of the number of nuclei surrounding the paramagnetic center. One has to remark that the combined analysis of the intensity and frequency modulation is a suitable procedure that greatly reduces the ambiguity in determining both number and distances; moreover, the agreement between the data obtained from two-pulse and three-pulse patterns can be assumed as a proof of the consistency of the procedure. In this study some uncertainty remains due to the approximations introduced to simplify the calculations and to reduce the computer time: the possibility of misalignment between the nuclear quadrupole and dipolar hyperfine tensors[15,17] was neglected; only a limited number of nuclear shells were allowed to surround the paramagnetic center, and the spherical model approximation was used. These approximations appear not to be critical in the analysis of disordered systems.

Relevant differences were found in the solvent arrangement around the –NO fragment between the unadsorbed and adsorbed systems. In solution, a packed situation occurs, and the formation of a "complex" between one solvent molecule and the radical is clearly revealed. In the adsorbed systems, significant changes from this structure were found. The degree of change was greater in the case of charged radicals; the differences in the structure can be attributed to the electric interactions between the cavity wall and the radicals.

One should note that the quantitative estimations obtained in this work are in good agreement with the general conclusions derived from CW ESR measurements. This confirms the usefulness of using both these magnetic resonance techniques to gain a more complete description of the studied systems.

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Artificial Layer Surface of Periodic Cu–TiO_2 for Catalytic Decomposition of Methanol

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Periodic thin-layer composites of Cu and TiO_2 were fabricated by alternating depositions in a form of regularly distributed small spots (150 μm in diameter) in order to obtain artificially modulated catalytically active surfaces. The periodic surfaces perpendicular to the deposition direction were applied to the catalytic decomposition of CH_3OH. The thickness of a Cu unit layer was changed in the range 3–10 nm, while that of the oxide support was kept at 10 nm with the total number of accumulated layers being 45. The periodic modulations of as-deposited and heat-treated composites were characterized by means of small-angle X-ray diffraction, Auger electron spectroscopy, secondary ion mass spectrometry, X-ray photoelectron spectroscopy, and scanning electron microscope observations. It was shown that the artificial layer structures were stable upon heat treatment in vacuo and in a H_2 atmosphere at high temperatures. In the catalytic reaction on the Cu phases at low pressures, an interesting feature was the appearance of a maximum in the selectivity of H_2CO formation at a medium thickness of the Cu layer. The effects of the periodic structures are discussed.

Introduction

In view of a current desire to fabricate a well-designed microstructure, artificial layering to produce superlattices has been developed in the semiconductor field and has been applied even to constituents with large differences in their lattice parameters.[1] Such a one-dimensional composite-modulated thin film can be described as a new material, not only because of the artificial designation of layer compounds, but also because of the periodic structures that hardly occur naturally. In the fabrication of modulated thin films, alternating deposition of the constituents was performed, and the periodic modulation becomes normal to the deposited layers so that composite surfaces can be exposed in the direction perpendicular to their accumulated layers. Such artificially designed surfaces are undoubtedly interesting, but so far there seems little attempt to apply this procedure to surface phenomena involving adsorption and catalysis. When the accumulated layers are constructed as a great number of small columns, the density of the modulated surfaces is considerably increased. For instance, provided that the diameter of the column is 50 μm and the total number of the accumulated layers with a thickness of 5 nm is 100, the area of the side surface becomes a few square centimeters when deposited on a 100 cm^2 substrate: the composite-modulated surface area is of the same order of magnitude as a single crystal. With a decrease in the column diameter, the available modulated surface area becomes much larger. In this manner, one is able to obtain artificial periodic surfaces that depend on the thickness of each accumulated ultrathin film. These multilayer structures have advantages in modifying electronically and geometrically catalytic active phases, since it is possible to change their thickness and the number of accumulated layers, and since it is to be expected that the sandwich structures with the same or different kinds of oxide supports will give rise to a stronger or weaker support effect. This provides a model for the effects of metal–support interactions.

In the present work, Cu was used as the catalytically active phase, and TiO_2 oxide (or SiO preliminarily) as support. A series of the metal–oxide catalysts was prepared to have alternating layer structures in which the thickness of a Cu unit layer was varied, while that of the oxide was kept constant. Their periodicity and layer structures were examined by means of small-angle X-ray diffraction, Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopic (SEM) observations. The catalytic reaction of methanol decomposition was examined at low pressures in a ultrahigh vacuum (UHV) system, because of the interesting selective catalysis by Cu metal for this reaction.[2,3]

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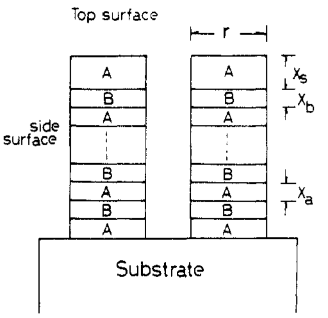

Figure 1. Schematic representation of a multilayer catalyst: A = TiO_2 or SiO; B = Cu; X_s = 20 nm; X_a = 10 nm; X_b = 3–10 nm; r = 150 μm.

Experimental Section

A Cu/TiO_2 thin multilayer was prepared by sequential depositions of the metal and oxide on a single crystal of Si(111) or Corning 7059 glass as substrates. A high-vacuum apparatus was constructed that had two evaporation sources, a small reaction space, a deposition plate, and a thickness monitor. High-purity Ti metal was heated with an electron-beam gun in the shroud, evaporated through the reaction space, which was filled with an ambient pressure of oxygen (2.7×10^{-3} Pa) enough to react with evaporated Ti metal atoms, and then deposited as thin metal oxide on the substrate. A differential pumping system was used to evacuate the introduced oxygen. Copper metal was evaporated from the other source by using resistance heating. Two shutters were employed to avoid contamination upon preheating and to separate one beam of the evaporated particles from the other. The thickness of the deposited layers was monitored by means of a quartz thickness monitor, Sloan 200, which was placed as nearly as possible to the substrate. The substrate was washed ultrasonically in cleaning solutions (Semicoclean 23 and 56 from Fru-uchi Chem. Co.), rinsed with distilled water, and then mounted in the center of the superposed position of the two particle beams. A Mo mask that has holes (150 μm in diameter) arrayed regularly with a rectangular unit cell of 440 μm × 260 μm was used to produce the small spots of the accumulated layers. The layer ultrathin coherent structures, as is schematically shown in Figure 1, were prepared by alternate layering of the support oxide and Cu. The thickness was kept constant at 10 nm for the oxides, while it was varied from 3 to 10 nm for the metal. The total number of the accumulated layers was 45, unless otherwise specified. The outermost surface was covered with the inert oxide support film as thick as 20 nm so as to prevent the direct exposure of the catalytically active Cu phase on the top surface. Hereafter the catalysts are described as (thickness of metal layer expressed in terms of nanometers of Cu/thickness of oxide layer expressed in terms of nanometer of oxide), such as (10-Cu/10-TiO_2). The coherent structures of the prepared multilayer were characterized by means of low-angle X-ray diffraction (Rigaku RAD III) method, Auger electron spectroscopy (Ulvac. Co., AQM 808), X-ray photoelectron spectroscopy (PHI ESCA 5300), and secondary ion mass spectrometry (Hitachi IMA-2S). The low-angle etching method to visualize the periodic structures of the multilayer was also employed. Most of the experiments were done for the Si substrate, and no significant differences were observed in the periodic structures between the substrates.

The catalytic reaction of methanol decomposition was carried out in an ultrahigh-vacuum apparatus equipped with a quadrupole mass spectrometer (Anerva, AGA 360). The system was pumped with an ion pump and a turbomolecular pump, and the background pressure was maintained below 1.3×10^{-7} Pa after baking. Prior to a catalytic run, the thin films were pretreated at 623 K in a H_2 atmosphere. The reactant and pretreatment gases were introduced through a leak valve to a quartz reaction cell. The catalysts were heated with an external electric furnace and its temperature was measured by a chromel–alumel thermocouple in contact with the substrate of the layer catalysts. The peak intensity of the mass spectra was taken as a measure of the amounts of gaseous components, and the spectra were corrected for the interfering fragment peaks of CH_3OH and CH_2O.[4]

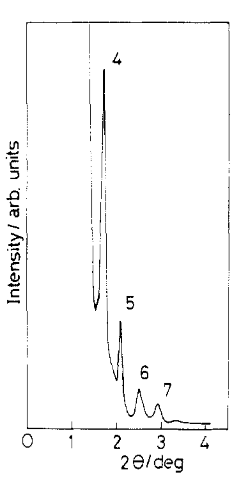

Figure 2. X-ray diffraction of (10-Cu/10-TiO_2) at low angles. The sample was reduced in H_2 at 673 K and then evacuated at 773 K.

TABLE I: Artificial Lattice Distances Evaluated from X-ray Diffraction Peaks for (10-Cu/10-TiO_2) Catalysts

	d/nm		
n	as deposited	heat treated in vacuo[a]	heat treated in H_2[b]
4		23.1	20.8
5	22.6	23.0	21.0
6	22.5	22.6	21.2
7	22.7	22.1	21.2

[a] At 673 K. [b] At 673 K and then evacuation at 773 K.

Results

The positions of X-ray diffraction peaks due to the artificial lattice with length of *d* are given by

$$\sin \theta = n/2(\lambda/d) \qquad (1)$$

where an integer *n* is the order of the reflection, and λ is the wavelength of the X-ray (λ = 0.15405 nm for Cu).[1] For the as-deposited (10-Cu/10-TiO_2) catalyst, the average artificial distance was calculated from the position of diffraction peaks to be 22.5 nm, which was fairly close to the value, 20 nm, of the deposition parameters obtained by the thickness monitor. In a similar way, the artificial lattice distances of as-deposited (3-Cu/10-TiO_2) and (6-Cu/10-TiO_2) catalysts were evaluated respectively as 13.5 and 16.3 nm and were consistent with the thickness of their deposition parameters. When the (10-Cu/10-TiO_2) sample was heated in vacuo at 673 K, the positions of the diffraction peaks remained almost unchanged, but their intensities became stronger. Figure 2 shows a small-angle X-ray diffraction pattern for the (10-Cu/10-TiO_2) catalyst after heat treatment in a H_2 atmosphere at 673 K and then evacuation at 773 K. The diffraction peaks were associated with the fourth to seventh reflection peaks. A comparison with as-deposited films exhibited that their peak positions shifted slightly to higher angles, which corresponded to a decrease of about 6% in the artificial lattice distance. The calculated artificial lattice distances are summarized in Table I. These results indicate that heat treatment has little effect on the present coherent artificial layer structures.

Figure 3 shows the depth profiles of the (10-Cu/10-TiO_2) catalyst analyzed by SIMS. The analysis was performed by using Ar ions accelerated at as low as 5 kV in order to avoid excess damage of the thin-layer structures. The peaks ascribable to Ti^+ and Cu^+ appear alternatively with sputtering time, and the

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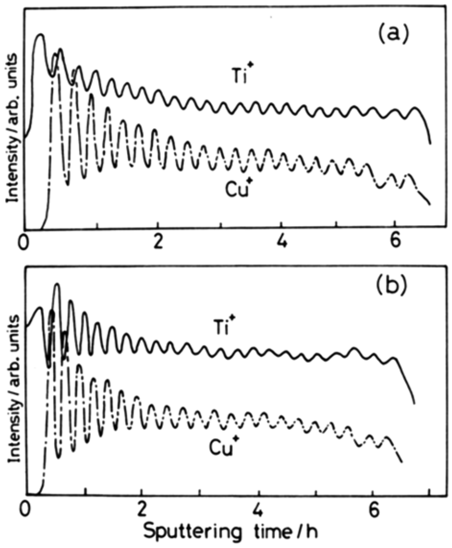

Figure 3. SIMS depth profiles of (10-Cu/10-TiO_2): (a) as deposited, and (b) heat treated in vacuo at 673 K. Sputtering at 5 kV.

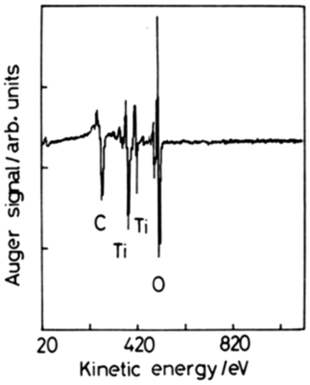

Figure 4. AES spectra of the top surface of H_2-reduced (10-Cu/10-TiO_2).

numbers of the peaks are consistent with those of the corresponding deposited layers. Almost the same peak width is observed for each respective peak. The heat-treated catalyst shows almost the same depth profile, which is indicative of the preservation of the artificial layer structures. The SIMS analysis was also employed on the (10-Cu/10-TiO_2) sample after the catalytic reaction, and little change was observed in the periodic structures. Figure 4 shows the Auger electron spectrum for the outermost surface of the H_2-reduced catalyst. The large peaks due to Ti $L_3M_{23}M_{23}$ and $L_3M_{23}M_{45}$ and to O $KL_{23}L_{23}$ Auger transitions were observed, whereas the AES peaks of Cu atoms were negligibly small. Upon sputtering at 5 kV by Ar ions, the periodic changes in the peak intensities of the respective components appeared: each maximum of Ti and O peaks was positioned at the minimum of the Cu peak, and vice versa, as is shown in Figure 5. The AES results also showed that a trace of impurity carbon existed only at the outermost surface regions. In order further to visualize the composite structures, Cu/TiO_2 samples were sputtered with a wide round-shaped beam of accelerated Ar ions, and the resulting cut-section was examined by scanning electron microscopy. As is shown in Figure 6, a stripe pattern exhibiting the alternating appearance of Cu and TiO_2 layers is clearly observed. The XPS spectra of the as-deposited (10-Cu/10-TiO_2) catalyst showed that the binding energy of the Ti 2p level was nearly the same as that of bulk TiO_2 oxide. As for the Cu phase, the multilayer was sputtered from the top surface to the interior until the XPS signals of Cu began to appear. There was no satellite peak in the Cu 2p region, and the binding energy of Cu $2p_{3/2}$ was 932.7 eV, which is near that observed for Cu metal (932.6 eV).

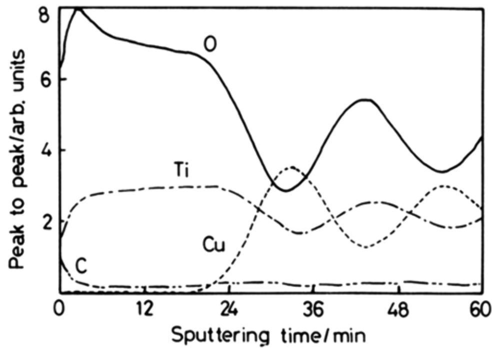

Figure 5. Changes in peak-to-peak Auger intensity with sputtering time for a sample of H_2-reduced (10-Cu/10-TiO_2).

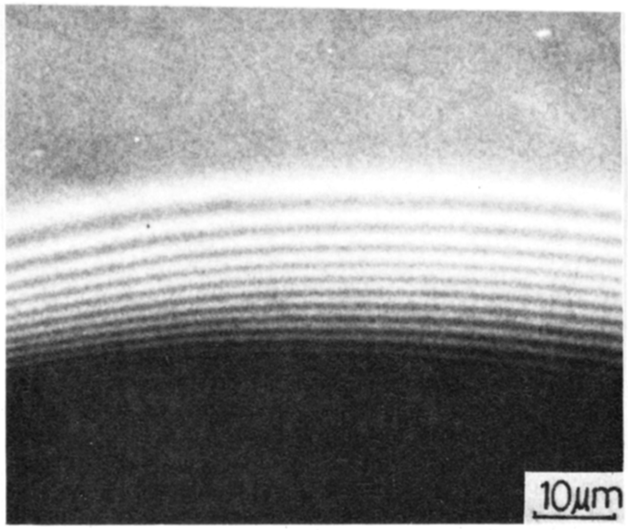

Figure 6. SEM image of multilayer after low-angle Ar ion etching. The white line is the TiO_2 phase.

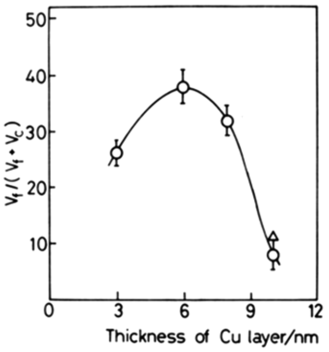

Figure 7. Change in catalytic selectivity as a function of thickness of Cu phase. Sample: ○, Cu/TiO_2; △, Cu/SiO. Conditions: $T = 723$ K; $P = 8 \times 10^{-4}$ Pa. The error bars are for the repeated runs of reaction.

The catalytic decomposition of CH_3OH on (*L*-Cu/10-TiO_2) ($L = 3, 6, 8,$ and 10) was carried out at 723 K and at 8×10^{-4} Pa. The same reaction was also examined on the catalyst with different oxide support, (7-Cu/10-SiO), where the total accumulation number of the layer was 15. The decrease in the mass peak intensity of CH_3OH was followed by an appreciable increase in the peak intensities of H_2CO and CO and a small peak of CH_3OCH_3. The mass peak at m/e 60 which is identified as methyl formate was not detected. There were no significant variations in the formation of CH_3OCH_3 among the Cu/TiO_2 catalysts with different thickness of the Cu layer. Figure 7 shows the change in the selectivity of the reaction as a function of the Cu layer thickness, in which the selectivity is defined as the ratio, $V_f/(V_f + V_c)$, where V_f and V_c are respectively the initial rates of H_2CO and CO formation. The selectivity increased with increasing thickness of the Cu phase, passed through a maximum at 6 nm, and then decreased. It is to be noted that almost the same selectivity was obtained for TiO_2 and SiO supports at the same thickness of the Cu phase.

Discussion

The small-angle X-ray diffraction of the sequentially deposited Cu–TiO_2 multilayers provided the reflection peaks due to the artificial lattice structures, of which distances are fairly close to the values evaluated from the deposition parameters. The appearance of these reflection peaks is consistent with the finding that the periodic structures of a Ti–SiO_2 system give rise to X-ray diffraction peaks in small-angle regions when their artificial lattice distances are between 3.0 and 21.1 nm.[5] Upon H_2 treatment and evacuation at higher temperatures, the artificial Cu–TiO_2 lattice was slightly decreased, compared to that of the as-deposited films. This contrasted with a remarkable decrease, as large as 20% by annealling at 673 K, observed for the Ti–SiO_2 multilayer films that were prepared by sputtering with an Ar + H_2 mixture.[5] Thus it is suggested that neither reorientation of each layer nor interface diffusions between Cu and TiO_2 to produce new phases occurred to a great extent in the present system. The artificial periodic structures of the H_2-reduced and as-deposited Cu–TiO_2 multilayers were revealed in the depth profiles by SIMS and AES and in the SEM observations after a low-angle Ar^+ etching. These results indicate the stability of the multilayer at high temperatures. It was also shown that the periodic structures were preserved after the catalytic reaction. In the AES analysis, no peak ascribable to Cu constituents was detected on the top surface of the accumulated layers, thus indicating that no Cu atoms are exposed at the outermost layer. In the XPS spectra of the as-deposited multilayers, there were no satellite peaks characteristic of Cu oxides, and the binding energy of the Cu $2p_{3/2}$ level was almost the same as that of Cu metal. Thus, the Cu thin layers sandwiched by the TiO_2 support are considered to be in a metallic state rather than in an oxidized state.

Browker and Madix reported that the desorption of formaldehyde from methanol adsorbed on a clean Cu(110) surface occurred at around 643 K, although it was enhanced remarkably with the presence of preadsorbed oxygen.[6] In the present multilayer catalysts, the selectivity was similar for Cu/TiO_2 and Cu/SiO as far as the layer thickness of the Cu phase was concerned. Thus, these results indicate that the decomposition reaction proceeds on the Cu phase at the periodic-composite surfaces. Carrizosa et al. showed that the catalytic reaction of methanol on TiO_2 oxides produced dimethyl ether, water, and methane at around 623 K as the main products.[7] It is plausible that a small amount of CH_3OCH_3 resulted from reaction on the TiO_2 support. The invariance of the rate of CH_3OCH_3 formation with the changes in Cu thickness is in line with this view.

One of the interesting structures in the Cu–TiO_2 multilayer compounds is the interface at which Cu and TiO_2 phases were brought into contact. Owing to the constant total number of the accumulated layers, the density of the interface region was the same for all the examined catalysts. The fact that the reaction selectivity varied from catalyst to catalyst indicates that the interface regions, which might have a bifunctional character of metal and oxide, have little contribution as catalytically active sites in this case.

In the dehydrogenation of methanol to methyl formate over Cu/SiO_2 catalysts,[8] it was shown that the turn over frequency, activation energy, and the selectivity remarkably varied when the surface area of Cu metal became larger than 400 m^2/g (corresponding to a particle diameter of 1.7 nm). This variation was explained in terms of the generation of a strong interaction between Cu and SiO_2. Thus, it is likely that similar effects are present in the Cu–TiO_2 layers, and a plausible explanation for the appearance of a maximum in selectivity with the Cu layer thickness can be given on the basis of the metal–oxide support interactions. The adsorption of methanol on Cu surfaces is reported to proceed via the adsorbed methoxide,[9,10] and formaldehyde is produced by the subsequent abstraction of hydrogen[6,11]

$$CH_3O(a) \rightarrow CH_2O(a) + H(a)$$

where the higher selectivity of CH_2O formation is obtained by the feasible desorption of $CH_2O(a)$ species before its decomposition. Such adsorbed formaldehyde is proposed to interact through a carbonyl lone pair,[12] and its stability is closely related to the electronic states of the Cu atoms. For a smaller Cu thickness, the fraction of the Cu atoms under influences of the TiO_2 support is large. If one assumes that the Cu atoms become slightly cationic through an interaction with oxygen of the oxide, it may be reasonable to expect that a stronger adsorption of $CH_2O(a)$ takes place, which results in a feasible decomposition. With increasing Cu thickness, the effects of the metal–support interaction are diluted, and the formation of CH_2O is increased. For much thicker Cu layer, the effects seem to be negligibly small, and the nature of the Cu atoms resembles that of bulk metal. This view is in line with the fact that there was no significant difference in the catalytic selectivity between TiO_2 and SiO supports with the thick Cu layer. It is to be expected that the density of hollow sites existing on lattice planes is increased for the thick Cu layer, which is suggested from a view point of a geometric effect to facilitate the abstraction of hydrogen from the chemisorbed CH_2O.[13] This apparently leads to a lower selectivity.

The formation of the periodic layer structures of Cu–TiO_2 was well confirmed in the bulk phases. However, it is not excluded that ambiguity remains for the thinner layer of Cu and for the artificial surface structures: agglomeration or an islandlike deposition of Cu might take place or there might be disordering in periodic arrangements of Cu and TiO_2 surfaces. In this regard, further improvements for the preparations and characterizations of the exposed composite surfaces are needed. Nevertheless, the present results strongly suggest that the observed selectivity change reflects the characteristics of the artificially modulated Cu–TiO_2 surfaces.

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