Selective Oxidation of Methanol by Extra Oxygen Species on One-Dimensional Mo Rows of a Mo(112)–(1 \times 2)-O Surface

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Selective oxidation of methanol on oxygen-modified Mo(112) was investigated by temperature-programmed reaction (TPR) and under the catalytic reaction conditions at constant pressures of CH₃OH and O₂ ($10^{-6}-10^{-5}$ Pa). Low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were also used. A Mo(112)–(1 × 2)-O surface ($\theta_0 = 1.0$) has a characteristic structure with alternating one-dimensional Mo rows of Mo_{2C} and Mo_{NC}. The Mo_{2C} rows are affected by preadsorbed oxygen atoms ((1×2)-O), whereas the Mo_{NC} rows served as the adsorption and reaction sites. Formaldehyde (H₂CO) was a major product with 50% selectivity in TPR of methanol on the Mo(112)–(1×2)-O surface, whereas CH₄, H₂, C(a), and O(a) were the products at lower oxygen coverages than the (1×2)-O coverage. Extra oxygen species on the Mo_{NC} row of Mo(112)–(1×2)-O increased the selectivity to formaldehyde to 88% and decreased the activation energy for the rate-limiting C–H bond scission of methoxy species. In a constant flow of methanol alone, the reaction proceeded for several cycles, but eventually the surface was deactivated by accumulation of carbon. Selective catalytic oxidation of methanol successfully proceeded on Mo(112)–(1×2)-O in a constant flow of O₂ and CH₃OH without deactivation because of the presence of the extra oxygen atoms on the Mo_{NC} rows during the reaction.

Introduction

Control of the reaction path of catalytic reactions by atomlevel design of catalyst surfaces is a key issue crucial to success in surface science. The surface, designed by optimizing the structural and electronic properties, may provide information on the origin of activity and selectivity and may show a new catalytic performance that may surpass that of existing catalysts.¹ Molybdenum is a main promoting key element in many industrial catalysts for various kinds of reactions, partly because of its wide range of chemical reactivity and oxidation states.^{2,3} We have succeeded in modeling selective catalytic oxidation of methanol by modifying a Mo(112) surface with ordered oxygen atoms to form a one-dimensional reaction field; this is the first example of a selective oxidation reaction on Mo singlecrystal surfaces.^{4–6}

The Mo(112) surface has a ridge-and-trough structure, where in the top layer the Mo atoms form close-packed atomic rows along the [111] direction separated from each other by 0.445 nm; adsorbed oxygen atoms produce a Mo(112)–(1 × 2)-O ordered surface, where oxygen atoms occupy quasi-three-fold sites of one second-layer and two first-layer Mo atoms.⁷ The model of the (1 × 2)-O surface ($\theta_0 = 1.0$), shown in Figure 1a was proposed on the basis of low-energy electron diffraction (LEED) patterns and CO titration experiments.⁸ Every second Mo row is coordinated by oxygen atoms (Mo_{2C}) on both sides, whereas the other Mo rows have no oxygen atoms directly coordinated (Mo_{NC}). This structure preserves adsorption sites on Mo_{NC} for such molecules as CO, ammonia, and methanol. Selective blocking of the second-layer Mo atoms by oxygen atoms suppresses bond breaking of C–O or N–H and stabilizes $CH_3O(a)$ or $NH_X(a)$ species at temperature up to 500 K.^{5,9}

The majority of commercial processes that produce formaldehyde from methanol use molybdates, $Fe_2(MoO_4)_3$ and MoO_3 , as a catalyst. This catalyst shows kinetics and selectivity similar to those observed with MoO_3 for methanol oxidation,¹⁰ which suggests that Mo-O sites play an important role in the reaction. MoO_3 has a layered structure along the (010) plane, but the surface is not reactive because there is a lack of unsaturated Mo sites.¹⁰ Perhaps differences of activities between Fe_2 - $(MoO_4)_3$ and MoO_3 can be attributed to the number of unsaturated Mo atoms, given the small difference in turnover frequency (TOF) observed for these catalysts.¹¹

On Mo metal single-crystal surfaces such as (100),^{12,13} (110),¹⁴ and (112),⁵ the major products in methanol reactions are H₂, CO, and CH₄; little formaldehyde (H₂CO) is produced. On slightly oxidized Mo(100), methoxy is reportedly stabilized on the surface but yields only a small amount of molecular CO.¹³ Desorption of a negligible amount of H₂CO has been reported on Mo(100)–(1 × 1)-O ($\theta_0 = 1.5$),¹² but most of the methanol was desorbed intact, probably because of considerable steric blocking by oxygen modifiers. Although desorption of a small amount of H₂CO on slightly oxidized Mo(110) surfaces has been reported, the major product was methyl radical.^{14,15} On the other hand, on the Mo(112)–(1 × 2)-O surface ($\theta_0 = 1.0$), H₂CO was a major product, with 50% selectivity in temperature-programmed reaction (TPR) of methanol.^{4–6}

Examination of methanol reactions on oxygen-modified metal surfaces such as Cu(110),¹⁶ Cu(111),¹⁷ Cu(100),^{18,19} Ag(110),²⁰ Ru(001),²¹ Rh(111),²² and Fe(100),²³ has shown that the oxygen atoms enhance the formation of methoxy intermediate by extracting the hydroxyl hydrogen of methanol to form OH(a),

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Figure 1. (a) Model of a Mo(112)-(1 × 2)-O surface ($\theta_0 = 1.0$) with a top view and a plane view. Quasi-three-fold sites with Mo–O distance of 0.21 nm are postulated.⁸ (b) Extra oxygen species adsorbed on Mo_{NC} rows of the Mo(112)–(1 × 2)-O surface ($\theta_0' \approx 0.22$).

which is desorbed as H₂O. Recent observation of the methanol reaction on a Cu(110) surface scanning tunneling microscopy (STM) suggests that methoxy is formed at an edge of a (2 × 1)-O domain.^{24,25} Another effect of oxygen modification is to stabilize the methoxy species, as observed on Ni(110),²⁶ Mo(100),¹³ and W(112).²⁷ On an Fe(100) surface, the stabilization of methoxy by oxygen atoms leas to a change of selectivity in the methanol reaction.^{23,28}

In the present study we report the selective oxidation of methanol by extra oxygen species on one-dimensional Mo rows of a $Mo(112)-(1 \times 2)$ -O surface (Figure 1b). We found that extra oxygen atoms greatly increased the selectivity to formaldehyde and lowered the activation energy of the selective oxidation. By supplying extra oxygen atoms on the surface, selective catalytic oxidation of methanol successfully proceeded without deactivation.

Experimental Section

The experiments were performed in a stainless steel ultrahighvacuum chamber equipped with LEED/Auger electron spectroscopy (AES) optics and a quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD) and TPR. A Mo(112) sample was cleaned by cycles of Ar⁺ ion sputtering and annealing to 1300 K after an initial cleaning procedure of high-temperature annealing.⁸ The sample can be cooled to 150 K with liquid N₂ and resistively heated at a linear ramp rate between 0.5 and 15 K s⁻¹. The cleanliness of the surface was checked by AES. The clean surface exhibited a sharp and wellcontrasted (1 × 1) LEED pattern, indicating that the surface preserved the bulk-truncated structure.⁸ A Mo(112)–(1 × 2)-O



Figure 2. Coverage of extra oxygen atoms (θ_0') on Mo(112)–(1 × 2)-O determined by AES as a function of O₂ exposure at 300 K. Insets are LEED photographs of (a) Mo(112)–(1 × 2)-O ($E_p = 101 \text{ eV}$) and (b) Mo(112)–(1 × 2)-O after exposure to 14 langmuirs of O₂ ($E_p = 124 \text{ eV}$). LEED photograph (c) was obtained after the surface of (b) was annealed at 800 K ($E_p = 138 \text{ eV}$).

structure ($\theta_0 = 1.0$) was prepared by repeatedly exposing the clean surface to O₂ at 300 K and subsequently annealing to 800 K. Typically, the total exposure was 1.7 langmuirs (1 langmuir = 1.33×10^{-4} Pa*s).⁸ Oxygen coverages were monitored by O(KLL)/ Mo(MNN) peak ratios and LEED patterns.

Oxygen and methanol gases were dosed through variableleak valves. The QMS was enclosed in a glass cap with an aperture 9 mm in diameter. The sample was positioned in front of the aperture for recording the mass signals were recorded. This reduced contributions from sources other than the sample. The base pressure after the exposure to oxygen or methanol was maintained below 2×10^{-7} Pa. The pressure of the gases introduced into the chamber is not calibrated and the value measured by a B–A gauge is shown in this study.

A temperature-jump method was adopted to measure the amount of catalytic reaction products during the feed of CH₃OH and O₂ ($10^{-6}-10^{-5}$ Pa) on Mo(112)-(1×2)-O.²⁹ Constant pressures of CH₃OH and O₂ were introduced to the chamber through two variable-leak valves on the (1×2)-O surface at 450 K, where no reaction occurred; then the sample temperature was jumped to a given reaction temperature for several minutes, and decreased to 450 K again. Therefore, the area of a mass signal over the baseline, which is bound between the signals at 450 K, corresponds to the amount of a product in the catalytic reaction at the surface. Data were accumulated by repetition of temperature jumps.

Results

Modification of a Mo(112)– (1×2) -O Surface with Extra **Oxygen Species.** A Mo(112)– (1×2) -O ($\theta_0 = 1.0$) surface was exposed to oxygen at 300 K and the coverage of extra oxygen (θ_0') adsorbed on the surface was measured by AES. Figure 2 shows the change of θ_0' as a function of oxygen exposure. Note that the total oxygen coverage at the beginning of the exposure ($\theta_{O}' = 0$) is 1.0. The extra oxygen was saturated at 0.5 monolayer (ML), which corresponds to the number of Mo atoms in Mo_{NC} rows. Figures 2a and 2b are LEED photographs of the surfaces before and after adsorption of extra oxygen, respectively. The surface after 14 langmuirs of exposure also showed sharp subspots of (1×2) , indicating that the substrate preserved a (1×2) structure. These results suggest that the extra oxygen species are adsorbed on Mo_{NC} rows of the Mo(112)– (1×2) -O surface (Figure 1a), as in the case of other molecules such as CO and NH₃.^{8,9} Although the



Figure 3. (a) TPD spectra of CO from Mo(112)–(1 × 2)-O with different coverages of extra oxygen atoms (θ_0). (b) Saturation coverage of CO as a function of the coverage of extra oxygen.

 $Mo(112)-(1 \times 2)$ -O surface was stable up to 1100 K, the (1 \times 2) LEED pattern of the surface with extra oxygen (Figure 2b) changed drastically by annealing above 800 K, being accompanied by faceting of the surface (Figure 2c).

Figure 3 shows TPD spectra of CO from the Mo(112)–(1 × 2)-O surface with preadsorbed extra oxygen. No CO molecule was dissociated on the surface.⁸ The adsorption energy of molecular CO was reduced by extra oxygen and CO was desorbed at lower temperatures, probably because of charge transfer from Mo atoms to electronegative oxygen atoms, which reduced back-donation from the substrate to $2\pi^*$ orbital of CO. Thus, the extra oxygen species modified electronic states of the Mo atoms in the Mo_{NC} rows.

Surface Reactions of Adsorbed Methanol. Temperature-Programmed Reaction. Figure 4a shows TPR spectra of methanol from the Mo(112)– (1×2) -O surface after exposure to 4 langmuires of methanol at 200 K. Our previous experiments with isotope-labeled methanol suggested that only the methoxy species were left on the surface at 500 K, and these decomposed at 560 K to give H₂CO, CH₄, CO, and H₂ as desorption products.^{4–6} Hydrogen atoms formed by dissociation of O-H bond of methanol were recombinatively desorbed as H₂ at 380 K. Desorption of CO at 800 K resulted from the recombination of C(a) and O(a) left on the surface by nonselective decomposition of methanol. As shown in Table 1, a major product was H₂CO with 50 (\pm 2%) selectivity; formation of H₂O was not observed at any temperature. Except for the recombinative desorption of CO at 800 K, oxygen atoms in the (1×2) -O structure were not incorporated in the reaction products. Therefore, the (1×2) -O atoms did not react with methanol but worked as modifiers on the surface. Incidently, H₂CO was not formed on Mo(112) surfaces modified with lower oxygen coverages than the (1×2) coverage. We concluded previously that effective blocking of the second-layer Mo atoms, which are supposed to show higher electronic fluctuation and



Figure 4. TPR spectra after exposure of Mo(112)–(1 × 2)-O (a) and Mo(112)–(1 × 2)-O with 0.2 monolayer of preadsorbed extra oxygen (b) to 4 langmuirs of CH₃OH at 200 K. Heating rate was 5 K s⁻¹. A fragment of H₂CO (35% of 30 amu) also contributes to a 28 amu peak around 560 K.

 TABLE 1: Distribution in TPR for Products of Methanol

 Reaction Around 560 K on the Mo(112) Surfaces Modified

 with Oxygen

	yield/monolayer (selectivit/%)				
products	$(1 \times 2)-O$ surface ($\theta_0 = 1.0$)	extra oxygen ($\theta_0' = 0.20$) + (1 × 2)-O surface ($\theta_0 = 1.0$)			
H ₂ (g)	0.10	0			
$H_2CO(g)$	0.09 (50)	0.05 (88)			
$H_2O(g)$	0	0.05			
$CH_4(g)$	0.04 (22)	≪0.01 (5)			
CO(g)	0.02(11)	≪0.01 (7)			
C(a)	0.03 (17)	0 (0)			
O(a)	0.07	0^a			

^{*a*} θ_0 ' after TPR was 0.15.

thus higher activity,³⁰ leads to formation of formal dehyde on the Mo(112)–(1 \times 2)-O surface.⁵

The extra oxygen adsorbed on the Mo(112)– (1×2) -O surface drastically changed the selectivity of the reaction. Figure 4b shows TPR spectra of methanol from the (1×2) -O surface with 0.20 monolayer of preadsorbed extra oxygen after exposure to 4 langmuirs of methanol at 200 K. Figure 4b differs from Figure 4a in several points: considerable reduction of the peaks for CH_4 and H_2 at 560 K, disappearance of the peak for recombinative desorption of CO at 800 K, and appearance of the peak for H₂O at 580 K. The amounts of desorption products are summarized in Table 1. Selectivity for H₂CO increased to 88% (\pm 6%). In particular, reduction of recombinative desorption of CO at 800 K indicates that complete decomposition of methoxy to C(a) and O(a) was considerably suppressed by the presence of extra oxygen. Detection of H₂O and suppression of H₂ suggest that hydrogen is effectively desorbed as H₂O by the reaction with extra oxygen. In separate experiments using NH₃ as a reactant, we found that extra oxygen reacted to form H₂O at 520 K, whereas oxygen atoms that were incorporated in the (1 \times 2)-O structure reacted at 650 K.³¹ Therefore, we consider that the more-reactive extra oxygen species changed the selectivity of the reaction and were desorbed as H₂O during the reaction.

Once the (1×2) -O structure with extra oxygen was destructed by heating above 800 K (Figure 2c), the extra oxygen became less reactive and H₂O was no longer formed below 600 K. TPR spectra of methanol from the destructed surface showed lower selectivity for H₂CO (~50%), with products distribution similar to that on the (1×2) -O surface without the extra oxygen species.

Activation Energy for Methoxy Decomposition. The simultaneous desorption peaks observed at 560–580 K in Figure 4 were of reaction-limited desorption. The peak temperatures of these peaks did not depend on the coverage of methoxy species. These results indicate that the desorption rate (reaction rate) on both surfaces has a first-order relation to the coverage of methoxy species. As Redhead describes,³² an activation energy (E_a) and a preexponential factor (ν) for a first-order process should have the following relation:

$$\ln(T_{\rm p}^{2}/\beta) = E_{\rm a}/(RT_{\rm p}) + \ln[E_{\rm a}/(R\nu)]$$
(1)

where $T_{\rm p}$, β , and R represent peak temperature, heating rate, and the gas constant, respectively. We measured the peak temperature for formaldehyde desorption from the Mo(112)-(1 \times 2)-O surface and from the (1 \times 2)-O surface with 0.20 monolayer of extra oxygen at heating rates from 2 to 15 K s⁻¹, using both CH₃OH and CD₃OD as reactants. Figure 5 shows plots of $\ln(T_p^2\beta^{-1})$ vs T_p^{-1} . From eq 1, we calculated E_a and ν for each case. On both surfaces, the energy difference for CH₃OH and CD₃OD was not clear because the error bars were greater than the typical zero-point energy difference of 4-5 kJ mol⁻¹ between the C-H and C-D bonds. But the peak temperatures for CD₃OD were always higher (left-hand curves in Figure 5) than those for CH₃OH, strongly suggesting that the C-H (C-D) bond cleavage of methoxy is the rate-limiting step of the reaction. Extra oxygen atoms lowered the activation energy by 20-24 kJ mol⁻¹ (Figure 5). However, the reaction rate itself decreased by the presence of preadsorbed extra oxygen because of the smaller frequency factor. This is also apparent from the shift of peak temperature from 561 K (Figure 4a) to 579 K (Figure 4b).

Catalytic Reactions at Constant Pressures. We have examined catalytic reactions of methanol on a Mo(112)–(1 × 2)-O surface under a constant flow of CH₃OH and O₂ (10^{-6} – 10^{-5} Pa). The amount of reaction products was measured as a function of reaction time by a temperature-jump method as described above. Figure 6 shows plots of the reaction rates as a function of time at different reaction conditions. Each rate corresponds to an averaged rate for product formation during each temperature–jump. The total amounts of the products are summarized in Table 2.

When only CH₃OH was fed, the reaction rate exponentially decayed with reaction time, as shown in Figures 6a and 6b. After the reaction ceased in both conditions, the surfaces were covered with nearly 1 monolayer of C(a) (Table 2), and the sharp (1 × 2) subspots of the surface before the reaction (Figure 7a) almost disappeared in the increase in background intensity (Figure 7b). As shown in Table 2, selectivity of the reaction at 560 K was similar to that obtained by TPR (Table 1). Other than the products given in Table 2, a negligible amount of C_2H_6 (total amount <0.1 monolayer) was observed. Other products



Figure 5. Plots of $\ln(T_p \, {}^2\beta^{-1})$ vs T_p^{-1} for TPR of methanol on (a) $Mo(112)-(1 \times 2)$ -O and (b) $Mo(112)-(1 \times 2)$ -O with 0.2 monolayer of preadsorbed extra oxygen. T_p : desorption peak temperature of formaldehyde; β : heating rates, ranging from 0.5 to 15 K s⁻¹. CH₃OH and CD₃OD were used for reactants. Activation energy and preexponential factor obtained by using eq 1 are indicated.



Figure 6. Rates of the formation of products from methanol on $Mo(112)-(1 \times 2)$ -O as a function of time on stream at reaction temperatures. Reaction conditions: (a) $P_{CH_3OH} = 2.1 \times 10^{-5}$ Pa, 560 K; (b) $P_{CH_3OH} = 2.1 \times 10^{-5}$ Pa, 700 K, (c) $P_{CH_3OH} = 2.1 \times 10^{-5}$ Pa, $P_{O_2} = 6.5 \times 10^{-6}$ Pa, 560 K; and (d) $P_{CH_3OH} = 2.1 \times 10^{-5}$ Pa, $P_{O_2} = 6.5 \times 10^{-6}$ Pa, 700 K.

such as dimethoxymethane and dimethyl ether, which are commonly observed on a MoO₃ powder catalyst,¹¹ were not seen. C(a) species formed with 26% selectivity covered the surface, resulting in an exponential decay of the reaction rate.

TABLE 2: Product Yields and Selectivities in Catalytic Methanol Reactions on Mo(112)-(1×2)-O

				yield/monolayer (selectivity/%)						
<i>Р</i> _{СН3ОН} /Ра	P _{O2} /Pa	$T_{\rm R}^{a}/{ m K}$	time/s	H ₂ CO(g)	CH ₄ (g)	CO(g)	$H_2(g)$	$H_2O(g)$	C(a)	O(a)
2.1×10^{-5}		560	1110	1.7 (43)	0.9 (22)	0.3 (8)	3.2	1.7	1.05 (26)	< 0.05
2.1×10^{-5}	6.5×10^{-6}	560	1650	7.3 (69)	2.1 (20)	0.6 (6)	3.5	5.8	0.55 (5)	0.40
8.1×10^{-6}	1.6×10^{-5}	560	2010	4.5 (84)	0.3 (5)	0.4 (8)	0.4	5.0	0.20 (4)	0.30
2.1×10^{-5}		700	2200	5.3 (59)	1.4 (16)	1.1 (13)	7.9	2.6	1.10 (12)	-0.15
2.1×10^{-5}	6.5×10^{-6}	700	1870	15.2 (89)	<0.1 (0.3)	1.7 (10)	1.3	15.9	0.05 (0.3)	0.15

^a Reaction temperatures.



Figure 7. Change in LEED patterns of Mo(112)–(1 × 2)-O by methanol reaction. (a) As prepared Mo(112)–(1 × 2)-O ($E_p = 101$ eV). (b) After the reaction in $P_{CH_3OH} = 2.1 \times 10^{-5}$ Pa at 560 K for 1100 s ($E_p = 98$ eV). (c) After the reaction in $P_{CH_3OH} = 2.1 \times 10^{-5}$ Pa and $P_{O_2} = 6.5 \times 10^{-6}$ Pa at 700 K for 3000 s ($E_p = 102$ eV). All photographs were obtained at 200 K.

O(a) species also formed on the surface but were desorbed as H_2O by reaction with hydrogen atoms. Neither C(a) nor a small amount of O(a) changed the selectivity in this case.

When CH_3OH was fed with O_2 , the selectivity for H_2CO increased in any conditions in this study that lengthened the lifetime of the reaction (Figures 6c and 6d). As expected by the results of TPR (Table 1), the extra oxygen atoms that formed on the surface enhanced the selectivity for H_2CO and reduced the accumulation of C(a). As shown in Figure 6d and in the



Figure 8. Pressure dependence of the initial rates for the catalytic formaldehyde formation on Mo(112)–(1 × 2)-O in a flow of CH₃OH and O₂ at 700 K. The empty square in (a) indicates the initial rate obtained at $P_{\text{CH}_3\text{OH}} = 8.3 \times 10^{-5}$ Pa and $P_{O_2} = 2.7 \times 10^{-5}$ Pa. Lines drawn in (a) and (b) are for visual comparison only.

bottom of Table 2, formaldehyde was formed with 89% selectivity and without significant deactivation. C_2H_6 was not detected in the presence of O_2 gas. Although the pressures of both CH₃OH and O_2 were the same in Figures 6c and 6d, the ratio of extra oxygen to methoxy on the surface differed. In Figure 6c, the reaction was deactivated because of preferential adsorption of methoxy in this condition. When the oxygen pressure was higher than the methanol pressure, the selectivity to H₂CO increased, as shown in the third line of Table 2. In Figure 6d, the coverages of methoxy and extra oxygen were well balanced, and the reaction proceeded without deactivation. The surface preserved relatively sharp (1 × 2) subspots after the reaction lasted for 3000 s in this condition (Figure 7c).

Pressure-dependence of the initial rate of formaldehyde formation was measured around the condition obtained in Figure 6d. As shown in Figure 8a, the initial rate showed a linear relation with methanol pressure at the low-pressure region. However, the rate deviated from this at the higher-pressure region, probably because of the decrease of extra oxygen species, which led to lower selectivity for H₂CO. As an empty square point in Figure 8a shows, the initial reaction rate was increased by increasing the oxygen pressure from 6.5×10^{-6} to $2.7 \times 10^{-$



Figure 9. Arrhenius plots for the catalytic methanol oxidation to form formaldehyde on Mo(112)–(1 × 2)-O. Shown are the reaction rates at $P_{\rm CH_{3}OH} = 8.3 \times 10^{-5}$ Pa (\bullet) and at $P_{\rm CH_{3}OH} = 8.3 \times 10^{-5}$ Pa and $P_{\rm O_2} = 2.7 \times 10^{-5}$ Pa (\bullet). The activation energies calculated from the linear slopes are indicated.

 10^{-5} Pa. In Figure 8b, the presence of 6.5×10^{-6} Pa of O₂ increased the initial rate, but the higher oxygen pressures decreased the rate because of the increase of adsorbed oxygen atoms, which blocked the adsorption of methoxy species.

Figure 9 shows Arrhenius plots of the reactions with and without oxygen feed. The pressures of methanol and oxygen are nearly four times those in Table 2. The initial rate of formaldehyde formation was measured 8 s after the first temperature jump for each condition. In the rather flat regions observed under both reaction conditions in Figure 9, the reaction rate was limited by adsorption of methanol. The apparent activation energies for the H₂CO formation, as determined from the linear slopes, were 54 ± 12 and 51 ± 5 kJ mol⁻¹ for CH₃OH and CH₃OH + O₂, respectively.

Discussion

Reaction Scheme of Methanol on Mo(112) $-(1 \times 2)$ -O in **TPR.** In the previous paper,⁵ we suggested the following reaction path in TPR on Mo(112) $-(1 \times 2)$ -O without extra oxygen. The first step is dissociation of methanol to form CH₃O(a) + H(a), which is followed by recombinative desorption of the adsorbed hydrogen:

$$CH_3OH(a) \xrightarrow{>300 \text{ K}} CH_3O(a) + H(a)$$
 (2)

$$H(a) \xrightarrow{>380 \text{ K}} \frac{1}{2} H_2(g)$$
 (3)

Therefore, only methoxy species are left on the surface at temperatures above 480 K. The major reaction path with 50% selectivity is formation of formaldehyde:

$$CH_3O(a) \xrightarrow{560 \text{ K}} CH_2O(a) + H(a)$$
 (4)

$$CH_2O(a) \rightarrow H_2CO(g)$$
 (5)

$$H(a) \rightarrow {}^{1}/_{2}H_{2}(g) \tag{6}$$

where step 4 is the rate-limiting step of the reaction, as noted above. CO is formed probably by further dehydrogenation of $CH_2O(a)$:

$$CH_2O(a) \rightarrow CO(g) + 2H(a)$$
 (7)

In isotope-scrambling experiments using a mixture of $CH_3O(a)$ and $CD_3O(a)$, the amount of CH_2D_2 produced was much less than those of CH₄, CH₃D, CD₃H, and CD₄.⁵ Methane is probably formed as follows:

$$CH_3O(a) + H(a) \rightarrow CH_4(g) + O(a)$$
 (8)

or

$$CH_3O(a) \rightarrow CH_3(a) + O(a)$$
 (9)

$$CH_3(a) + H(a) \rightarrow CH_4(g)$$
 (10)

The desorption temperature of methane in the TPR of methanol coincides with that of other products, even when CD_3OD is used as a reactant.⁵ Thus, step 8 can be understood as the reaction path initiated by the H(a) produced in step 4. If we assume that steps 9 and 10 are major processes, then the activation energy and preexponential factor for step 9 should be similar to those for step 4, and $CH_3(a)$ should react with the H(a) in from other steps. Note that formation of C(a) can be understood more easily by a competing step to step 10:

$$CH_3(a) \rightarrow C(a) + 3H(a)$$
 (11)

When extra oxygen species are coadsorbed with methanol, some modifications of the reaction steps are needed. A promotion effect of adsorbed oxygen atoms on the formation of methoxy from methanol has been reported on some oxygen-modified metal surfaces.^{16–25}

$$CH_3OH(a) + O(a) \rightarrow CH_3O(a) + OH(a)$$
 (12)

Such an effect may not be important on Mo(112)– (1×2) -O, where methoxy coverage is low (Table 1). However, the hydrogen atom formed by step 2 is probably trapped by extra oxygen atom (O_e(a)),

$$H(a) + O_e(a) \rightarrow O_eH(a)$$
(13)

because desorption of H₂ below 400 K was not detected (Figure 4b). Given that the selectivity for formaldehyde is as high as 88% in the presence of extra oxygen, we should consider only the reaction path from methoxy to formaldehyde. The fact that the activation energy of hydrogen extraction from methoxy is reduced by 20-24 kJ mol⁻¹ in the presence of extra oxygen suggests that hydrogen is extracted at 580 K by an extra oxygen atom (step 14) or by a Mo atom that is electronically modified with the extra oxygen atoms (step 15):

$$CH_3O(a) + O_e(a) \rightarrow CH_2O(a) + O_eH(a)$$
 (14)

$$CH_3O(a) + Mo_m \rightarrow CH_2O(a) + H(a)$$
 (15)

This is followed by desorption of H_2CO (step 5). When the hydrogen atoms released from methoxy species in step 15 are trapped with extra oxygen atoms (step 13), step 14, and step 15 cannot be differentiated. Alternatively, the hydrogen atoms react with $O_eH(a)$ to produce $H_2O(g)$ by step 16.

$$O_e H(a) + H(a) \rightarrow H_2 O(g)$$
 (16)

 $H_2O(g)$ is also produced by dehydration of 2 $O_eH(a)$ species (step 17).

$$2O_eH(a) \rightarrow H_2O(g) + O_e(a)$$
 (17)

It is also possible that CH₃O(a) reacts with O_eH(a) to produce

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H₂CO and H₂O at 580 K (step 18).

$$CH_3O(a) + O_eH(a) \rightarrow H_2CO(g) + H_2O(g)$$
 (18)

Kinetics of Selective Catalytic Oxidation of Methanol on $Mo(112)-(1 \times 2)$ -O. Reaction steps 2 to 11 are also relevant to the catalytic reaction of methanol in a flow of CH₃OH, even though the steps 3 and 6 can no longer be separated anymore. The net reaction for dissociative adsorption of methanol is expressed by step 19:

$$CH_3OH(g) \rightarrow CH_3O(a) + H(a)$$
 (19)

Recombinative desorption of methoxy and hydrogen,

$$CH_3O(a) + H(a) \rightarrow CH_3OH(g)$$
 (20)

becomes one of major processes because the concentration of hydrogen atoms on the surface in the flow-reaction conditions is higher than in TPR. Assuming that the rate-limiting step is C-H bond scission of methoxy (step 4), the initial rate of formaldehyde formation (v) plotted in Figure 9 can be expressed by

$$v = v S_{H,CO} \theta_{CH,O} \exp(-E_a/RT) = A \exp(-E/RT)$$
(21)

where ν and $E_{\rm a}$ are the preexponential factor and activation energy of C-H bond scission of the methoxy species obtained by TPR (ν : 7 × 10^{15±1} s⁻¹, E_a : 175 ± 13 kJ mol⁻¹), respectively, and S_{H2CO} is the selectivity for H2CO. E is an apparent activation energy for the H2CO formation determined from the linear slope in Figure 9 (54 \pm 12 kJ mol⁻¹), and A is a constant. After determining S_{H_2CO} determined by the measured rates of the formation of products (H₂CO, CH₄, CO, and C(a)) at each temperature, we can calculate $\theta_{CH_{3O}}$ from eq 21. $\theta_{CH_{3O}}$ decreased from 0.06 at 560 K to 0.01 at 600 K, values much smaller than the observed maximum coverage of methoxy species (~0.25 monolayer). The methoxy species are formed by dissociative adsorption (step 19) and consumed by reaction (step 4 and step 8, or step 9) or recombinative desorption (step 20). The coverage of H(a) indirectly affects the coverage of methoxy species. The desorption energy of hydrogen atoms by step 6 was estimated by TPR as $92 \pm 5 \text{ kJ mol}^{-1}$, assuming a typical preexponential factor of 1 \times 10⁻² cm² s⁻¹. Using these values, we calculate $\theta_{\rm H}$ from the measured H₂ formation rate. $\theta_{\rm H}$ stays almost constant (0.001) from 560 to 600 K. The rate of recombinative desorption (step 20) estimated to maintain $\theta_{\rm CH_{3}O}$ as a constant value was determined by using $E_{\rm ad}$ as a parameter and assuming a typical preexponential factor of 1 \times 10^{-2} cm² s⁻¹. The initial rate of formaldehyde formation (v) was simulated by using these values.

When a mixture of CH₃OH and O₂ is supplied, the extra oxygen atoms produced on the Mo_{NC} rows simplify the reaction paths. Hydrogen atoms produced by dissociative adsorption of methanol (step 19) are immediately trapped by the extra oxygen atoms (step 13). A minority of them recombine with methoxy to be desorbed as methanol (step 20), and only a small amount of H₂ is detected during the reaction. Methoxy decomposition to form H₂CO by steps 14 or 15 (followed by step 5), or step 18 showed a high selectivity of 89% when steps 7–9 for byproduct formation were suppressed. With sufficient amounts of extra oxygen and a small coverage of O_eH(a) in the catalytic reaction conditions, the contribution of step 18 would be much lower than that of step 14 or step 15. The initial rate of formaldehyde formation (v') plotted in Figure 9 is given by eq 22, which is similar to eq 21:

$$\nu' = \nu' S'_{H_2CO} \theta_{CH_3O} \exp(-E_a'/RT) = A' \exp(-E'/RT)$$
 (22)

where ν' and E_a' are the preexponential factor and activation energy of C-H bond scission (step 14 or, equally, step 15 + step 13) obtained by TPR (ν' : 2 × 10^{13±2} s⁻¹, E_a' : 155 ± 18 kJ mol⁻¹), respectively, and S'_{H₂CO} is the selectivity for H₂CO. E' is an apparent activation energy for the H_2CO formation, determined from the linear slope in Figure 9 (51 \pm 5 kJ mol⁻¹), and A' is a constant. The coverage of extra oxygen is not included in the rate because it is a constant in steady-state. S'_{H_2CO} is almost unity in these conditions. $\theta_{CH_{3}O}$, calculated from eq 22, decreased from 0.09 at 560 K to 0.03 at 600 K. $\theta_{\rm H}$, calculated similarly to the method mentioned above, was less than 10^{-4} . Then, methoxy is formed by dissociative adsorption (step 19) and consumed by reaction (step 14 or step 15). The extra oxygen atoms are adsorbed competitively with methoxy species on one-dimensional Mo_{NC} rows. The coverage of extra oxygen was estimated by the simulation to be 0.28, 0.33, and 0.30 at 560, 580, and 600 K, respectively. The decreased at the higher temperature was due to a higher reaction rate for oxygen desorption as H_2O .

The TOF of the reaction (moles of the products per surface reaction site per second) can be compared with that on a MoO₃ powder catalyst. The preexponential factor and activation energy of methanol oxidation on a MoO₃ powder catalyst were determined by TPR to be $2 \times 10^7 \text{ s}^{-1}$ and 86.2 kJ mol⁻¹, respectively.³³ These Arrhenius parameters reproduce the TOF of the reaction on the MoO₃ catalyst at 473 K ($3.3 \times 10^{-3} \text{ s}^{-1}$),³³ but the desorption peak of formaldehyde from the MoO₃ catalyst at 493 K is much lower than that on Mo(112)–(1×2)-O. However, the TOF on Mo(112)–(1×2)-O becomes comparable with that on a MoO₃ catalyst at 560–590 K and has much larger values at 700 K if we postulate the rate constant obtained by TPR (with or without extra oxygen).

Role of Extra Oxygen Species on Mo(112)–(1 × 2)-O in Selective Oxidation of Methanol. In previous studies,^{8,9} we have suggested that molecules such as CO or NH₃ adsorb exclusively on Mo_{NC} rows in Figure 1 because of considerable steric blocking of oxygen atoms on Mo_{2C} rows (see the van der Waals sphere of an oxygen atom in Figure 1). The saturation coverages of extra oxygen (0.5 monolayer) and methoxy (~0.25 monolayer) suggest adsorption on the Mo_{NC} rows for these species also. The adsorption sites of these species are not clear in the present study. Oxygen atoms tend to occupy higher coordination sites at low coverages on other Mo surfaces.³⁴ Preferential adsorption of methoxy on higher coordination sites is also reported on some metal surfaces.^{35–38} In any case, these two species are competitively adsorbed on the one-dimensional Mo_{NC} rows.

TPR results in Figure 4 indicate that 0.20 monolayer of extra oxygen (40% of the adsorption sites on the Mo_{NC} rows) was enough to inhibit C–O bond scission of the methoxy species. The coverage of extra oxygen atoms during the catalytic reaction in the best conditions (bottom line in Table 2) was estimated to be 0.22 monolayer. These results may be explained if a strong interaction working attractively between an extra oxygen atom and a methoxy group is postulated, i.e., if an oxygen and a methoxy form a pair on a Mo_{NC} row. This does not seem to be the case, however, because CH₄ (a nonselective product) was detected by TPR when the amount of preadsorbed extra oxygen was reduced to 0.1 monolayer (the coverage of methoxy was <0.1 monolayer in this case). Figure 10 shows a model of the Mo(112)–(1 × 2)-O surface coadsorbed with extra oxygen atoms and methoxy species, with coverages similar to those in



Figure 10. (a) Supposed arrangement of methoxy species and extra oxygen atoms on Mo(112)–(1 × 2)-O ($\theta_0' \approx 0.21$ and $\theta_{CH_3O} \approx 0.07$, respectively). (b) Sectional view at A–A' in (a), also showing the van der Waals spheres for the extra oxygen atoms. Methoxy species are drawn with the van der Waals sphere of each element by assuming the same bond distances as those of methanol. Extra oxygen and methoxy are located at bridge sites on the Mo_{NC} rows with a Mo–O bond at 0.21 nm.

TPR of Figure 4b ($\theta_0 \approx 0.21$ and $\theta_{CH_3O} \approx 0.07$, respectively). This model suggests that C–O bond scission of the methoxy was inhibited not through steric blocking but through electronic modification of Mo atoms by the extra oxygen atoms. As noted above, C(a) species accumulated on the Mo(112)–(1 × 2)-O surface during the catalytic reaction with CH₃OH feed alone (Table 2), but, in contrast to extra oxygen species, C(a) did not inhibit C–O bond scission of methoxy species. This result also excludes the possibility of steric blocking as a major reason of the inhibition. Effective trapping of hydrogen atoms by extra oxygen atoms (step 13) may increase the selectivity of methoxy dehydrogenation to formaldehyde if step 8 is the major path for CH₄ formation.

The extra oxygen decreases the activation energy of C–H bond scission of the methoxy species, which is the rate-limiting step of the selective methanol oxidation, and the extra oxygen was desorbed as H₂O during the catalytic reaction. Thus, the selective catalytic oxidation of methanol may involve the direct extraction of a hydrogen atom by an extra oxygen atom (step 14), which is similar to the mechanism proposed in oxidative dehydrogenation of methanol on oxide surfaces.³ One-dimensionality of the Mo_{NC} row may increase the probability of direct interaction between methoxy and extra oxygen species. TPD spectra of CO indicate that extra oxygen species reduce the electron density of Mo atoms in Mo_{NC} rows. This modification causes the decrease of the activation energy for the methoxy dehydrogenation.

On the other hand the extra oxygen atoms decrease the preexponential factor of the reaction. A high preexponential factor of $7 \times 10^{15\pm1}$ s⁻¹ was observed on the Mo(112)–(1 × 2)-O surface without extra oxygen. A high preexponential factor was also reported on CO desorption from Ru(001) and was explained by high mobility of transition state species on the surface.³⁹ Methoxy species in the transition-state are probably weakly bound to the surface and may diffuse freely along a Mo_{NC} row. The extra oxygen atoms may restrict the diffusion

of transition-state species, resulting in a lower preexponential factor $(2 \times 10^{13\pm2} \text{ s}^{-1})$. Considering that dissociation of C–H and C–O bonds of methoxy occurs on the Mo atoms in a Mo_{NC} row, effective motion of the methoxy for dissociation may be a frustrated rotation along the Mo_{NC} row. Extra oxygen atoms may restrict the diffusion and frustrated rotation of methoxy even at the lower coverage, given to the one-dimensionality of the Mo_{NC} row.

Conclusion

The results presented here indicate that methanol reaction paths are dramatically sensitive to the coverage and arrangement of oxygen modifiers and the surface structure. On Mo(112)- (1×2) -O, methoxy species are stabilized by the oxygen modifiers in the (1×2) -O phase, which selectively block the Mo atoms with high coordination and form one-dimensional reaction sites on the surface. This type of modification contributes to the formation of H₂CO on the surface, but with 50% selectivity. The extra oxygen species adsorbed on the (1 \times 2)-O surface increase the selectivity to 88% and decrease the activation energy for the rate-limiting C-H bond scission of methoxy species. Selective catalytic oxidation of methanol proceeds in a constant flow of O2 and CH3OH without deactivation. Thus the present results suggest that we can control the reaction paths by designing a reaction field with two types of coadsorbed oxygen.

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