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CO dissociation activities of clean Pt {430}, {320}, {520}, {310}, {410} and {210}: a comparison with the predictions of Banholzer's orbital symmetry model

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Banholzer et al. used an orbital symmetry model to predict the activity of various Pt faces for the dissociation of adsorbed NO. The predictions were later extended to the adsorption system CO/Pt. Our experimentally observed activities for the dissociation of CO on clean Pt {430}, {320}, {520}, {310}, {410} and {210} do not follow these predictions. However, the measured activities agree well with the predictions of the C_6 "atomic site" model.

Keywords: CO dissociation activities; Pt catalyst, Banholzer's orbital; symmetry model

In the following, a brief outline will be presented of the orbital symmetry model by Banholzer et al. [1,2] and its predictions of face specific dissociation activities for the adsorption systems NO,CO/Pt. It will be demonstrated that our experimental data of the CO dissociation on Pt {430}, {320}, {520}, {310}, {410} and {210} do not follow these predictions. It will be shown that they rather follow the predictions of the C_6 "atomic site" model.

In 1983, after Woodward and Hoffmann [3] and Fukui [4] had shown that the conservation of orbital symmetry can be used advantageously to determine favourable reaction pathways in organic and inorganic systems, Banholzer et al. attempted to apply the method to surface reactions [1,2]. (For a general treatment of the subject matter see, for example, refs. [5] and [6]). Banholzer et al. selected for their investigations the dissociation of NO on Pt because of its experimentally proven, pronounced face specificity. They derived symmetry rules for various Pt faces using models of surface electronic structures, which had been developed by Bond [7]. Questions by Richardson [8] concerning the validity of parts of their model were rebutted by Masel [9]. The Banholzer model requires the NO molecule, which is attached through the N atom to the Pt surface, to bend over and to acquire a side-on adsorption position before

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Table 1
Activity predictions based upon Banholzer's orbital symmetry model. The predictions were originally made for the adsorption system NO/Pt and later extended to CO/Pt [15]. Dissociation activities of face groups, S-[m{hkl}×{hkl}], and of individual faces. The positions of the face groups and the individual faces within the unit stereographic triangle are shown in fig. 2. The face group codes are used in figs. 1 and 2. The models of the faces marked by (*) are incorrect in the corresponding original papers [11,12].

Face group code	Analyzed face or face group	Correspond. crystal zone ⟨uvw⟩	Predicted dissociation activity	Analyzed faces within face group	Predicted activity trend among individual faces
–	{111}	⟨110⟩	Inactive	–	–
–	{110}	⟨100⟩⟨100⟩	Inactive	–	–
–	{100}	⟨100⟩⟨100⟩	Moderat. active	–	–
–	{210}	⟨100⟩	Moderat. active	–	{210} ≪ {410}
A	S-[m{111}×{111}]	⟨110⟩	Inactive	{11, 11, 9} {13, 13, 11}	–
B	S-[m{110}×{100}]	⟨100⟩	Highly active (increase from {110} to {210})	–	–
C	S-[m{100}×{110}]	⟨100⟩	Unusually highly active (maximum at {410})	{410}	{410} ≫ {210}
D	S-[m{100}×{111}]	⟨100⟩	Active (decrease from {100} to {111})	{411} * {511} *	{411} ≈ {211} {511} ≈ {100}
E	S-[m{111}×{100}]	⟨100⟩	Active (increase from {111} to {100})	{211}	{211} ≈ {411}

dissociation can occur. If the molecule finds in this side-on position appropriately oriented symmetric and antisymmetric surface orbitals with energies near the Fermi edge, the dissociation is said to be "symmetry allowed", if not, it may be "partially allowed" or "totally symmetry forbidden" [1,10].

Banholzer et al. analyzed {111}, {100}, {110} and some major groups of stepped faces of the type S-[$m(hkl)\times(hkl)$] [1]. As more experimental results became available, the model was tested on additional faces [10–12]. Table 1 shows a summary of all activity predictions. (The discrepancy between prediction and experiment, which had been observed for {11 11 9} [13] and {13 13 11} [14], was partially attributed to experimental problems [15].) The most striking prediction concerns the unusually high activity of {410}. Its indicated activity is considerably higher than that of {210}, the fcc face with the largest surface roughness.

In addition, some important model details were published. The most significant one concerned the alignment of the molecular axis of the side-on adsorbed

NO. On {100}, the ⟨100⟩ direction was found to provide optimal conditions [11]. If one takes into consideration that on a stepped surface the N atom of the side-on adsorbed NO must be attached to a Pt ledge * atom in order to optimize symmetry effects [1], then above alignment constraint limits the group of faces with an unusually high dissociation activity, S-[m{100} × n{110}], to those with $m > n + 1$ [10]. Dealing with monatomic step heights, i.e., $n = 1$, m must be larger than 2. Thus, the alignment constraint explains on the one hand the comparatively high activity of {410} [10], on the other hand, however, it excludes {210} from the group of highly active faces. At the time, the prediction appeared to be consistent with the experimental findings on {210} [11,17,18].

In 1984, after an analysis of the existing experimental results, it was concluded "that Pt{410} has an unusual activity for C–O bond breaking as well" [15]. The predictions of the Banholzer model were extended to the dissociation of CO on Pt: "CO has a nearly identical molecular orbital structure to NO so the same symmetry arguments apply" [15]. Identical model predictions were made for the dissociation of NO and CO on Pt [15]. In addition, it was noticed that also the dissociation of CO on Ni seems to obey the Banholzer model ("., clearly there is an apparent agreement with our model" [15]): A high activity had been observed on Ni{510} and Ni{310} [16]; both are S-[m{100} × {110}]-faces.

In 1985, the concept of "orbital availability" was introduced for the system NO/Pt [19,20]. Especially the "site average orbital availability" (SAOA) permitted a quantitative comparison with experimental results. (The larger the SAOA of a face, the larger its capability to dissociate NO.) Fig. 1 shows the SAOA (solid line; from ref. [20]) for the surface areas located on the boundary zones of the unit stereographic triangle. The SAOA reflects in a more quantitative fashion the trends displayed in table 1. The {410} face has the largest dissociation capability. It is about twice as active as {210}. (Fig. 2 displays the positions of analyzed faces, face groups, and the corresponding crystal zones within the unit stereographic triangle. As in fig. 1, the face group codes introduced in table 1 (A, B, C, D, and E) are utilized.)

Since the activity predictions of the Banholzer model had been extended to the system CO/Pt ("Again the relative activity of the various single crystal planes for C–O bond breaking is in general accord with the model of Banholzer et al.", [15]), it appeared useful to compare them with our most recent experimental results of CO dissociation on clean Pt. The investigations had been carried out on a variety of kinked surface areas by means of field electron microscopy (FEM).

If the dissociation of an adsorbate is accompanied by a reasonable work function change, the process can be conveniently observed and measured in a FEM. The FEM has the advantage that, in one micrograph, a complete unit

* The "ledge" is the monatomic "vertical strip" connecting the "upper" and "lower horizontal" terraces. Synonymously used is sometimes "step edge".

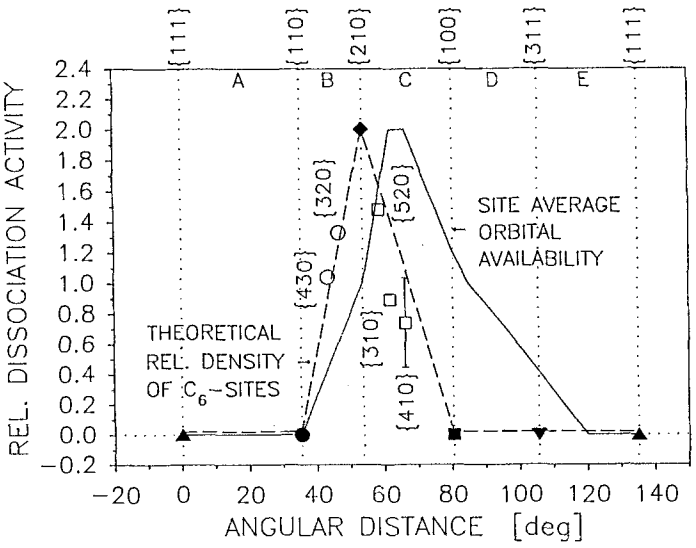

Fig. 1. Comparison of experimentally determined dissociation activities (CO/Pt) with model predictions. Activities of {430}, {320}, {210}, {520}, {310} and {410} have been measured with FEM [24]. Represented are areas along the boundary zones of the unit stereographic triangle (see fig. 2). Solid line: "Site average orbital availability" (SAOA) of Banholzer's model (from ref. [20]). Dashed line: "C_6-site density" (atomic site model). Face group codes: A ≡ S-[m{111}×{111}], B ≡ S-[m{110}×{100}], C ≡ S-[m{100}×{110}], D ≡ S-[m{100}×{111}] and E ≡ S-[m{111}×{100}]. Filled symbols mark major crystallographic faces.

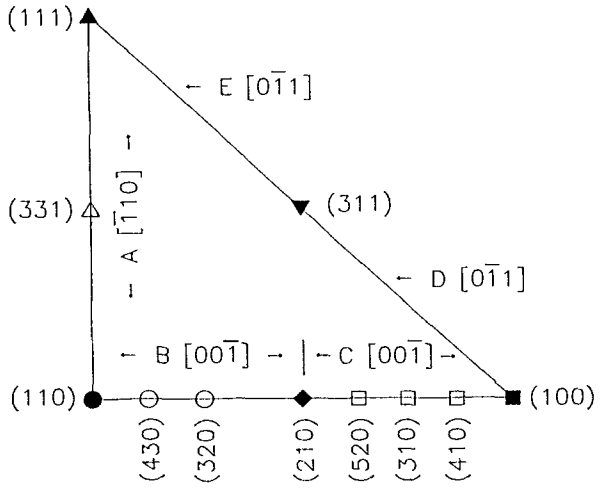

Fig. 2. Schematic drawing of the unit stereographic triangle. Shown are the locations of the face groups (A, B, C, D, and E) and their corresponding zones, [*uvw*], as well as the locations of measured, individual faces. Filled symbols mark major crystallographic directions. Face group codes: A ≡ S-[m{111}×{111}], B ≡ S-[m{110}×{100}], C ≡ S-[m{100}×{110}], D ≡ S-[m{100}×{111}] and E ≡ S-[m{111}×{100}].

stereographic triangle can be studied, i.e., all major crystallographic directions can be analyzed simultaneously under the same gas phase and surface conditions. The sample investigated by FEM is the rounded single crystal region at the apex of the field emitter needle. Because of its size and shape, it can be used for simulating the surface properties of larger, rounded catalyst particles.

Primarily, results obtained by FEM on the dissociation of CO on ultrapure ("FEM-clean" [21–23]) Pt surfaces will be used. Details of experimental set-up, procedures, and the theoretical basis for the interpretation of experimental results have been reported earlier [24–28]. Therefore, only the most essential information shall be given here. — Pt sample purity, 99.999% (Materials Research Corp.); CO (99.97%, J.T. Baker); residual gas pressure: 10^{-11} Torr range; radius of the fairly blunt, rounded Pt crystal $r \approx 5000$ Å; preparation of initial "FEM-clean" surface [21–23] by heating and flashing sample close to its melting point followed by rapid quenching; to avoid field effects, all sample heating was carried out without the application of an imaging field; at room temperature, the sample was exposed to CO for 2 min. at 8×10^{-7} Torr to achieve saturated adsorption; the gas pressure was then reduced to the 10^{-11} Torr range and the sample heated stepwise for 30 sec at increasing temperatures. —

During the dissociation of CO on Pt, a work function increase could be observed because of the formation of oxygen. Relative dissociation activities of crystal face groups (or complete crystal zones segments) could be determined by comparing FE-micrographs that had been taken before and after the appearance of dissociation. By measuring the work function increase ("oxygen-peak height", OPH [24]) on individual crystal faces, quantitative information could be obtained. The results of both methods are summarized in table 2. Relative dissociation activities of {320} and {430} (S-[m{110} × {100}]-faces), of {520}, {310} and {410} (S-[m{100} × {110}]-faces), and for {210} (as calculated from corresponding OPH-values) are plotted in fig. 1. The results will be discussed below.

A variety of models have been used to explain the experimentally observed face specificity of catalytic reactions. In 1986, Masel investigated for NO on Pt the suitability of these models to explain the dependence of the dissociation rate on the crystallographic direction [20]. Only Banholzer's orbital symmetry model could justify the extraordinary activity sequence, {410} ≫ {210} [11]. Another model, which Masel, in his review [20], termed C_6 "atomic site" model, predicts face activities somewhat similar to those of the Banholzer model. However, it ranks {210} highest on its activity scale. The atomic site model investigates to how many first nearest lattice neighbours a surface atom is attached. All surface atoms are characterized by a symbol C_i, in which the subindex, i, indicates the number of first nearest lattice neighbours [29]. If one considers only regular lattice sites, then $i = 6$, 7, 8, 9, 10 and 11. The symbol C_6 describes a kink site atom! (C_{11}-sites, which always accompany C_6-sites and also show a maximum on

Table 2
Activity measurements. Dissociation activities of face groups, S-[m{hkl}×{hkl)], and of individual faces for the system CO/Pt. Measurements on the high-index faces were carried out by FEM [24]. Quantitative values are plotted in fig. 1. The positions of the face groups and the individual faces within the unit stereographic triangle are shown in fig. 2. The face group codes are used in figs. 1 and 2. (w.e.l ≡ within error limits.)

Face group code	Measured face or face group	Measured dissociation activity	Measured faces within face group	Measured activity trend among individual faces	References
–	{111}	Zero	–	–	[17,18]
–	{110}	Zero w.e.l.	–	–	[24]
–	{100}	Zero	–	–	[17,18]
–	{210}	Maximal	–	–	[24]
–	{311}	Zero w.e.l.	–	{311} ≈ {110}	[24]
A	S-[m{111}×{111}]	Zero or minimal	{331}	{331} ≈ {311}	[24]
B	S-[m{110}×{100}]	Active	{430}	{430} < {320}	[24]
		(increases from	{320}	{320} < {210}	[24]
		{110} to {210})			
C	S-[m{100}×{110}]	Active	{520}	{210} > {520}	[24]
		(decreases from	{310}	{520} > {310}	[24]
		{210} to {100})	{410}	{310} > {410}	[24]
D	S-[m{100}×{111}]	Zero or minimal	–	–	[24]
E	S-[m{111}×{100}]	Zero or minimal	–	–	[24]
			{211}	{211} ≈ {100}	[17]

{210}, can be disregarded as independently active dissociation sites: They appear at the straight edges of the completely inactive S-[m{111} × {111}]-faces as well.) The appropriately scaled C_6-site density for the faces located on the boundary zones of the unit stereographic triangle (fig. 2) are plotted in fig. 1 (dashed line).

According to fig. 1, the dissociation activity of the measured areas along the ⟨100⟩ zone increases when one moves from {110} to {210} and decreases when one moves from {210} to {100}. The {210} is the most active area while {410} shows the smallest activity among the investigated faces. Our experimental data do not follow the predictions of the Banholzer model very well. They are predicted better by the C_6-model. (Details, including the effect of thermal roughening, etc., will be discussed in an ensuing, more comprehensive paper [30]. It will be shown that also the activities of the S-[m{111} × {311}]-faces, {741}, {321} and {11 9 5}, follow the C_6-model very well.)

A comparison of the predictions of the Banholzer and the C_6 model (see fig. 1) shows agreement within the S-[m{111} × {111}] face group, partial agreement within the S-[m{111} × {100}] face group, and disagreement within the S-[m{100} × {111}], the S-[m{110} × {100}], and the S-[m{100} × {110}] face groups. In the S-[m{100} × {110}] group, the question of the activity sequence of the corresponding faces, especially the one involving {410} and {210}, is the most crucial

one. Most recent experimental evidence [31,32] shows that the dissociation activity of {210} is larger than the one of {410} not only in the system CO/Pt but also in the systems NO/Pt [32] and NO/Rh [31,32]. (As in the case of Ni [15], it is believed that the Banholzer model can be applied also to Rh [31,33].)

What could have been the reason for {210}, which is thermally a very stable face [18,34], to show in the above quoted older investigations a considerably lowered dissociation activity? The answer may lie in three recently established facts: (i) One of the major contaminants in most Pt samples is Si [21–23,35]; (ii) Si selectively poisons {210} [25,26]; and (iii) because of an overlap of the 93 eV peak of Pt and the 92 eV peak of Si, an Si contamination is extremely hard to detect on Pt surfaces by Auger Electron Spectroscopy (AES) [21,23]. Auger Electron Spectroscopy is used as a standard technique in surface science for establishing surface cleanness. Interesting in this connection is the observation that Pt{210}, on which a reduced dissociation activity had been detected, adsorbed unusually large amounts of oxygen [17]. There are indications that impurity Si, once segregated to the surface of Pt, readily and strongly interacts with oxygen [27,35–38].

In conclusion, using an orbital symmetry model, Banholzer et al. [1,2] predicted the activity of individual surface areas for the dissociation of NO on Pt. The activity predictions were later extended to the system CO/Pt [15]. Our measured dissociation activities for CO on kinked Pt faces (see table 2) do not agree with the predictions of the Banholzer model (see fig. 1). The measurements were carried out by FEM on ultrapure, rounded Pt single crystals. They included the areas: {430}, {320}, {520}, {310}, {410} and {210}. While our measurements are not in agreement with the Banholzer model, they fit the predictions of the C_6 "atomic site" model [e.g., 20] (see fig. 1). Our most crucial finding, i.e., activity {210} $\gg$ activity {410}, is supported by very recent experimental observations of other research groups on NO/Pt and NO/Rh [31,32]. Earlier experimental findings of a smaller dissociation activity of {210} may be explained by the presence of a hard to detect Si surface contamination [21–23,25,26].

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