which provide a unique way to derive detailed kinetic information, for example, enabling us to modulate reactant fluxes in a flexible way, determine exact reaction probabilities, or detect reaction products in a collision free manner. In order to perform such experiments on supported model catalysts, we use a molecular beam system at the Fritz-Haber-Institute (Berlin), which allows us to cross up to three beams on the sample surface and perform time-resolved reflection absorption IR spectroscopy (TR-RAIRS) and angle resolved/integrated gas phase detection simultaneously.⁶⁶ Recently, we have applied the molecular beam approach to the CO oxidation on supported model catalysts.^{67,68}

Here, we discuss methanol decomposition as an example of a more complex reaction system. In brief, molecular adsorption is followed by the formation of methoxy species on the Pd particles. This first intermediate is stable up to temperatures of 200 K. At higher temperatures, decomposition proceeds via two competing reaction pathways. Dehydrogenation as the dominating reaction channel results in rapid formation of CO. Depending on the CO formation and desorption rate (i.e., the surface temperature), a significant steady state coverage of CO adsorbed on the Pd particles is built up, which can be monitored via *in situ* TR-RAIRS.

As a second pathway, we observe slow breakage of the carbon-oxygen bond, leading to formation of adsorbed carbon and hydrocarbon species. This assumption is corroborated by three observations: first, weak features in the CH-stretching frequency region indicate the presence of CH_x-species [IR: $\tilde{\nu} = 2945 \text{ cm}^{-1}$, 2830 cm⁻¹ (C—H)]. Such hydrocarbon species have been shown to be stable up to 500 K. Secondly, in a TPD experiment we observe desorption of hydrocarbons (15 amu, 700 K) and recombinative desorption of CO (28 amu, 800 K), which is characteristic for the presence of atomic carbon.⁶⁹ Finally, carbon formation has been monitored by X-ray photoelectron spectroscopy.⁷⁰

It is essential to note that during CO exposure under identical conditions no carbon formation is observed on the same Pd particle system.⁶⁷ From this we infer that the carbon deposits do not originate from CO decomposition, but from breakage of the C—O bond during the dehydrogenation process.

The question arises where on the nanoparticles the carbon deposits are located. This question is answered by RAIRS using CO as a probe molecule. The corresponding spectra for the pristine Pd particles and after prolonged exposure to methanol are compared in Figure 5.

For the pristine sample (Fig. 5, open symbols), the spectrum is dominated by a sharp absorption feature at $1960 \,\mathrm{cm}^{-1}$ (1) with a broad low-frequency shoulder (2) (1930 to 1840 cm^{-1}) and an additional weak feature at 2080 cm^{-1} (3). Previously, the features between 1930 and 1840 cm⁻¹ (2) have been assigned to CO adsorbed on hollow and possibly some bridge sites on Pd(111), and the absorption peak at 2080 cm^{-1} (3) to on-top CO on Pd(111).^{56,71} A detailed comparison with previous work shows that the prominent absorption band at $1960 \,\mathrm{cm}^{-1}$ (1) originates from a superposition of bridge bonded CO on (100) facets and CO adsorbed at defect sites such as particle edges or steps.^{56,71} The contribution of (100) facets, however, is expected to be small due to the minor fraction of these facets and their tilted geometry (as a consequence of the surface selection rule, IR absorption is attenuated on small tilted facets, e.g., ref. 72). Following these arguments, we assume that the absorption feature at 1960 cm⁻¹ is dominated by CO adsorbed on defect sites, mainly steps and particle edges (see Fig. 4). Note, however, that the signals are expected to be strongly modified by dipole coupling effects.73 As a consequence, the relative intensities do not directly reflect the rela-



Fig. 4. (a) Schematic representation of the supported Pd nanoparticles and the blocking of defect sites by carbon species during methanol decomposition. (b) STM image of the Pd particles grown at 300 K on $Al_2O_3/NiAl(110)$ (20 \times 20 nm) from ref. 109.

tive abundance of the corresponding sites, but the defect feature at high frequency is expected to gain intensity at the expense of the regular absorption signal.

After extended exposure to methanol, drastic changes are observed (Fig. 5, solid symbols). The defect peak at 1960 cm^{-1} (1) vanishes almost completely, whereas the absorp-

tion signal in the on-top region (3) strongly increases (2090 cm^{-1}) . All other features in the spectrum, in particular the region below 1950 cm^{-1} (regular facets), remain practically unchanged. Although dipole-coupling effects mentioned above preclude a straightforward quantification, it is apparent from these observations that adsorption at particle defect sites



Fig. 5. RAIR spectra for CO adsorbed on Pd/Al₂O₃/NiAl(110) (sample temperature 100 K, after CO exposure at 300 K; open symbols: immediately after preparation; solid symbols: after prolonged exposure to methanol at 440 K).

(i.e., steps and edges) is blocked by carbon species formed via carbon-oxygen bond breakage. We conclude that these carbon species preferentially accumulate at defect sites.

In the next step we investigate the effect of carbon accumulation on the kinetics of both reaction pathways. Carbon formation results in a slowly decreasing CO absorption capacity, which allows us to follow the process *in situ* by TR-RAIRS.

In order to quantify the surface fraction covered by carbon, we calibrate the integral CO absorption as a function of coverage (θ_{CO} : fraction of Pd surface sites covered by CO; note that in RAIRS there is no simple relation between coverage and absorption due to dipole coupling effects⁷²). To do so, we combine a CO sticking coefficient measurement and a TR-RAIRS experiment. The calibration is used to estimate the surface fraction covered by carbon ($\theta_{C}(t) = \theta_{CO}(0) - \theta_{CO}(t)$, $\theta_{CO}(0)$: initial CO coverage) as a function of exposure time to methanol. The result is shown in Figure 6. It is apparent that the initial rate of carbon formation is high, but drops rapidly with increasing carbon coverage. From this observation we conclude that the carbon-oxygen bond breakage is fast only at the defect sites, which are preferentially blocked during the reaction, but not at the regular facet sites. The next question to ask is whether the second reaction pathway, that is, the methanol dehydrogenation, is affected by carbon accumulation in a similar manner. For experimental reasons, the dehydrogenation rate is determined in an isotope exchange experiment combined with surface detection via TR-RAIRS. The setup comprises a ¹²CH₃OH beam and a ¹³CH₃OH beam of equal intensity. Switching between the two beams, we follow the exchange between the dehydrogenation products ¹²CO and ¹³CO, and determine the time constants for CO exchange τ_{CO} on the clean and the partially carbon-covered catalyst. Moreover, we can use the steady state coverages of CO (see above) to derive the corresponding rates of CO formation (or methanol dehydrogenation) as $R_{CO} = \theta_{CO} \tau_{CO}^{-1}$.

It is apparent that whereas the rate of carbon-oxygen bond breakage drastically decreases with increasing carbon coverage, the rate constant for CO exchange remains nearly unaffected by this process. The decrease in the dehydrogenation rate simply reflects the decrease in the carbon-free Pd surface area. Quantitatively, we find that the ratio between the rates of dehydrogenation and carbon-oxygen bond breakage R_{CO}/R_{C} increases from 30 on the pristine sample to approximately 1000 on the carbon-contaminated sample.



Fig. 6. Estimated carbon coverage as a function of exposure time *t* to the methanol beam (derived from TR-RAIRS, surface temperature of 440 K), $\theta_C = \theta_{CO}(0) - \theta_{CO}(t)$ per monolayer. From the slopes at $t \to 0$ and $t \to \infty$ the rates of carbon formation for the clean and the carbon-covered samples have been estimated.

A drawback of this approach,⁴ however, is the fact that the adsorbate distribution could not be monitored under reaction conditions, but has to be investigated at lower sample temperature after terminating the reaction. In the next example,⁵ this major shortcoming is avoided. We focus on the NO dissociation and reduction, which is of considerable scientific and technological interest in environmental catalysis.⁷⁴ On Pd surfaces, the reaction exhibits a pronounced structure dependence. Whereas on Pd(111) NO remains intact up to high temperatures, Pd(100) and stepped Pd surfaces exhibit much higher activity towards dissociation (see, e.g., refs. 75-79 and references therein). Consequently, prominent structure and size effects are expected for the supported Pd catalyst as well and have indeed been observed experimentally.^{80,81} Most importantly, however, the products of NO dissociation, atomic nitrogen and oxygen, have been shown to play a key role for the reaction kinetics, for example, in the case of the CO-NO reaction.⁸² Thus, the distribution of dissociation products on the particles under reaction conditions and their influence on the dissociation activity is a critical but still open question.

Combining molecular beam methods and *in situ* TR-IRAS we show that under conditions of NO dissociation on alumina-supported Pd crystallites, the dissociation products, atomic oxygen and nitrogen, preferentially occupy edge and defect sites on the particles. After selectively removing oxygen by applying a CO pulse, strongly bound nitrogen species remain and lead to reduced NO adsorption at the particle edges. Simultaneously, the rate of NO dissociation is found to be strongly enhanced.

In Figure 7 IRAS spectra are displayed, which were recorded during exposure of the pristine model surface to NO immediately after switching on the beam. No NO adsorption is observed for the clean alumina film at 300 K. For the Pd particles, three main absorption features in the N—O stretching frequency range are observed: (1) an absorption band, which shifts from $\tilde{\nu} = 1595 \text{ cm}^{-1}$ at a sample temperature of 300 K to



Fig. 7. IR spectra of the N—O stretching frequency region acquired during exposure of the clean alumina film and the Pd particles supported on the film to a beam of NO immediately after admission of the beam.

 $\tilde{\nu} = 1548 \text{ cm}^{-1}$ at 475 K; (2) a band between $\tilde{\nu} = 1656 \text{ cm}^{-1}$ (300 K) and $\tilde{\nu} = 1628 \text{ cm}^{-1}$ (475 K); and (3) a strong absorption band at $\tilde{\nu} = 1735 \text{ cm}^{-1}$ (300 K), which vanishes at sample temperatures exceeding 400 K.

Based on single crystal experiments on Pd(111) (ref. 83 and references therein) and theoretical calculations,^{84,85} bands (1) and (3) can be attributed to NO adsorbed at threefold hollow sites (1) and at on-top sites (3) on (111) facets, respectively. For absorption band (2) there are, in principle, two possible assignments. First, there is a large fraction of edge sites available (e.g., more than 30% of the top facet atoms are located at the particle edge, see Fig. 4). To some extent, this situation is comparable to NO adsorption at stepped Pd surfaces. For Pd(112), for example, Ramsier et al. found an absorption feature at elevated temperature between 1655 and $1670\,\text{cm}^{-1.75}$ In addition to the edge sites, a contribution due to the (100) facets is possible. At high coverage on Pd(100) single crystals, bridge bonded NO gives rise to a characteristic absorption feature between approximately 1630 and 1670 cm⁻¹.^{86,87} Based on the morphology of the particles, however, we can conclude that the contribution of the (100) facets is minor. In addition, the large tilting angle of the (100) facets leads to a suppression of the IR absorption as a result of the metal surface selection rule, which-due to the small thickness of the oxide film-also applies for the present model surface.⁷² Consequently, we assign band (2) to NO species predominately located at particle edges and a minor contribution from (100) facets. It should be pointed out that an exact quantification of the relative population of the different states is complicated because of dipole coupling effects, which may lead to some degree of intensity transfer between the bands.⁷³ Hence, we restrict ourselves to qualitative conclusions in the following discussion of the site-occupation.

In the next step we follow the kinetics of NO decomposition at 450 K. For this purpose IR spectra are recorded continuously during exposure to the NO beam (see Fig. 8). The integral intensity of the two absorption features (1) and (2) is displayed in Figure 8. On-top sites giving rise to band (3) are not populated at this sample temperature. From the data it is obvious that initially absorption band (2) decreases in intensity, followed by band (1) at later time. For sufficiently long exposure times both NO absorption features vanish completely.

The loss of NO adsorption capacity can be attributed to the accumulation of dissociation products, atomic nitrogen and oxygen, on the particles. The preferential loss of the absorption feature (2), mainly NO at particle edges, indicates that adsorption of the product species at these sites is favorable. This observation is consistent with a recent STM study of oxygen adsorption on the same Pd model catalyst, showing preferential adsorption at particle edges.⁸⁸ It should be pointed out that from the desorption behavior of oxygen from Pd single crystal surfaces (desorption between approximately 700 and 1000 K, e.g., refs. 78, 79), it can be concluded that the rate of oxygen desorption is negligible under the reaction conditions applied in this work. Nitrogen, however, can leave the surface via formation of N_2 or $N_2O_{,}^{78,79}$ with the ratio of both products sensitively depending on the reaction conditions and surface structure. In addition, strongly adsorbed nitrogen species have been observed both on single crystal surfaces and on supported particles^{79,82} (leading to high temperature N₂ desorption features in the range between approximately 500 and 650 K). These findings suggest that a fraction of the atomic nitrogen may remain on the particles under the reaction conditions applied here.

In order to investigate the role of adsorbed nitrogen and its influence on the dissociation kinetics a CO titration exper-



Fig. 8. (a) IR spectrum of the N—O stretching frequency region acquired during exposure of Pd model catalysts to a NO beam, taken immediately after admission of the beam. (b) Integral intensity of the two absorption bands in the N—O stretching frequency region as a function of time.

iment is performed, which is displayed in Figure 9. Again, the pristine catalyst is exposed to a continuous NO beam and the kinetics of NO decomposition is recorded via TR-IRAS (Fig. 9). The integral intensity of both absorption features is shown in Figure 9. At certain points in time a CO pulse is applied to the sample via a second beam source. The CO efficiently removes all adsorbed oxygen from the surface by oxidation to CO_2 (see ref. 65 and references therein). Note that carbon contamination due to CO dissociation or disproportionation can be excluded under these conditions.^{65,66} The corresponding CO_2 quadrupole mass spectrometer signal (Fig. 9) provides a measure for the oxygen coverage of the sample.

As discussed before, absorption band (2) (edges) immediately decreases upon NO exposure, whereas the (111) facet sites [band (1)] are affected at a later time. A first CO pulse applied at low NO exposures yields the expected low CO_2 signal, indicating that initially the surface is oxygen free. Besides, the CO pulse has a negligible effect on the rate of NO decomposition.

A second CO pulse is applied after the surface is completely covered by the reaction products. The substantial CO_2 production indicates a high oxygen coverage. After removal of the surface oxygen, IR absorption band (1) is fully restored, whereas absorption band (2) is only restored to about 60% of its original intensity and remains blue-shifted by approximately 8 cm^{-1} . From this we conclude that strongly bound nitrogen species remain preferentially adsorbed in the vicinity of edge sites on the particles and modify the adsorption properties of these sites.

It is remarkable that a constant CO_2 yield is found for subsequent CO titration experiments (Fig. 10). From this observation it follows that the NO dissociation capacity is constant, that is, there is no further accumulation of nitrogen beyond the well-defined level formed in the initial part of the exposure.

Another striking result from this experiment is that after initial oxygen removal, the rate at which the surface is covered by reaction products becomes much faster. As shown by CO titration the same amount of NO dissociates in each cycle. Thus, this difference must be due to an increased dissociation rate and not due to a loss in adsorption capacity. An estimate of the dissociation probability is shown in Figure 10. On the partially nitrogen-covered particles, an increase in the dissociation probability by approximately a factor of five is found with respect to the pristine surface.

These observations suggest that atomic adsorbate species preferentially bound in vicinity of particle edges critically control the dissociation activity. Specifically, we may consider two effects, which could contribute to the increase in the dissociation rate. First, the presence of strongly bound nitrogen may lead to a reduced NO coverage at the active sites and thus to reduced site blocking and faster NO dissociation. Secondly, we have to take into account that atomic nitrogen and oxygen species coadsorbed in the vicinity of the active sites may have different effects on the activation barrier for dissociation. Thus, a possible scenario would be that during the first pulse (starting from N- and O-free particles) a large fraction of the dissociation sites are decorated by oxygen whereas in subsequent pulses (after removing the atomic oxygen) there is preferential decoration by nitrogen. Future theoretical calculations may help to identify the exact role of these effects for the dissociation kinetics. The implications of the current results for the catalytically important CO-NO coadsorption and reaction system will be discussed elsewhere.8



Fig. 9. Time resolved IRAS experiment showing the development of the integral intensity of the two absorption bands in the N—O stretching frequency region as a function of time and CO pulsing. Insets: CO_2 mass spectrometer signal recorded during CO pulsing.

The last example for site-specific adsorption and reactivity deals with the bimetallic nanoparticles whose morphology has been discussed above. Here, a very important ingredient is the surface composition of the particles because this composition provides the sites for adsorption and reaction and it may also change in this process.

In order to verify the surface composition of our model systems, we performed temperature programmed desorption experiments using CO as a probe molecule. In this context, it is important to note that CO prefers *different adsorption sites* on the two metals. On Pd, the molecule is bound preferentially to threefold hollow sites, followed by bridge sites, and finally atop sites.^{90,91} On Co the order is reversed: CO is bound preferentially to atop sites, followed by more highly coordinated sites.^{92,93}

A series of TPD spectra from the bimetallic is plotted in Figure 11, that is, the deposition sequence 1^{st} Co/ 2^{nd} Pd. At the top, CO desorption from pure Pd particles is shown. At the bottom, the equivalent data for pure Co particles are shown. While for the pure Pd clusters the assignment is well



Fig. 10. Absolute NO dissociation probability as a function of CO pulsing.

established, in that the peak near 450 K stems from threefold hollow sites and the long tail towards lower temperature from CO bound in on-top positions, the situation for Co has only been clarified recently. Figure 12 shows the TPD traces as well as IRAS data for CO adsorption on pure Co particles.⁹⁴ At low temperature an increasing CO coverage leads to the formation of two bands 2015 and 2068 cm⁻¹, respectively. After annealing to room temperature the band shifting from 2015 to 2000 cm⁻¹ prevails, indicating that the larger peak in the TPD spectra above 300 K is associated with this species, and the peak at 1980 cm⁻¹ is associated with the TPD feature with a maximum at 275 K. It is interesting to note that the abundance as revealed in TPD anticorrelates with peak intensities in the IRAS spectra. As we have discussed elsewhere, in comparison with ab initio calculations, the two bands originate from CO bound to on-top sites within the surface (2015 cm⁻¹) and from



Fig. 11. Temperature-programmed desorption spectra of CO from bimetallic Pd-Co particles supported on Pd/Al₂O₃/NiAl(110). The particles were prepared by depositing 2 Å Co (1 Å Co = 9.0×10^{14} cm⁻²) first and various amounts of Pd subsequently. The spectra for pure Pd and Co particles are also shown for reference. An exposure of 20L CO (1L = 10^{-6} torr) was given at 100 K prior to TDS. The heating rate was 1.5 Ks^{-1} .



Fig. 12. TPD and IRAS spectra of Co (2Å) deposited onto alumina at room temperature. (a) TPD spectra after exposure to CO, with quantitative evaluation of the desorbing CO. (b) IRAS spectra in the range of CO stretching frequencies taken at 44 K and after annealing to 300 K.

CO bound to isolated Co atoms as $Co(CO)_n$ with $n \ge 3$ carbonyl species (2068 cm⁻¹).⁹⁵ The latter information has been confirmed with isotopic labeling experiments.⁹⁴

Upon evaporation of small amounts of Pd onto the Co pre-exposed surface, a new desorption peak from CO atop sites evolves at lower temperature (a), which can be assigned to Co particles partly covered by Pd.⁴⁶ The shoulder at the original desorption temperature, still visible in the first spectrum of the series, apparently results from areas on the particles not covered at this stage. The shift of the maximum to lower temperature induced by Pd can again be understood in terms of two contributing effects, which may be responsible for the different adsorption and desorption behavior of an alloy as compared to the pure metals: electronic and structural effects.^{96,97} The first contribution, also called ligand effect, is encountered if the interaction between an adsorbate and a particular adsorption site is modified by a second metal surrounding that site. Because bimetallic bonding generally weakens the strength of the CO-metal bond the downshift of the desorption maximum can be explained by a ligand effect of Pd covering the Co particles. The second effect, called ensemble effect, is relevant only for highly coordinated sites, that is, bridge or hollow sites. It is effective if one of the atoms constituting such a site is exchanged by the second metal so that the site is eliminated. For example, a threefold hollow site would be strongly affected by this effect. In the present case this is not so obvious, but if one looks at TPD spectra for the reverse deposition sequence, that is, first Pd then Co (not shown, see ref. 46), the Pd particles are well ordered and exhibit facets with a high attendance of threefold hollow sites, and one finds a very pronounced suppression of such sites even for small Co depositions.⁴⁶

As the Pd coverage increases and its electronic influence becomes stronger, the desorption shifts to even lower temperatures and the desorption from pure Co vanishes. Finally, when a Pd shell completely covering the Co cores is formed, desorption from Pd threefold hollow sites is detected in the spectra. At a first glance, it might be surprising that relatively large amounts of Pd are needed to observe this site. Two reasons, however, can be responsible for that: the strong ensemble effect expected for this site, as mentioned above, and the smaller and less ordered particles as compared to the other deposition order, which possibly offer less intact threefold hollow sites.⁴⁶

These Co-Pd bimetallic systems have been used in reactivity studies, that is, the Fischer-Tropsch reaction for which a combination of Pt or Pd to Fe or Co has been shown to increase the selectivity for methanol formation from synthesis for gas at high pressure. Supported bimetallic Co-Pd catalysts have previously been studied in non-UHV conditions.^{48–52,98–102} It has been proposed that the addition of Pd promotes the reduction of Co oxide by activating hydrogen.^{48–52,103–106} Magnetic measurements⁵¹ and temperatureprogrammed reduction¹⁰³ have shown that CoO is more easily reduced when Pd is added as a cocatalyst.

In order to shed light on this question we have studied adsorption and reaction of molecules relevant for a Fischer-Tropsch scenario, that is, oxygen, hydrogen, carbonmonoxide, and ethene.⁶ Here, we summarize some of the results and stress some particularly striking points. The important point to note is the pronounced influence of oxygen and the concomitant oxidation of the Co/Pd alloy particles on the adsorption and reaction behavior of other molecules. We exemplify this here by looking at hydrogen desorption with TPD.

The interaction of hydrogen with the pure and bimetallic particles is dependent on the bimetallic composition, as demonstrated by TPD (Fig. 13a). We have used deuterium in place of hydrogen in order to avoid detecting subsurface hydrogen already present from the background gases. On unoxidized 2Å Co particles, desorption peaks can be seen at 280 and 340 K. On the open Co(1010) face, hydrogen has been observed to form an ordered $c(2 \times 4)$ overlayer at 0.5ML, a (2 \times 1)p2mg overlayer at 1ML, and cause a reconstruction at a saturation coverage of 1.5ML.¹⁰⁷ In contrast to Pd, ^{108,109} hydrogen does not form a subsurface species on the open face of Co.^{107,110} The two desorption peaks in Figure 13a are most likely due to the depopulation of one adsorbate phase after another, though the structure on the particles is probably not the same as on Co(10-10). On the 2Å Pd particles, a broader feature can be seen with a peak at 290 K; the desorption before the peak temperature has previously been assigned to subsurface hydrogen.¹¹⁰ The interaction of surface-adsorbed hydrogen with Co appears stronger than the interaction with Pd.

The high-temperature desorption feature of hydrogen from Co is affected by the addition of Pd. When 0.1 Å Pd forms a shell on top of 2Å Co particles, the high-temperature desorption peak from the 2Å Co particles is attenuated (Fig. 13a), indicating that Pd ad-atoms suppress that adsorption state, for example, by site blocking or preventing the formation of a higher-compression phase. Further, when 1 Å Pd forms a shell on top of 2Å Co particles, the high-temperature feature present in the desorption spectrum from 2Å Co particles is almost completely suppressed. When 1 Å Co forms a shell on 2Å Pd particles, this feature is further seen again, although in this case, it may arise from Co particles that have nucleated between existing Pd particles, and are thus made of pure Co. The lower-temperature desorption feature of hydrogen from 2Å Co particles does not appear to be affected by the addition of 0.1 Å Pd or 1 Å Pd, though it is certainly possible that different adsorption states result in similar desorption temperatures.

Subsurface hydrogen adsorption is also affected by the addition of Co to Pd particles.^{108,109} The lower-temperature tail of hydrogen desorption from pure Pd particles, attributable to subsurface hydrogen,¹¹⁰ is reduced by the addition of 1Å Co to 2Å Pd particles (Fig. 13a). The desorption of surface-bound hydrogen from Pd threefold sites also seems to be reduced by the addition of 1Å Co to 2Å Pd particles; this could be explained by an ensemble, or site-blocking effect. Furthermore, subsurface hydrogen adsorption appears suppressed when 1Å Pd is covering 2Å Co particles. Because pure Co cannot carry subsurface hydrogen,¹⁰⁷ this suggests that the bimetallic Co-Pd particles have less carrying capacity for subsurface hydrogen than does Pd alone.

The interaction of hydrogen with the pure and bimetallic particles^{108,109} is sensitive to the presence of chemisorbed oxygen, as demonstrated by TPD (Fig. 13b). When the particles are exposed to 30L of O2 at 300 K before the D2 dose and TPD measurement, no D₂ desorption is detected from the 2Å Co particles or the 2Å Pd with a 1Å Co shell on top (Fig. 13b). Only very small amounts of D_2 desorption are detected from the oxygen-covered 2Å Pd particles (Fig. 13b); apparently, hydrogen can still adsorb, to a limited extent, on the particles having faces with ordered $p(2 \times 2)$ -O overlayers. It is possible that the small amount of hydrogen adsorption occurs at the particle edges or boundary with the substrate, because we would expect a larger amount if it were actually adsorbing within the p(2 \times 2)-O structure. A small amount of D₂ desorption is also detected from 2Å Co particles covered with 1Å Pd at the same temperature as the desorption from the pure 2Å Pd particles. It is possible that this is also due to adsorption of hydrogen on edges of the Pd. In contrast, no D_2 desorption from 2Å Co was detected, as we might expect from the fully-oxidized Co particles. However, it is slightly more surprising that only 1 Å Co added to 2 Å Pd particles also results in a complete suppression of D₂ adsorption when oxidized. Because Co nucleates not only on top of existing Pd particles, but also between them, the Pd particles are most likely not fully covered with Pd. Thus, an incomplete layer of Co ad-atoms on top of Pd particles is sufficient to completely suppress adsorption of D2. The consequences of the two experiments with bimetallic particles for the Fischer-Tropsch reaction is that Pd added to the Co-catalyst would have to be well-exposed to the surface in order to trap hydrogen and thereby facilitate reduction of CoO.7,14,40,44,48,58,106,111,112 In none of the cases was the evolution of deuterated water, a possible reaction product, detected.

The adsorption of ethylene on the bimetallic particles is not as drastically affected by previous oxidative treatment as the adsorption of CO or H₂. The desorption of ethylene from 2Å Pd particles results in a broad desorption feature (Fig. 14), which has previously been assigned to pi-bonded (T < 230 K) and di-sigma bonded ($T \approx 270 \text{ K}$) ethylene.¹¹⁰ It is possible that the broadness of the peak results from these two binding modes at different binding sites on the particles. At 300 K there is desorption of H₂ when ethylidyne is formed from the disigma bonded ethylene¹¹⁰ on the Pd particles.^{108,109} Further H₂ desorption is due to the stepwise decomposition of ethylidyne to surface carbon. A similar formation of ethylidyne on Co surfaces has also been observed.¹¹³ The desorption of ethylene from Co particles is similar to the desorption from Pd particles in that there are a number of desorption states that are followed by a liberation of H_2 (Fig. 14). The liberation of H_2 near 300 K is most likely due to the formation of ethylidyne and subsequent decomposition, the latter step occurring more readily on Co particles than on Pd particles (Fig. 14). When



Fig. 13. (a) TPD of D_2 from the pristine system surface. (b) TPD of D_2 from the deposited aggregate after exposure to oxygen to induce oxidation.

1 Å Pd is covering 2 Å Co particles or vise-versa, there is also a desorption of ethylene from pi-bonded and di-sigma states, as well as the evolution of hydrogen at 300 K, indicative of ethylidyne formation. However, the evolution of hydrogen, indicative of the formation of ethylidyne, occurs at 277 K on the bimetallic particles, rather than at 300 K, as on the pure Pd particles or at 293 K as on the pure Co particles. This small but clear difference indicates a facilitation in the reaction of ethylene conversion to ethylidyne on these nonoxidized bimetallic particles. This suggests that the enhancement in Fischer-Tropsch reactivity of Co catalysts with added Pd may also be due to properties other than CoO reduction. On oxygen-covered Pd particles, the amount of pi-bonded ethylene remains the same as that on the nonoxidized particles, while the relative amount di-sigma bonded ethylene is reduced (Fig. 14). This is probably due to the site-blocking effect of oxygen in Pd threefold sites.^{49,114} There is a small shoulder due to ethylene desorption around 270 K (Fig. 14) on the Pd particles, suggesting that an oxygen-overlayer on Pd particles hinders the formation of di-sigma bonded ethylene but does not fully suppress it. The desorption of ethylene at 270 K followed by evolution of hydrogen at 300 K is further reduced when the surface has been exposed to D₂ before being exposed to C_2H_4 (Fig. 14). This might be the result of a site blocking effect or due to the fact that part of the ethylene is hydrogenated at lower temperature and thus not available for ethylidyne formation.

On the oxidized Co particles and bimetallic Co-Pd particles, the amount of adsorption into the pi-bonded state is roughly the same as on the nonoxidized particles, but the formation of di-sigma bonded ethylene is fully suppressed. A predose of D_2 before the ethylene TPD run on the oxidized Co and Co-Pd bimetallic particles (Fig. 14) makes no difference to the ethylene desorption spectrum, because the D_2 cannot adsorb on these particles (Fig. 13b), excepting Pdcovered Co; in the latter case, however, the amount of D_2 adsorption was shown to be low.

An attempt was made at reducing the oxidized particles through a TPD of ethylene up to 320 K. However, the second TPD spectrum of ethylene from the oxidized particles is similar to the first (data not shown). This suggests that CoO cannot be reduced by pi-bonded olefins such as ethylene.

TPD of CO after a predose of ethylene and annealing to 320 K shows an attenuated and shifted signal compared with the clean particles. The attenuation of the CO-desorption feature in the pure and bimetallic particles suggests ethylidyne has formed and is taking up space on the surface. Further, the CO-desorption feature is slightly shifted to higher binding energy, particularly on the bimetallic particles, suggesting a favorable adsorbate-adsorbate interaction. The hydrogenation of ethylene with preadsorbed hydrogen is observed on all prepared materials. On the bimetallic particles the overall amount of ethylene hydrogenation is slightly less than on the pure Co or Pd particles.

However, in contrast to the unoxidized particles no reaction is observed on the oxidized Co-containing particles when O_2 is predosed before an ethelene TPD. On the oxidized Cocontaining particles, hydrogen adsorption is inhibited, thus also inhibiting hydrogenation. In short, the oxidized Cocontaining particles are unreactive—even when there is partial Pd shell present. These reaction studies indicate that the reduction of CoO to the metal is of prime importance for the Fischer-Tropsch reaction.



Fig. 14. (a) TPD spectra of C_2H_4 and H_2 from the unoxidized (left panel) system. The H_2 signal has been corrected for the cracking contribution of C_2H_4 and is plotted on a different scale. (b) TPD spectra of C_2H_4 and H_2 from the system after exposure to oxygen (middle panel). The surface was only heated to 320 K. Desorption of H_2O and H_2 was not observed. (c) TPD spectra of C_2H_4 after also dosing D_2 on the oxidized system (right panel). Desorption of D_2 , H_2O , and H_2 was not observed. H_2 desorption was only seen for Pd. The H_2 -signal has been corrected for the cracking pattern of C_2H_4 and is plotted on a different scale.

Conclusions

In the present article we have demonstrated that model catalysts are well suited to derive structure-reactivity relationships. This has been shown for pure Pd nanoparticles with respect to the influence of particle facets and corners/edges on the selectivity of reactions both by probing *ex situ* and also *in situ*. A third example for the formation, characterization, and reactivity of bimetallic Pd/Co particles has been presented. It is shown how the stoichiometry and the interaction with oxygen influence reactivities in such systems.

In summary, model catalyst investigations have a lot to offer and it is important to ever increase the complexity of the system in an attempt to finally reach the complexity of "real" systems. It is, however, also clear that starting with "real" systems—in other words the reverse approach—does not offer a practical alternative because the reverting control of the system is lost.

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