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Atomic Aspects on Surface Chemical Reaction

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Development of surface science has provided us atomic scale surface images and helped us understand the surface reaction in an atomic scale. It was believed that there were two big gaps between the real catalyst systems and surface science targets, pressure gap and material gap. But these gaps are being filled now. Non-linear optical phenomenon (SFG), glancing angle x-ray and scanning probe techniques have enabled the ambient pressure measurements of surface. Great efforts on electron analysis techniques have made it possible to carry out the XPS measurements in the presence of the gas phase oxygen and other reactants. Recent development in surface analysis techniques for non-conducting targets enables us to investigate the metal clusters on well-defined oxide surfaces to fill the material gap. We are now able to control and to initiate the surface reactions intentionally by adjusting physical parameters.

Surface science has reached a new stage not only to determine the surface structure, electronic properties and reaction mechanisms but to synthesize the highly active surfaces and to control the catalytic reactions artificially.

1. Introduction

Recent developments in surface science techniques have provided us atomic scale surface images and confirmed our understanding of the surface phenomena based on the atom and molecular levels. The modern surface science is based on three techniques,

1. Electron analysis techniques such as LEED(Low energy electron diffraction) RHEED(reflection high energy electron diffraction), HREELS(High resolution electron energy loss spectroscopy), XPD(X-ray photoelectron diffraction), UPS(Ultraviolet photoelectron spectroscopy) and XPS(X-ray photoelectron spectroscopy) which are surface sensitive due to electron's small escape depth from the material [1];
2. Preparation and characterization techniques of well-defined single crystal surfaces;
3. Ultra-high vacuum(UHV) technique.

In spite of the great success in surface science, it is believed that there are still gaps between the surface science and real catalytic systems. [2] One is "pressure gap" and the other is "material gap". Many surface science techniques require UHV conditions while the practical catalytic reactions occur at ambient or higher pressure than 1 atm. Thus there are 10^{13} order difference between them called as "pressure gap"!! As for "material gap", surface science uses well defined flat surfaces to decrease complexity while practical catalyses occur on inhomogeneous complex materials with a lot of pores, multielement and multiphases to increase the activities and selectivities.

Recent challenges are addressed to fill these gaps. [2] In this plenary talk, I review some examples of these challenges to fill the pressure and material gaps in oxidation catalysts. In the last part I will discuss the future aspect of surface science in oxidation reactions - possibility of fine synthesis of highly active surface structure and artificial control of the surface reaction which are the greatest advantages of the surface science.

2. To overcome the pressure gap.

Why does the surface science require the UHV conditions? It is because the clean surface is rapidly contaminated unless the UHV condition is satisfied and because electron is easily scattered by the gas phase components. The first reason can be overcome by strictly keeping the UHV conditions around the sample just before the reaction starts. Once the clean well defined surface is prepared and characterized by surface science techniques, the reaction can be then carried out under the ambient conditions. Somorjai and Goodman have revealed the structure dependence of reactivities of single crystal surfaces in this way. [3; 4] The second difficulty is overcome in two ways. One way is to use other surface sensitive techniques than electron spectroscopy, such as scanning probe techniques and light spectroscopies.

Fig.1a shows the TiO_2(110) surface structure.[5] Big and small filled balls are oxygen and Ti atoms, respectively. Protruding oxygen atoms (called as bridging oxygen) make a row running along the [001] direction while the 5-fold Ti atoms exposed to the surface also make another line parallel to the [001] direction. Fig. 1b and c shows STM images of the clean TiO_2(110) and the CH_3COOH adsorbed surfaces, respectively. [6] The bright spots in Fig.1b make a line corresponding to the 5-fold Ti atoms and the dark bands between the bright lines corresponding to protruding oxygen atoms running along the [001] directions. Note the STM can observe Ti atoms owing to the electronic effect though Ti atoms are below the protruding atoms. [5] One can find the bright spots in the dark bands which correspond to the oxygen defects or OH groups which have a large tunneling probability. When it is exposed to CH_3COOH, it is dissociatively adsorbed on the two 5-fold Ti atoms to form a bridging acetate. The adsorbed acetates form a uniform lattice structure with twice as large a periodicity as that the substrate in the [001] direction, (called 2x1 structure) as shown in Fig.1d. The STM can give the atomic scale pictures of surfaces including the surface defects and adsorbates. Onishi and Hendersson et al. observed the photo decomposition reaction of trimethylacetate in the presence of oxygen and discussed the role of oxygen. [7]. Aizawa et al. revealed the formate decomposition reaction on the TiO_2(110) surface. They concluded that the monodentate formate species was the reaction intermediate for the decomposition reaction. [8; 9]

Light is not so strongly affected by the presence of gas phase. RAIRS(Reflection-absorption infrared spectroscopy) can give the surface vibrational information about the adsorbate.[10] In order to distinguish surface adsorbate and gas phase signals, polarization-modulated RAIRS(PM-PARIS) are adopted because adsorbate vibrational mode only absorbs the p-polarized light while gas phase can absorb both polarizations. SFG(Sum frequence generation) is a more surface sensitive technique because SFG signal only arises from the surface region where the inversion center is lacking. Ruppenrechter et al. studied CO, CH_3OH, CH_4 oxidation reaction under the ambient pressure by PM-PARIS and SFG [11-13]

The x-ray diffraction, scattering and absorption can give the structure information. However, X-ray can penetrate deeply into the material and is not usually surface sensitive. When the flat surface is used and the X-ray hits the surface in a grazing angle or with the incident angle less than the critical angle, δ_c (normally 10 mrad), the total refection of X-ray occurs. In this case the X-ray can not penetrate deeply into the bulk of the material (penetration depth <a few nm) and X-ray becomes surface sensitive. [14] Thus the grazing angle X-ray diffraction gives the surface lattice structure more precisely than LEED(Low energy electron diffraction) because the latter technique is suffered from the multiple scattering. The relaxation of TiO_2(110) surface was determined by the surface X-ray diffraction techniques. [15; 16] The bridging oxygen and 5-fold Ti are relaxed upwards by 0.010 nm and downward by 0.011nm, respectively.[16] I will discuss the polarization dependent total reflection fluorescence X-ray absorption fine structure spectroscopy(PTRF-XAFS) method which is suitable for the structure analysis of metal

species highly dispersed on the flat substrate in the next section. [17-19]

The other way to overcome the second difficulty is to reduce the distance between the sample and electron analyzer and to use the electron lens. Fig. 2 shows the schematic drawing of the ambient XPS. [20] Photoelectron excited by the x-ray goes into the XPS instrument. The electron lenses placed before the energy analyzer collect the ejected electron to focal points. Pin holes are put on these focal points so that the differential pumping becomes possible before and after the pin holes without the loss of photoelectron. Consequently the pressure around the sample can be kept at high pressure (> 1mbar) while XPS analyzer system is under high vacuum.[21-25] Atop CO was observed at 286.6 eV in the presence of 1 mbar CO by the ambient XPS which was never observed under the high vacuum. [26]

The desorption angle and translational energy analysis of the reaction products can give us the reaction site information if the product suffers repulsive interaction from the surface like CO_2. [27] Mastushima et al. intensively studied the angular distribution of CO oxidation reaction. CO oxidation reaction occurs in a Langmuir Hinshelwood mechanism where both CO and oxygen adsorbs on the surface. The CO_2 desorption occurs mainly along the perpendicular direction of Pd(110) surface after the CO oxidation reaction. The angular distributions along $[1\bar{1}0]$ and [001] are proportional to $\cos^3\theta$ and $\cos^{10}\theta$ at 420 K, respectively, indicating the CO_2 desorption distribution is sharp along [001] while it is wide in the $[1\bar{1}0]$ direction.[27] Here, θ is defined as an angle between the desorption direction and surface normal. This result means that the CO oxidation reaction takes place at the valley Pd atoms between the Pd ranges which are running along $[1\bar{1}0]$ direction. The infrared emission spectroscopy of the desorbed gas can provide the information about vibrational and rotational states of the desorbed products[28; 29] which conveys the structure of the reaction intermediate. If CO and oxygen react in a straight manner as shown in Fig.3a, antisymmetric vibrational mode is excited while those react in a side-on manner as shown in Fig.3b, bending and rotational modes are excited in addition to the antisymmetric mode. Nakao and Kunimori have revealed that CO oxidation reaction on Pd(111) goes with a side on collision at high temperature while it occurs in a rather straight manner at low temperature. [30; 31]

If the vibrational and rotational states of the desorbed products are identified in an angle resolved way, one can determine the shape of the reaction intermediate and detail reaction mechanism as well as the reaction site structure. But the signal of angle resolved infrared emission is too small and hindered by the background infrared emission if it is measured in the angle resolved way. The angle resolved infrared emission spectroscopy of desorbed products was thus extremely difficult. Yamanaka challenged this difficulty by cooling down the entire system to a liquid N_2 temperature and successfully measured angle-resolved infrared emission. [32-34] The intermediate state of CO_2 on the Pd (111) at 700 K is produced through a side-on manner between O and CO and has a molecular alignment with its molecular axis parallel to the surface. The angle resolved infrared emission provides more details view of the surface intermediate. The bending mode of the desorbed CO_2 is excited as shown in Fig.3(c) in the normal desorption while rotational mode is not excited. In the off-normal direction, the rotational mode is rather excited but the bending mode excitation becomes less.(Fig 3(c)) The CO_2 just before the desorption is bound to surface through two bonds at O and C(O) If the O –substrate bond is first cleaved, the rotationally excited CO_2 is desorbed in the off-normal direction. On the other hand if C(O)-substrate bond is cleaved first the CO_2 is desorbed with the bending mode highly excited.

3. To fill the material gap

The largest difference in the real systems from the single crystal surfaces can be found in the supported metal catalysts. The real system is composed of nanoclusters with different surface structures involving the corners and the steps supported on the porous inorganic oxide while the single crystal system is basically flat. The periodic steps and kinks can be made on the single crystal surfaces but the nanoscale particle size tremendously affects the catalyses as is found in Au nanoparticles. [35] The deposition of the metal on the flat metal oxide surface gives the model supported metal system. When the oxide surface has an electric conductivity, the STM (Scanning tunneling microscopy) is available to provide the size and morphology of nanoparticles deposited on the surface. But many oxides, such as MgO, SiO_2 and Al_2O_3, are insulators so that we can not directly observe the oxide surface by STM. The preparation of well-defined oxide thin film on the metallic substrate is one way to observe the oxide surface by STM. [36] Sterrer prepared MgO(100) thin film on Ag(100) surface and observe the defect present in the MgO (100) surface. The defect energy levels are dependent on its location. [37] The Al_2O_3 thin film is grown on the surface by the oxidation of NiAl(110) .[38] The SiO_2 thins film grown on the Mo(112) has an isolated structure linked to Mo surface through Si-O-Mo bond. [39-41] The TiO2 thin film can be grown on the Mo(112) to give the well-order (8x2) structure[41-43]. Chen et al. revealed that 2 monolayer Au deposited on the TiO_2/Mo showed very high activity for CO oxidation reaction. [43] The other way is to use NC-AFM(non-contact Atomic force microscopy). NC-AFM is a method which does not require the electric conductivity and has beenapplied to the MoO_3, NiO, CeO_2, Al_2O_3 and TiO_2 surfaces. [44-51] Recently, the ambient condition STM and AFM are applicable to the surface science studies.[52-54] NC-AFM study on the Au on fully oxidized TiO_2 (110) shows the high Au mobility under the presence of air at room temperature while Au particles are immobile under a high vacuum. [54]

When Ni is deposited on the TiO_2 (110) surface, the surface Ni clusters with a certain size is produced at lower coverage(0.03ML) as shown in Fig. 4 and then the number of the Ni clusters increases with the further deposition of Ni. We call such a growth mode of Ni on

TiO_2(110) as a self-regulated growth mode. [55] The interaction between Ni clusters and TiO_2 (110) surface may stabilize the cluster with a definite size and may cause such a self-regulated growth mode. However, the atomic scale information about the interaction between Ni cluster and the substrate is lacking in the STM observation. The X-ray absorption fine structure(XAFS) spectroscopy gives the structure information around the X-ray absorbing atom. [56] XAFS intensity has X-ray polarization dependence. When the angle between x-ray electric vector and bond direction is θ, XAFS intensity is proportional to $3\cos^2\theta$. When the metal particles are deposited on the flat oxide substrate system and the polarization direction is set at the parallel to the oxide surface, the XAFS signal of the deposited metal is dominated by the metal-metal interaction as shown in Fig. 4b. When it is set at the normal to the surface, the metal-substrate structure is mainly elucidated as shown in Fig.4c. The polarization dependent total reflection fluorescence XAFS(PTRF-XAFS) is applied to the Ni clusters on the TiO_2(110) surface to understand the self-regulated growth mechanism.[57-59] The Ni clusters are found with a structure shown in Fig.4d where 86 % Ni atoms in the cluster has bondings with the protruding oxygen atoms of the TiO_2(110) surface which stabilize the surface cluster structure. Such interaction between metal cluster and protruding oxygen atoms was found in a Cu cluster on the TiO_2(110) surface. [60] The TPRF-XAFS can provide the information about the structure change during the reaction because X-ray can go through the gas phase reactant. Mo dimer is created on the TiO_2 (110)

surface and catalyzed the CH_3OH oxidation reaction. [17; 61-65] In situ TPRF-XAFS under the oxidation reaction reveals that the reaction takes place in the Mars-van Krevelen mechanism where the Mo dimer structure is broken by the reaction with CH_3OH and is regenerated after the oxidation process as shown in Fig. 5.

4. Future aspect of surface science in catalysis- synthesis of highly active structure and artificial control of the surface reaction.

The flat substrate has a merit for easy characterization and easy control of preparation. The above development of surface sciences has made it possible to carry out the surface in situ characterization under the reaction conditions. The demerit of the flat surface might be the low surface area and the low activity. But if one can precisely synthesize the surface species with a very high activity, it will be the most efficient catalyst. Hara et al. prepared a well-defined Pd complex on the Si (111) surface linked with bisoxazoline molecule and demonstrated the possibility to synthesize the highly active species on the flat surface. [66-68] The small Si tip(5x5mm^2) with the Pd complex converted benzyl alcohols to benzyl aldehyde by gas phase oxygen with nearly 100 % conversion and TON=410,000. Lithographic techniques which have succeeded in the fabrication of electronic devices can be applied to surface science preparation of well-defined inhomogeneous surfaces. [69-71] $VSbO_x$ undergoes the selective ammoxidation of propane. [72] The remote control mechanism is proposed for the selective oxidation in which the oxygen activated in the Sb_2O_4 phase diffuses to the $VSbO_4$ surface and is used for the selective oxidation reaction. [73] The size and arrangement of $VSbO_4$ and Sb_2O_4 phases are finely adjusted by the lithography.[74] Fig. 6 shows the preliminary result of the dependence of propene selective oxidation activity to acrolein on the separation of Sb_2O_4 line. [75] The width of Sb_2O_4 lines is designed by lithography, keeping the total surface areas of $VSbO_4$ and Sb_2O_4 constant as shown in Fig.6(a). There is an optimum separation of Sb_2O_4 lines in this reaction as shown in Fig.6(b), indicating the possibility of the reaction control in the μm or sub μm size created by the lithography.

The other merit of using a flat surface is to control of the catalytic reaction with in-situ monitoring of the reaction and giving the external impulses such as light, electric potential and reactant pressure. Rotermund et al. successfully control and modify the reaction by monitoring the surface reaction using EMSI(Ellipsomicroscopy for surface imaging). [76-79] They observed the reaction pattern formation during CO oxidation reaction by EMSI. Then the laser light was shed at a small point of the surface to initiate and modify the reaction by increasing the local temperature.

The pulse infrared laser can control the surface reaction not only through the temperature rise but through the selected excitation of a specific vibrational mode. MoO_3 has 5 Mo-O bonds with different vibrational modes. The infrared laser emitted from the free electron laser system tuned to a specific vibrational bond can initiate the C_2H_5OH decomposition reaction though no reaction occurs when wavelength of the infrared laser is detuned from the vibrational mode. [80; 81]

5. Conclusions

In summary, surface science is not only dedicated to the ideal model systems which create and demonstrate catalytically important concepts but also provide a new way to prepare a well defined and highly active structure as well as an artificial way to control the surface reaction. **Surface science has reached a new stage not only to determine the surface structure, electronic properties and reaction mechanism but to synthesize the highly active surface catalyst molecule and to control the catalytic reaction artificially.** In this purpose, surface science will make progress in the cooperation with fine chemical syntheses, semiconductor device fabrication methods, laser and molecular beam technologies and colloidal chemistry as well as the improvement of its original methods.

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Figure captions

Figure 1. (a) TiO_2 (110) surface a large and a small filled balls are oxygen and Ti atoms, respectively.(b) STM image of a clean TiO_2(110). (c) STM image of a CH_3COOH-adsorbed TiO_2(110).

Figure 2. Schematic drawing of the ambient XPS system.

Figure 3. Vibrational and rotational states of desorbed CO_2 after the CO oxidation reaction. (a) The oxygen atom collides with CO in a straight manner. (b) The oxygen atom collide with CO in a side-on manner. (c) The desorption angular dependency of energy states of vibrational and rotational modes of desorbed CO_2. The energy is expressed by the temperature. (d) A schematic explanation of the desorption direction and the excitation mode.

Figure 4. (a) STM image of Ni cluster on TiO_2(110) surface. Ni coverage is 0.03 ML. (b) and (c) indicated the polarization direction and the cluster structure. (d) Model structure for Ni cluster on the TiO_2(110) surface.

Figure 5. Upper panel shows the PTRF-XAFS oscillations for Mo dimer after the oxidation reaction (upper left) and Mo monomer after the reaction with CH_3OH(upper right). Lower panel shows schematic drawing of the structure change during the reaction.

Figure 6. SEM picture of lithographic Sb_2O_4-$VSbO_4$ surfaces (a) and the acrolein formation activity dependence on the separation of Sb_2O_4 lines(b) 2.5 x10^{-3} Pa C_3H_6 and 7.5 x10^{-3} Pa O_2 are reacted on the surface with the temperature of 673 K.

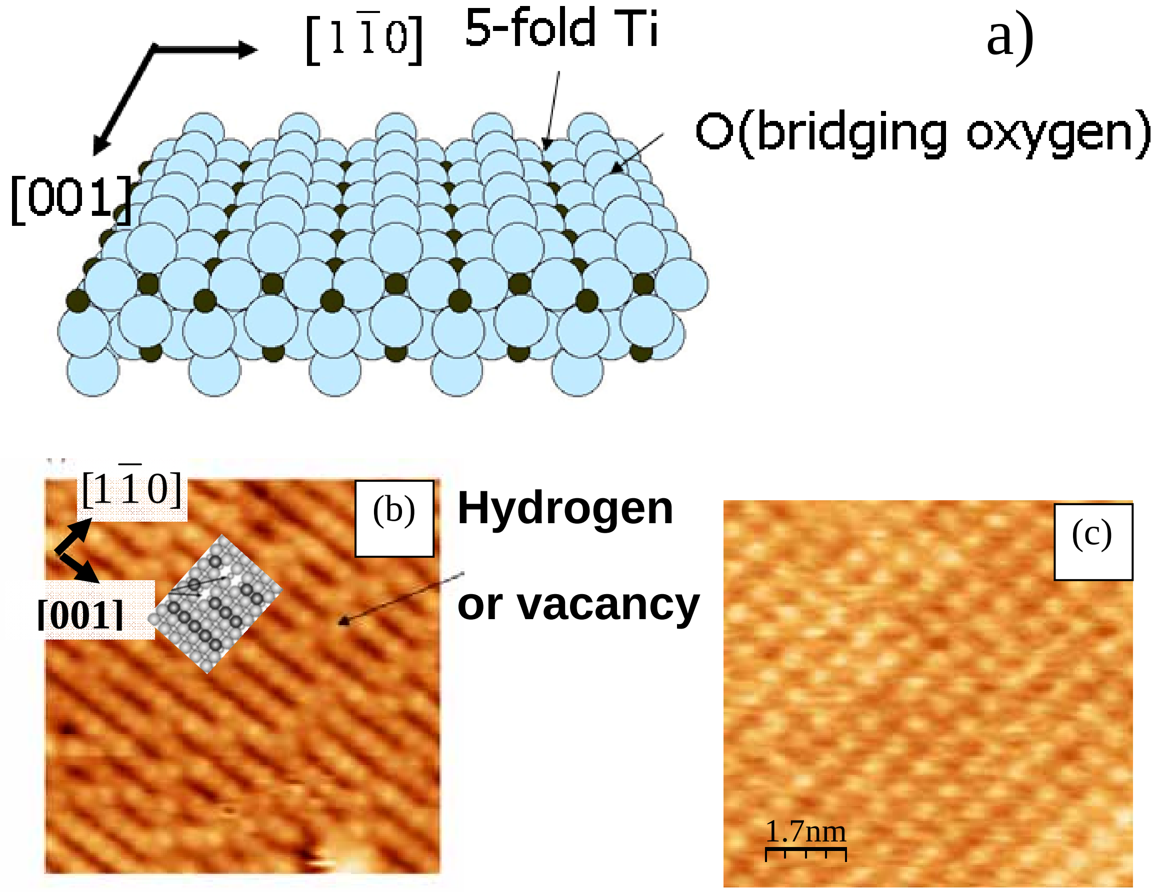
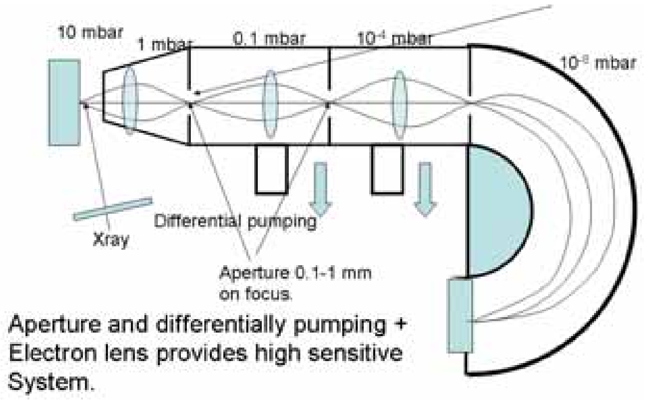

[1$\bar{1}$0]
5-fold Ti
a)
[001]
O(bridging oxygen)
[1$\bar{1}$0]
[001]
(b)
Hydrogen
or vacancy
(c)
1.7nm

Figure 1.



Aperture and differentially pumping +
Electron lens provides high sensitive
System.

Figure 2.

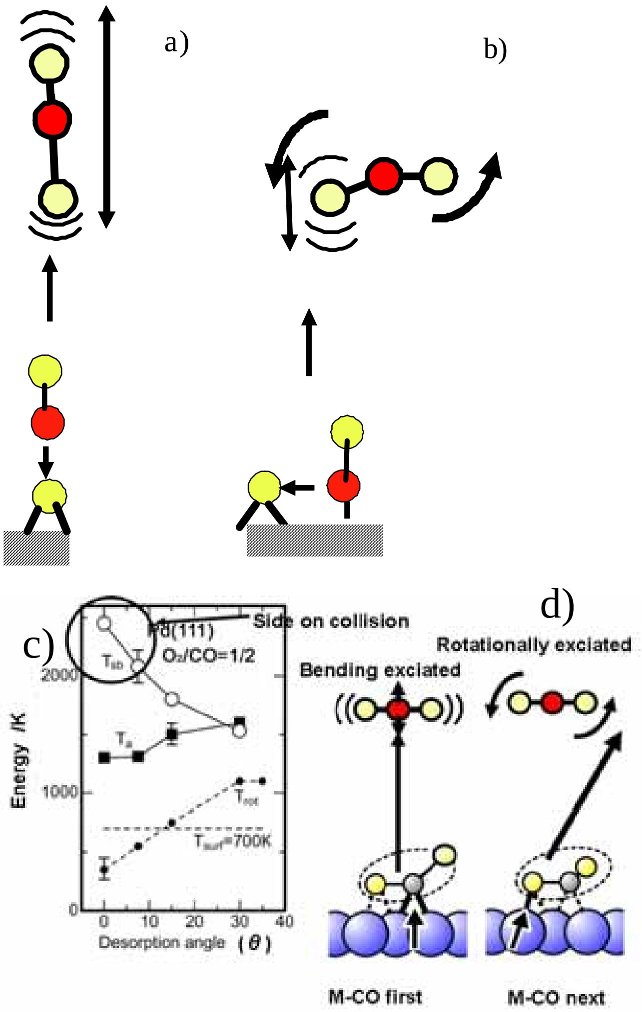

a)
b)
c)
d)
Side on collision
Pd(111)
O₂/CO=1/2
T_sb
T_a
T_rot
T_surf=700K
Energy /K
2000
1000
0
0
10
20
30
40
Desorption angle (θ)
Rotationally exciated
Bending exciated
M-CO first
M-CO next

Figure 3.

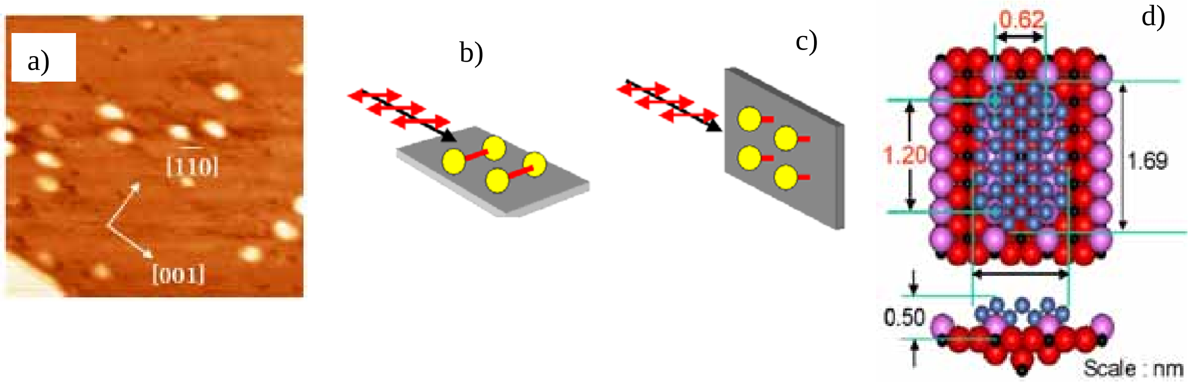


Figure 4.

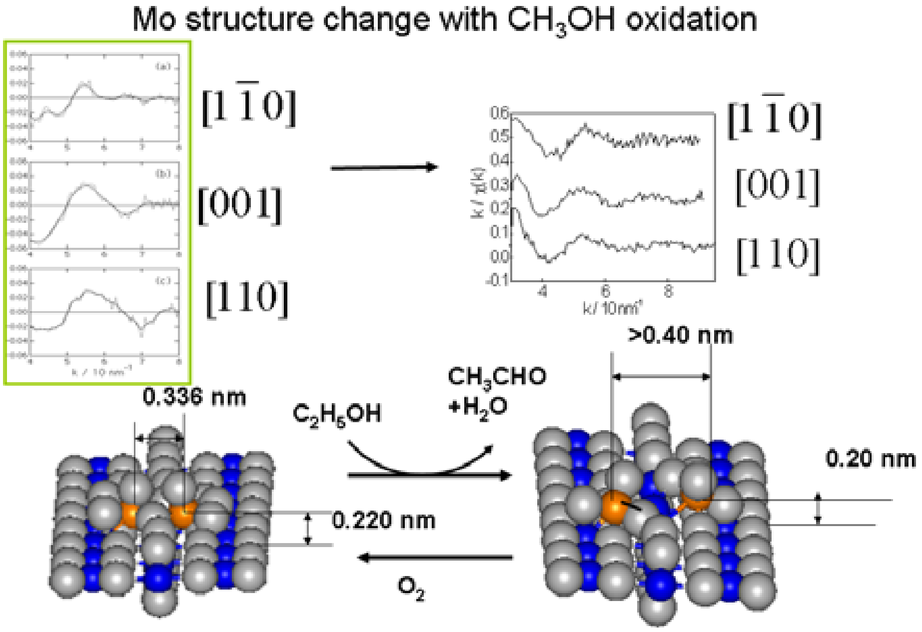


Figure 5

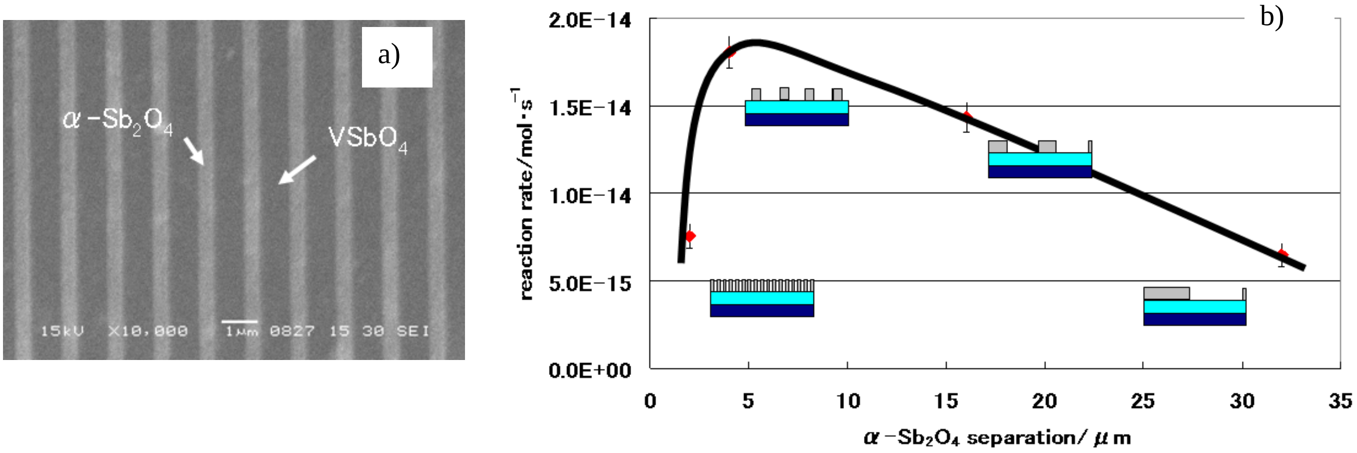


Figure 6

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