J|A|C|S
COMMUNICATIONS

Adsorption Mode of Cinchonidine on Cu(111) Surface

Qing-Min Xu,† Dong Wang,†,§ Li-Jun Wan,*,† Chun-Li Bai,*,† and Yuan Wang‡

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received September 4, 2002

Chiral modification of solid catalysts has gained considerable attention as one of the most promising strategies for heterogeneous enantioselective catalysis. Two typical systems for enantioselective hydrogenation reaction are tartaric acid modified Ni catalysts[1−3] and Pt/Al_2O_3 catalysts in the presence of different cinchona alkaloids.[4] From the experimental and theoretical studies of tartaric acid on Cu(110) and Ni(110), it is proposed that the chiral surface was introduced by the self-assembly of modifier or relaxation of the surfaces due to adsorption.[1−3] On cinchona alkaloid-Pt catalyst, the adsorption of 10,11-dihydrocinchonidine on Pt(111) was studied by XPS, LEED, and NEXAFS in UHV environment.[5,6] The molecule was found to bind by the quinoline ring lying parallel to the surface. Recently, other in situ methods such as reflection-adsorption infrared spectroscopy (RAIRS) and attenuated total reflection IR spectroscopy (ATR-IRS) were also employed to study the adsorption of cinchonidine in solution.[7−9] The effect of solvent and coverage on the adsorption mode was discussed. By using the molecular mechanism method, the interaction between cinchonidine and pyruvate was modeled.[10] The "shielding effect" model was reported to elucidate the enantioselective reaction mechanism. As a result, it is generally proposed that the enantioselectivity of the cinchona/Pt system mainly stems from the interaction of modifier and reactant. However, owing to the lack of direct experimental evidence, the adsorption mode of cinchona modifier on catalyst surfaces is still unclear.

Recently, we have obtained direct evidence on the adsorption mode of cinchonidine on Cu(111) by using scanning tunneling microscopy (STM) in solution. Aqueous solution was chosen to minimize the effect of the solvents. Cu(111) substrate was used because the higher mobility of adsorbates on the surface is helpful to form ordered adlayer.[11−13] The internal structure and coordination of the molecules with Cu(111) were clearly revealed in a high-resolution STM image. The result presented here could serve as a model to understand the catalysis process of the cinchona alkaloid-based catalysis system.

A commercial Cu(111) single-crystal disk with a diameter of 10 mm (from Mateck Co., Germany) was used as a working electrode for in situ STM observation. A well-defined single-crystal surface was prepared by the electropolishing method. The STM experiment was carried out on a Nanoscope E instrument (Digital Instruments, Santa Barbara, CA). The tunneling tips were prepared by electrochemically etching tungsten wire (0.25 mm in diameter) in 0.6 M KOH. All of the experimental details were the same as those described in our previous studies.[11,12] The solution of $HClO_4$ (Cica-Merck, Kanto Chemicals) and cinchonidine (Fluka) was prepared with ultrapure Millipore water. All electrode potentials were reported with respect to the RHE (reversible hydrogen electrode). The structural model of cinchonidine was built by Hyperchem software and optimized by the AM1 method until a root-mean-square of less than 0.01 kcal/Å.

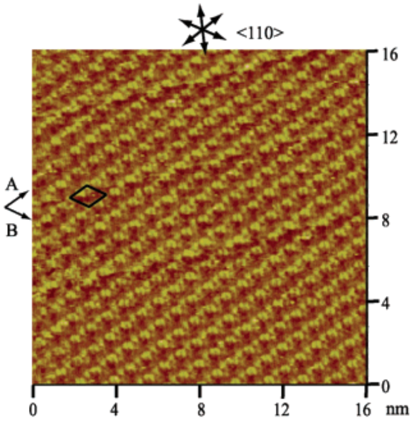

Figure 1. STM image of cinchonidine adlayer on Cu(111) in 0.1 M $HClO_4$ + 0.1 mM cinchonidine at −0.287 V with a setpoint of 10 nA.

After the examination of Cu(111)-(1 × 1) to determine the substrate lattice direction in 0.1 M $HClO_4$, a small amount of 2 mM cinchonidine solution was directly injected into the STM electrochemical cell, and the concentration of cinchonidine was adjusted to ca. 0.1 mM. A uniform cinchonidine adlayer was formed on a wide terrace of Cu(111) surface several minutes later. Figure 1 shows a typical STM image of cinchonidine adlayer in 0.1 M $HClO_4$ + 0.1 mM cinchonidine. It can be seen that the directions of molecular rows indicated by **A** and **B** are along close-packed directions of the Cu(111) lattice with a period of 1.01 ± 0.02 nm corresponding to 4 times the Cu(111) lattice. The angle between **A** and **B** is 60 ± 2°. Therefore, a (4 × 4) structure of the molecular adlayer can be concluded. A unit cell is outlined in Figure 1. In contrast, no ordered structure of cinchonidine was reported by LEED in UHV on Pt(111).[5] This can be attributed to the difference of substrates.[12,13]

To reveal the internal structure of cinchonidine molecules, higher-resolution STM images were acquired under particularly carefully adjusted experimental conditions. Figure 2 is one of the high-resolution images of the cinchonidine adlayer obtained at an electrode potential of −0.287 V. It can be clearly seen that each cinchonidine molecule consists of spots ***a***, ***b*** in ellipse shape and ***c*** in round shape. The distance between spot ***a*** and ***b*** is measured to be 0.48 ± 0.02 nm, while that between ***a*** and ***c*** is measured to be 0.83 ± 0.02 nm. According to the previous ATR-IR results, cinchonidine was anchored on the Pt surface by a quinoline ring with π electrons at low coverage.[8] Meanwhile, the adsorption of pyridine and naphthalene, the molecules with structural features similar to those of the quinoline moiety, on Cu(111) was investi-

---

* To whom correspondence should be addressed. Tel. & Fax: +86-10-62558934. E-mail: wanlijun@infoc3.icas.ac.cn.
† Chinese Academy of Sciences.
‡ Peking University.
§ Also in Graduate School at CAS, Beijing, China.

10.1021/ja028399+ CCC: $22.00 © 2002 American Chemical Society

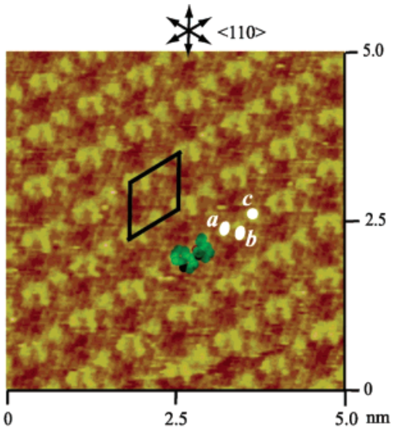

Figure 2. High-resolution STM image of cinchonidine molecules on Cu(111) in 0.1 M $HClO_4$ + 0.1 mM cinchonidine at −0.287 V with a setpoint of 10 nA.

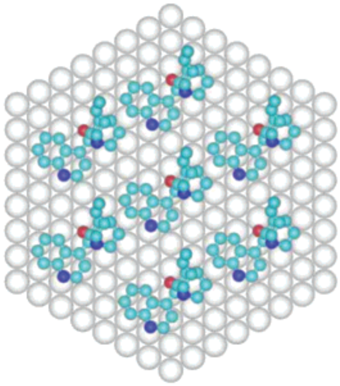

Figure 3. Structural model proposed for cinchonidine adlayer on Cu(111).

gated by in situ STM.[12,14] A flat-on conformation of the two molecules was proposed. The conformation of cinchonidine in different solvents was also investigated with NMR and ab initio simulation. Three preferable conformers in polar solvents were identified. In the present study, it is found that the molecular features in STM image agree well with the "close (1)" structure in ref 15, as schematically overlaid in Figure 2. On the basis of the above consideration, it is reasonable to propose that spots ***a*** and ***b*** correspond to two aromatic rings of the quinoline moiety with a flat-on orientation on the Cu(111) surface. As compared to the STM image with the chemical structure of cinchonidine, the spot ***c*** is thought to be produced by the quinuclidine group. Because of the special steric structure of cinchonidine, the quinuclidine moiety should extend out of the surface. A possible structural model for cinchonidine molecules on Cu(111) is tentatively proposed in Figure 3. The nitrogen atoms in quinoline moiety are located on atop sites.[14] The rings of quinoline are slightly shifted from the two-fold bridge sites of the Cu(111) lattice, similar to the adsorption geometry of naphthalene.[12] The line connecting the quinoline and quinuclidine is aligned along the close-packed direction of the underlying Cu(111) lattice as STM images revealed. In the model, quinoline rings take parallel orientation to the Cu(111) surface. However, the further investigation by other characterization methods or theoretical simulation is necessary to give a detailed and precise understanding of the coordination and bonding of cinchonidine on the surface.

The adsorption conformation of cinchonidine on the solid surface is the key issue for understanding the catalysis process and the mechanism of enantioselectivity. As demonstrated in the present and previous studies, the adsorption of cinchonidine by the quinoline moiety determines the quinuclidine group extending into solution. Thus, the interaction of ketoesters with cinchonidine modifier was facilitated by amine group in quinuclidine. The enantioselectivity stems from the chirality of the quinuclidine group, consistent with the theoretical simulation of the interaction between ketoesters and cinchonidine.[10,16] On the other hand, the catalysis efficiency is strongly dependent on coverage, temperature, solvent, and catalysis material because the conformation of modifier strongly depends on these factors and thus affects the catalysis process. For example, tartaric acid was initially found to form long-range ordered domains on a Cu(110) surface in vacuum.[1] Later, it was found the acid does not form ordered domains on a Ni surface.[3] In the present study, a well-defined cinchonidine adlayer is observed on Cu(111). The molecular conformation is related to the enantioselective catalysis. However, to get insight into the catalyst mechanism of cinchona alkaloid-Pt systems, it is necessary to extend the preliminary research to the real catalyst systems. The further study on the adsorption of cinchonidine as well as cinchonine on Cu and Pt is in progress.

In summary, the adsorption of cinchonidine on a Cu(111) surface has been investigated by in situ STM. It is found that cinchonidine molecules adsorb on Cu(111) and form a long-range ordered adlayer. The high-resolution STM images reveal the internal structure of the molecule. While the quinoline rings lie parallel to Cu(111), the chiral quinuclidine moiety extends out of the substrate surface. A structural model for the adlayer is tentatively proposed. The enantioselectivity of catalysts may relate to the special conformation of cinchonidine upon adsorption. The present study may supply structural information for understanding the enantioselective mechanism of real cinchona alkaloid-Pt catalysts.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Nos. 20025308, 20177025, 20121301), the National Key Project on Basic Research (Grant G2000077501), and the Chinese Academy of Sciences.

References

(1) Lorenzo, M. O.; Baddeley, C. J.; Muryn, C.; Raval, R. *Nature* **2000**, *404*, 376−379.
(2) Barbosa, L. A. M. M.; Sautet, P. *J. Am. Chem. Soc.* **2001**, *123*, 6639−6648.
(3) Humblot, V.; Haq, S.; Muryn, C.; Hofer, W. A.; Raval, R. *J. Am. Chem. Soc.* **2002**, *124*, 503−510.
(4) Kacprzak, K.; Gawroński, J. *Synthesis* **2001**, 961−968.
(5) Carley, A. F.; Rajumon, M. K.; Roberts, M. W.; Wells, P. B. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2167−2172.
(6) Evans, T.; Woodhead, A. P.; Gutiérrez-Sosa, A.; Thornton, G.; Hall, T. J.; Davis, A. A.; Young, N. A.; Wells, P. B.; Oldman, R. J.; Plashkevych, O.; Vahtras, O.; Ågren, H.; Carravetta, V. *Surf. Sci.* **1999**, *436*, L691−L696.
(7) Ferri, D.; Bürgi, T.; Baiker, A. *Chem. Commun.* **2001**, 1172−1173.
(8) Ferri, D.; Bürgi, T. *J. Am. Chem. Soc.* **2001**, *123*, 12074−12084.
(9) Kubota, J.; Zaera, F. *J. Am. Chem. Soc.* **2001**, *123*, 11115−11116.
(10) Margitfalvi, J. L.; Tfirst, E. *J. Mol. Catal. A* **1999**, *139*, 81−95.
(11) Xu, Q.-M.; Wang, D.; Wan, L.-J.; Wang, C.; Bai, C.-L.; Feng, G.-Q.; Wang, M.-X. *Angew. Chem., Int. Ed.* **2002**, *41*, 3408−3411.
(12) Wan, L.-J.; Itaya, K. *Langmuir* **1997**, *13*, 7173−7179.
(13) Yau, S.-L.; Kim, Y.-G.; Itaya, K. *J. Phys. Chem. B* **1997**, *101*, 3547−3553.
(14) Wang, D.; Xu, Q.-M.; Wan, L.-J.; Bai, C.-L. *Langmuir* **2002**, *18*, 5133−5138.
(15) Bürgi, T.; Baiker, A. *J. Am. Chem. Soc.* **1998**, *120*, 12920−12926.
(16) Vargas, A.; Bürgi, T.; Baiker, A. *New J. Chem.* **2002**, *26*, 807−810.

JA028399+