Japan Academy Prize to:

Maki Kawai
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for "Single-Molecule Spectroscopy Elucidating Chemical Reactions at Solid Surfaces"

Outline of the work:

Chemicals essential for our life are produced by chemical reactions involving catalysis. Discovery of ammonia synthesis catalysts saved Europe from starvation in the early 20th century, whereas polymerization catalysts have allowed us to produce synthetic fibers such as nylon that have changed our way of living. In recent years, catalysts work to protect our environment by converting nitrogen oxides, one of the causes of air pollution, into harmless molecules. Catalysts used in large-scale production are heterogeneous catalysts (solid catalysts). In this case, catalysis is a chemical reaction that takes place at the surface of the solid.

Dr. Maki Kawai has contributed to the fields of chemistry and materials science, especially in the fundamental understanding of physical chemistry at solid surfaces and elucidating the mechanism of catalytic reactions, through precise spectroscopic studies of molecules at solid surfaces. When adsorbed on surfaces, the electronic state, vibration state, and spin state of an adsorbed molecule change. This perturbation is the key to catalysis, and the difference between the original and the altered state of the molecule reflects its interaction with the surface. By accurately measuring these states, it is possible to determine experimentally the potential energy surface (PES) for reaction and/or the diffusion on surfaces. Dr. Kawai utilized infrared spectroscopy and electron-energy-loss spectroscopy to identify the vibrational energy of adsorbed molecules. Using carbon monoxide as an example, she estimated the PES for its surface diffusion. Among many interesting achievements, her study on single-molecule spectroscopy and reactions is highly evaluated. Dr. Kawai and her colleagues have developed a method to quantify the electronic structure and the vibrational state of individual molecules, which are spatially selected, and they have succeeded in specifying the reaction that is triggered by each specific chemical state of the molecule. Their research achievements realizing state-to-state chemistry at surfaces have been highly evaluated internationally. Followings are some examples of these research achievements.

Scanning tunneling microscopy (STM) provides a sub-Ångström spatial resolution and the ability to control precisely the acceleration energy of electrons. Dr. Kawai utilized STM to advance her research on single-molecule spectroscopy and chemistry. She developed a method for detecting the vibrational states of a single molecule, enhancing her study on chemical reactions originating from vibrational excitation. Furthermore, focusing on the interaction between substrate metals with continuous electronic states and adsorbed molecules with discrete states, she advanced our understanding of the spin state of the adsorption system. In particular, she determined the relationship between the molecular vibration excited by tunneling electrons and the reaction coordinate. When a molecule is vibrationally excited, a chemical reaction will take place with a certain probability. By experimentally obtaining the relationship between the reaction probability and the accelerating energy of the tunneling electrons, a vibrational spectrum is obtained, which is called an "STM action spectrum." Precise analysis was realized based on a theoretical simulation. The development of a method (action spectrum) for acquiring the vibration spectrum of a single molecule on the surface was a remarkable achievement that has been highly evaluated worldwide. Molecules with unpaired spins (magnetic molecules) interact with the electrons of the substrate metal to develop an electronic state unique to the adsorbed molecular system. Depending on the strength and symmetry of the adsorption, this spin state differs. If the interaction is too strong, the spin state disappears. If it is very weak, the spin state survives. A Fano-shaped Kondo state appears in between. Dr. Kawai studied the changes in these states and showed that the spin system depends on the distance between the isolated spin and the metal in the molecule, and that the degree of orbital freedom depends on the symmetry of the adsorption site. This led to the world's first discovery of the emergence of an exotic Kondo state, which contributed to the development of low-dimensional physical properties on solid surfaces.

In addition to single-molecular spectroscopy, Dr. Kawai has conducted research on the electronic state of oxygen defect sites on the surface of titanium dioxide (Titania), which is a well-known photocatalyst. By atomically specifying the electronic structure of Titania through STM, she found that the defect state appears in the band gap at the higher edge of the occupied state, where the state is found to spread wide to about five lattices. This is an important finding related to the properties of the small polaron formed in titanium dioxide.

As mentioned above, Dr. Maki Kawai has been conducting highly unique research on chemistry using solid surfaces as the reaction platform. Based on precise observations in spectroscopy, she has performed research on the reaction behavior of single molecules and microscopic studies on the electronic state of solid surfaces. Dr. Kawai has contributed not only to the field of chemistry, but also to condensed matter science. These outstanding achievements have been highly evaluated in Japan and abroad. She has been awarded the Chemical Society of Japan Award, Medal with Purple Ribbon, L'Oreal-UNESCO Women in Science Award, and AVS Medard W. Welch Award.

List of Main Publications

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4. "Molecular beam epitaxy study of $Bi_2Sr_2CuO_x$ using NO_2 as an oxidizing agent", S. Watanabe, M. Kawai and T. Hanada, *Jpn. J. Appl. Phys*. **29,** L1111–L1113 (1990).

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13. "Conduction and valence band positions of Ta_2O_5, TaON, and Ta_3N_5 by UPS and electrochemical methods", W.-J. Chun, A. Ishikawa, H. Fujisawa, T. Takata, J. N. Kondo, M. Hara, M. Kawai, Y. Matsumoto and K. Domen, *J. Phys. Chem. B* **107**, 1798–1803 (2003).
14. "Local chemical reaction of benzene on Cu(110) via STM-induced excitation", T. Komeda, Y. Kim, Y. Fujita, Y. Sainoo and M. Kawai, *J. Chem. Phys.* **120**, 5347–5352 (2004).
15. "Investigation of the electronic interaction between TiO_2(110) surfaces and Au clusters by PES and STM", T. Minato, T. Susaki, S. Shiraki, H. S. Kato, M. Kawai and K. Aika, *Surf. Sci.* **566–568**, 1012–1017 (2004).
16. "Excitation of molecular vibrational modes with inelastic scanning tunneling microscopy processes: Examination through action spectra of *cis*-2-butene on Pd(110)", Y. Sainoo, Y. Kim, T. Okawa, T. Komeda, H. Shigekawa and M. Kawai, *Phys. Rev. Lett.* **95**, 246102 (2005).
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