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Structure of surface tantalate species and photo-oxidation of carbon monoxide over silica-supported tantalum oxide

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Tantalum oxide (10 wt.% as Ta_2O_5) supported on silica was prepared and the structure and the photo-oxidation of carbon monoxide over the catalyst sample were investigated. XAFS analysis showed that surface tantalate is a TaO_4 tetrahedral species with a Ta=O bond which is a photoactive center. The initiation of the photo-oxidation of carbon monoxide is the photoadsorption of an oxygen molecule on the catalyst sample, elucidated by photoluminescence. EPR spectroscopy showed that the photo-excited center interacts with an oxygen molecule to form a T-type ozonide ion. A carbon monoxide ion attacks the ozonide ion to form an $[O_3-CO]^-$ paramagnetic intermediate to lead the production of carbon dioxide.

Introduction

Silica-supported vanadium oxide and silica-supported niobium oxide have been found to exhibit photocatalytic activity for the oxidation of alkanes,¹⁻³, alkenes,⁴⁻⁷ alcohols^{7,8} and carbon monoxide.⁹ The active site is assigned to the metal–oxo double bond ($M^{5+}=O^{2-}$),^{4,10} which is activated by ultraviolet light to form an exciton ($M^{4+}-O^{-}$). Although tantalum oxide, which belongs to the same group Va metal oxides as vanadium and niobium oxides, is expected to exhibit photocatalytic activity when it is dispersed on a silica support, there have been only a few studies^{11,12} dealing with supported tantalum oxide as a photoactive material for oxidation. In the present paper, we discuss the surface structure of tantalum oxide over a silica surface and photooxidation of carbon monoxide over the catalyst sample and report the photocatalytic activity of silica-supported tantalum oxide.

Experimental

Silica-supported tantalum oxide (10 wt.% as Ta₂O₅) was prepared by impregnating silica (specific surface area 550 m² g⁻¹) with an aqueous solution of tantalum oxalate, followed by calcination in a stream of dry air at 773 K. Prior to each reaction and measurement, the catalyst sample was heated at 673 K in vacuo, followed by treatment under a 60 Torr oxygen atmosphere. The photo-oxidation of carbon monoxide was performed with a conventional closed circulating system made of a glass tube equipped with a quadrupole-type mass spectrometer which allows the quantitative analysis of isotope distribution. The catalyst sample was spread over the flat bottom of the reactor made of quartz and UV irradiation was applied from the bottom from a 250 W ultra-high pressure Hg lamp. Each spectroscopic measurement was carried out with a sample manipulated without exposure to the air. X-ray absorption experiments were carried out with the X-ray absorption fine structure (XAFS) spectrometer installed on the BL01B1 beam line¹³ with an Si(111) two-crystal monochromator at SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan. The stored current and electron energy in the synchrotron radiation ring were 20–17 mA and 8 GeV, respectively. Computational analysis of the XAFS spectra was carried out using the mainframe computer at Kyoto University Data Process Center as described elsewhere.¹⁴ The photoluminescence spectra were recorded at 77 K with a Hitachi Model 850 spectrofluorimeter equipped with a phosphorescence attachment with a delayed chopper of 1 ms. X-band electron paramagnetic resonance (EPR) spectra were recorded at 77 K with a JEOL JES-3BS-X spectrometer.

Results and discussion

The structure of tantalum oxide on a silica surface

The coverage of silica with tantalum oxide is only 6% and it is expected to be highly dispersed on the surface. To examine the dispersion and the structure of tantalum oxide, we carried out the analysis of XAFS spectra at the Ta L-edge of the catalyst sample. Fig. 1 shows the k^3 -weighted extended XAFS (EXAFS) spectrum at the Ta L_3 -edge of the catalyst sample together with those for tantalum pentaoxide and tantalum oxalate solution. The EXAFS spectrum of the catalyst sample exhibits an oscillation at low frequency whereas those of reference compounds exhibits low frequency oscillations in the low k region and high frequency oscillations in the high k region. The low frequency oscillations show the presence of short bonded ligands, i.e., oxygen atoms. The high frequency oscillations in the high k region show the presence of the heavy atom at a longer distance than that of oxygen atoms. In the case of the catalyst sample, it should be noted that a beat is observed in the oscillation amplitude and a beat-node can be found at around 10 $Å^{-1}$. Since the beat results from the simple sum of plural sine waves at different frequencies, the beat in the oscillation indicates the existence of at least two kinds of Ta-O bonds. Assuming that two Ta-O bonds are present, the difference in the bond distance, Δr , can be estimated using the following equation:15

$k_{\rm node}\,\Delta r=\pi/2$

where k_{node} is the position of the node, $10 \pm 0.5 \text{ Å}^{-1}$, and Δr can be evaluated as $0.16 \pm 0.01 \text{ Å}$.

Phys. Chem. Chem. Phys., 1999, 1, 5235–5239 5235



Fig. 1 Ta L_3 -edge k^3 -weighted EXAFS spectra of the catalyst sample, tantalum oxalate solution and tantalum pentoxide.

Fourier transformation was performed on these EXAFS data to obtain radial structure functions (RSF) as shown in Fig. 2. The peak at around 1.5 Å found in all the RSF is due to the electron backscattering by neighboring oxygen atoms. The peaks in the region 3.2-3.7 Å are due to the presence of tantalum atoms and these are missing for the RSF of the catalyst sample. This shows that tantalum atoms are not aggregated on the silica surface but highly dispersed as an isolated form, although the tantalum ions in the tantalum oxalate solution are present as polynuclear species.

Fig. 3 shows the X-ray absorption near edge structure (XANES) spectrum at the Ta L_1 -edge for silica-supported tantalum oxide and those for the reference compounds. The striking point of the XANES spectral features of the catalyst sample is an intense shoulder peak, which is seen at the low energy side of the rising edge. This peak is attributed to the 2s-5d electron transition. The presence of the intense peak shows that tantalum ions are located at a center of distorted symmetry. 16 In the case of $\mathrm{Ta_2O_5}$ and tantalum oxalate solution, the peak is smaller than that of the catalyst sample and tantalum cations in these reference samples are expected to be localized at the center of distorted oxygen octahedra. By comparison of the peak intensities, tantalum atoms in the catalyst samples are concluded to be coordinatively unsaturated. Furthermore, the characteristic of the rising edge of two peaks shows that tantalum atoms are located at the center of oxygen tetrahedra, as found in the case of vanadium and niobium complexes.17

From the XAFS result mentioned above, we conclude that tantalum atoms in 10 wt.% Ta_2O_5 -SiO₂ are present as an isolated TaO_4^{3-} tantalate species, in which at least two kinds



Fig. 2 Fourier transforms of Ta L_3 -edge k^3 -weighted EXAFS spectra of the catalyst sample, tantalum oxalate solution and tantalum pentoxide.



Fig. 3 Normalized XANES at Ta L_1 -edge spectra of the catalyst sample, tantalum oxalate solution and tantalum pentoxide.

of Ta–O bonds exist. To estimate the Ta–O bond distances, we performed curve-fitting analysis using the empirical parameter for a W–O bond extracted from Na_2WO_4 . The best fits were obtained with two Ta–O shells and a trial with a single shell did not give a satisfactory result. The evaluated data are summarized in Table 1. TaO_4^{3-} ions possess one short Ta–O bond and three long Ta–O bonds. The difference in the bond lengths is 0.14 Å and this is consistent with the estimation by the beat-node method. The conclusion regarding the structure of the tantalate species on a silica surface is fundamentally the same as those of vanadate¹⁸ and niobate¹⁹ species.¹⁷

Photo-oxidation of carbon monoxide

The reaction was examined on the catalyst sample. Equimolar amounts of carbon monoxide and oxygen were admitted into the system and the catalyst sample was irradiated. After an induction period of 200 min, the oxidation of carbon dioxide proceeded stably at a rate of 38.4 μ mol h⁻¹ g(Ta₂O₅-SiO₂)⁻¹. On the other hand, in the absence of oxygen, oxidation of CO did not take place whereas over V_2O_5 -SiO₂, carbon dioxide was evolved even without oxygen.⁹ In the case of V_2O_5 -SiO₂, lattice oxygen of vanadium oxide was found to be incorporated into carbon dioxide regardless of the presence or absence of oxygen. To elucidate the active oxygen species of the present system, photo-oxidation of CO was carried out with ¹⁸O₂. At 1.5% conversion of CO, the ¹⁸O isotope distribution was $C^{16}O_2 : C^{16}O^{18}O : C^{18}O_2 = 27 : 73 : 0.0$. Ordinarily, CO₃ or CO₄ is thought to be a candidate for the intermediate which consists of CO, reactant O₂ gas and lattice oxygen. If such an intermediate were present, $C^{18}O_2$ should be produced, but the fact that $C^{18}O_2$ was not detected at all in the initial stage suggests that oxygen atoms in such an intermediate, if any, do not play an equivalent role.

Photoluminescence

It is often the case that a silica-supported metal oxide catalyst exhibits photoluminescence and the luminescent center works as an active site.^{2,6,10,20} We carried out the measurement of phosphorescent emission spectra of the sample in contact with reactant gas molecules. Fig. 4 shows the photoemission excitation spectra of the catalyst sample in vacuo. The excitation wavelength was changed, monitoring the emission intensity at 550 nm. Obviously two maxima were observed at 280 and 360 nm. The catalyst sample possesses two kinds of excitation sites. Subsequently, the photoemission spectra were recorded by exciting the sample at 280 and 360 nm as shown in Fig. 5. The catalyst sample exhibited phosphorescent emissions at 450 nm when it was excited at 280 nm (λ_{em} 450– λ_{ex} 280 nm pair) and at 550 nm when excited at 360 nm (λ_{em} 550– λ_{ex} 360 nm pair). The result shows that Ta2O5-SiO2 possesses two pairs of photoexcitation and photoemission sites. The similarity between the emission and excitation wavelengths of the λ_{em} 550– λ_{ex} 360 nm pair and those for $V_2O_5\text{--}SiO_2^{-2,10}$ and

Table 1Ta-Obond parameters of surface tantalate obtainedby curve-fitting analysis^a

CN^b	$\mathbf{R}^{c}/\mathbf{\mathring{A}}$	$\Delta \sigma^2/{ m \AA}^2$ d	RF ^e (%)
1.3	1.80	0.0004	9.0
3.4	1.94	0.0006	

^{*a*} A trial fit with a Ta–O single shell did not give an RF value less than 22%. The energy offset for ionization threshold was taken to be 9869.5 eV. ^{*b*} Coordination number within an error ± 0.5 . ^{*c*} Ta–O distance within an error ± 0.01 Å. ^{*d*} Relative Debye–Waller factor deviated from that for W–O bonds of orthotungstate within an error ± 0.0005 Å². ^{*e*} A measure of fitness. The definition can be found in ref. 14.



Fig. 4 Excitation spectrum of Ta_2O_5 -SiO₂ at 77 K *in vacuo* monitoring emission intensity at 550 nm.

 Nb_2O_5 -SiO₂⁶ catalysts may indicate that one of the luminescence-active species is the excited Ta=O in the triplet state. Both of the emissions were efficiently quenched by contact of the catalyst with CO and O₂ gases and Fig. 6 shows Stern–Volmer plot of the emission intensity against the



Fig. 5 Emission spectra of Ta_2O_5 -SiO₂ at 77 K *in vacuo* excited at (a) 280 and (b) 360 nm.



Fig. 6 Plots of the reciprocal intensity of the emission against (a) O_2 pressure and (b) CO pressure. Open symbols are for the $\lambda_{em} 555 - \lambda_{ex}$ 340 nm pair and closed symbols for the $\lambda_{em} 430 - \lambda_{ex}$ 280 nm pair. Symbols to the right of the lines are for the recovered emission after evacuation of the gases.

gas pressure. The reciprocals of the intensity of both the emissions are linear with respect to the gas pressure, indicating that both emission sites are present on the catalyst surface and interacted with these gas molecules. It is noted that although quenching by CO molecules was observed, the emission intensity was restored after evacuation of CO gas. This indicates that CO molecules do not interact with the emission sites chemically but do collide with the sites physically. This is consistent with the result that oxidation of CO does not take place in the absence of oxygen. On the other hand, in the case of quenching by oxygen, the slopes of the plotted lines are higher than those found with CO quenching. This is partly caused by the difference in the probe molecules. In particular, the slope of the line for emission at 550 nm was large. Furthermore, the intensity of the emission at 450 nm was restored after evacuation of oxygen whereas the intensity of the emission at 550 nm was not. The luminescent center of the $\lambda_{\rm em}$ $550-\lambda_{ex}$ 360 nm pair interacts chemically with an oxygen molecule and therefore oxygen molecules remained on the site even after evacuation. On the other hand, the site of 450 nm emission does not interact chemically and we assume that the λ_{em} 450- λ_{ex} 280 nm pair does not participate in the photooxidation. This site may be the same as the luminescent center on a silica surface reported by Yoshida *et al.*²¹ Here we conclude that the emission site of the $\lambda_{\rm em}$ 550– $\lambda_{\rm ex}$ 360 nm pair is the active site, presumably involving a Ta=O bond. However, its behavior is different from that for the case of V_2O_5 -SiO₂. Oxygen gas plays a significant role in the photo-oxidation of carbon monoxide over Ta_2O_5 -SiO₂ whereas in the case of V_2O_5 -SiO₂ catalyst oxygen was used for the reoxidation of the catalyst after having been reduced by CO.

Reaction intermediate

In the photo-oxidation of carbon monoxide, the reaction is initiated by the photoadsorption of oxygen. The formation of paramagnetic ionosorbed oxygen species is very likely and therefore we recorded EPR spectra of the catalyst sample in contact with reaction gases. No EPR signal was found for the catalyst with or without irradiation in vacuo at 77 K. One may conjecture that O⁻ species as an exciton hole could have been observed. However, owing to its extremely short life, it usually cannot be detected.²² Introduction of 2 Torr of O₂ gas and photoirradiation of the catalyst caused the appearance of an EPR signal assignable to O_3^- ion at 77 K, as shown in Fig. 7. From the g-values, the paramagnetic species is the T-type ozonide ion, which is formed by interaction of excited lattice O⁻ ions with a side-on attached oxygen molecule.²² After evacuation of the catalyst and introduction of CO, the photoirradiation results in the formation of a new anisotropic EPR signal with $g_1 = 2.0453$, $g_2 = 2.0066$ and $g_3 = 2.0021$, as shown in Fig. 8. The appearance and behavior of these paramagnetic species are the same as those observed with MoO_3 -SiO₂ by Gonzalez-Elipe *et al.*²³ and on plasma-bombarded silica by Ogata *et al.*²⁴ The anisotropic signal is assigned to CO₄⁻ ions structured with [O₃-CO]⁻, which was elucidated by theoretical calculation by Ben Taarit et al.25 Then the catalyst was annealed to room temperature and again cooled to 77 K. The CO_4^- signal disappeared and an end-on type O_2^- signal appeared instead, as shown in Fig. 9.

From these results, reaction is expected to proceed in the initial stage as follows. The oxygen molecule is adsorbed on a photoexcited Ta=O to form ozonide ions, Ta-O-O₂. The carbon monoxide molecule attacks the ozonide ion to form a Ta-O₃-CO species, detected by EPR via an O₃-CO intermediate. This intermediate possibly involves the ozone structure in which three oxygen atoms are equivalent. The reaction scheme is almost the same as the scheme on activated silica reported by Ogata et al.²⁴ The possible reaction scheme for the initial stage is illustrated in Fig. 10; the intermediate III





Fig. 7 EPR spectrum of adsorbed species on Ta_2O_5 -SiO₂ irradiated in the presence of 5 Torr O₂ at 77 K for 1 h.



Fig. 8 EPR spectrum of adsorbed species on Ta_2O_5 -SiO₂ irradiated in the presence of 7 Torr CO at 77 K after evacuation of O₂.



Fig. 9 EPR spectrum of adsorbed species on Ta_2O_5 -SiO₂ annealed to room temperature and subsequently cooled to 77 K.



Fig. 10 Possible reaction scheme for the initial stage of CO photo-oxidation over Ta_2O_5 -SiO₂.

was not detected. The presence of an O_3 -CO intermediate is one of the candidates which can explain the isotope distribution in the carbon dioxide formed from C¹⁶O and ¹⁸O₂.

Conclusion

Tantalum oxide (10 wt.%) is supported on silica in a highly dispersed form. The structure of the surface tantalum species is the same as that of vanadium and niobium oxides; a Ta ion is located at a center of an oxygen tetrahedron, one of which forms a Ta=O bond. The Ta=O species is photoactive but terminal oxygen does not participate directly in oxidation of CO, as elucidated by photoluminescence spectroscopy. The active species is an adsorbed oxygen molecule interacting with a photoexcited lattice oxygen to form a T-type ozonide ion. The ozonide ions are attacked by a CO molecule to form an O_3 -CO intermediate.

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