Migration of Methyl Species of Surface Methoxy Groups on Ta-TMS1

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$CH_3{}^{18}O$ methoxy group formed by adsorption of $CH_3{}^{18}OH$ on Ta-TMS1was converted to $CH^{16}O$ between 573 and 673 K, indicating the mobility of methyl groups by cleaving the C-O band of methoxy groups.

It is widely known that methoxy groups are formed by adsorption of methanol on various oxides [1-5]. Terminal (t)- and bridged (b)-methoxy groups are known to form on ZrO_2 ,[5-7] and they were found to convert their sites and were suggested to migrate on ZrO_2 surface at 573 K, in our previous IR work.[6, 7] The unit of migration, whether CH_3O or CH_3, was identified as CH_3O by using $CH_3{}^{18}OH$ adsorption; the C-^{18}O stretching bands kept unchanged under the condition where both t- and b-methoxy groups migrated.[7] Recently, thermally stable mesoporous materials consisting of oxides of transition metals such as Ti,[8] Mn,[9] Nb,[10] Zr,[11] and Ta[12] have been synthesized. Besides the expectation of these materials for providing of new reaction field, they seem to be suitable for spectroscopic characterization of adsorbed species as well as for supports due to their extremely high surface areas. The acid-base character and adsorption of molecules on any Ta_2O_5 powder have not been well investigated. Therefore, adsorption of methanol on a mesoporous tantalum oxide (Ta-TMS1) was studied by FT-IR in this study, in order to know the surface property of tantalum oxide and for the purpose of utilization of Ta-TMS1. The cleavage of C-O bond of the t-methoxy group upon migration on Ta-TMS1 between 573 and 673 K was observed, which is shown below.

Ta-TMS1 was synthesized according to the following procedure similar to the one described by Antonelli and Ying:[12] To a mixture of $Ta(OEt)_5$ and octadecylamine was added water and the resulting suspension was heated to 353 K for 24 h, 373 K for 24 h, and 453 K for 7 days. The product was recovered by filtration, washed with water, ethanol and diethyl ether and dried in air at 393 K. The surfactant was removed by the treatment of Ta-TMS1 with stoichiometric quantities of triflic acid in dimethoxyethane at 195 K followed by extensive washing with 2-propanol at room temperature. The XRD pattern for the triflic-acid treated sample had a very strong peak at 3.82 nm and its BET surface area was measured as 320 $m^2 \cdot g^{-1}$ after calcination in vacuo at 573 K for 30 min. Less than 5 mg of the sample was dispersed on a CaF_2 plate for IR measurement. Since a small amount of the surfactant still remained in the as-prepared sample (observed by IR), it was in-situ calcined in O_2 at 673 K for 1 hr followed by evacuation at the same temperature. Ta_2O_5 (Wako, purity> 99.8%) with 1.8 $m^2 \cdot g^{-1}$ of surface area was used as a reference. The crystal structure of Ta_2O_5 and Ta-TMS1 were confirmed by XRD (Rigaku Geigerflex RAD-1VB) as orthorhombic and amorphous, respectively. 64 scans were collected for a spectrum at 4 cm^{-1} resolution with an MCT detector.

Methoxy groups on Ta-TMS1 were produced by methanol adsorption at room temperature followed by evacuation at higher temperatures. Spectra (a) and (b) in Figure 1 were measured at 573 K for $CH_3{}^{16}O$ and $CH_3{}^{18}O$ methoxy groups formed by $CH_3{}^{16}OH$ and $CH_3{}^{18}OH$ adsorption, respectively. Since the background spectrum measured before methanol adsorption was subtracted in each spectrum in Figure 1, a negative band appeared at around 3720 cm^{-1} which is attributed to t-OH groups existing on Ta-TMS1 surface after pretreatment. The C-O stretching band of methoxy groups appeared at different frequencies, 1135 and 1098 cm^{-1} for $CH_3{}^{16}O$ and $CH_3{}^{18}O$ species, while two CH stretching bands were similarly observed between 2800 and 3000 cm^{-1} for both methoxy groups. One or several types such as terminal, bridged and tridentate methoxy groups were observed on several oxides and identified by their C-O stretching frequencies as listed in Table 1. The methoxy groups on Ta-TMS1 with high frequency C-O stretching bands are classified in

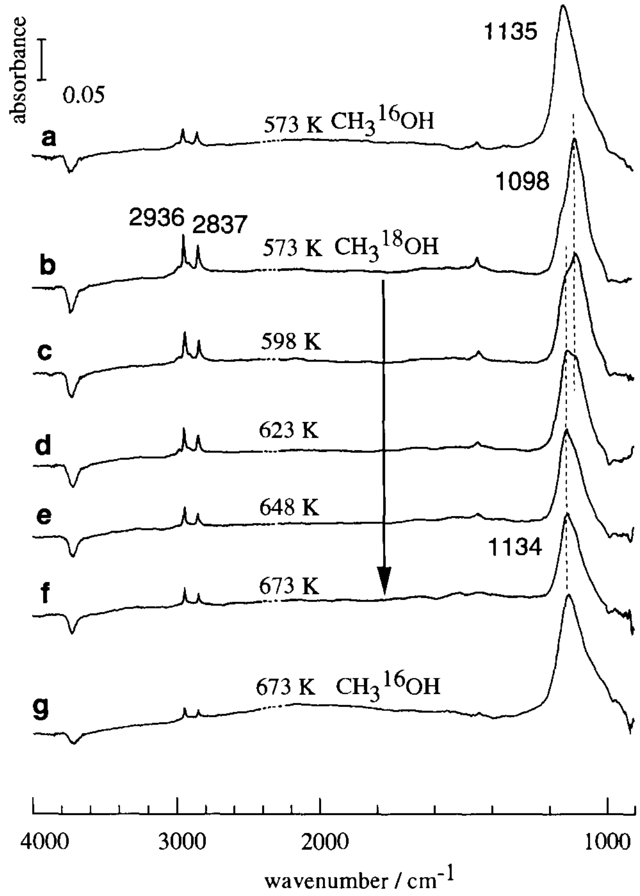

Figure 1. IR spectra of $CH_3{}^{18}OH$ adsorbed on Ta-TMS1.

Table 1. CO stretching frequencies of methoxy groups on oxides/cm^{-1}

	terminal			bridged			tridentate		
	$C^{16}O$	$C^{18}O$	ratio[a]	$C^{16}O$	$C^{18}O$	ratio[a]	$C^{16}O$	$C^{18}O$	ratio[a]
Ta-TMS1[b]	1135	1098	1.034						
ThO_2[c]	1124	1088	1.033	1061 1045	1029 1015	1.031 1.030	1013	985	1.028
CeO_2[c]	1104	1068	1.034	1057 1042	1025 1012	1.031 1.030	1013	985	1.028
ZrO_2[d]	1154	1107	1.042	1052	1015	1.036			

[a] $\nu(C^{16}O)/\nu(C^{18}O)$. [b] Present study. [c] Reference 3. [d] Reference 7.

t-methoxy species. The isotopic ratio of the bands at 1098 and 1135 cm^{-1}(1135 / 1098 = 1.034) is well in agreement with the other oxides (Table 1). Only the t-methoxy group was also observed on Ta_2O_5 powder.

When the methoxy-adsorbed Ta-TMS1 was heated to 673 K in evacuation, gradual peak shift was observed (spectra (b)-(f) in Figure 1); the band at 1098 cm^{-1} decreased in intensity and a new band simultaneously appeared at 1134 cm^{-1}. By comparing the spectrum of the methoxy group on Ta-TMS1 at 673 K (spectrum (f)) with that of $CH_3{}^{16}O$ which was formed by $CH_3{}^{16}OH$ adsorption and evacuation at 673 K (spectrum (g)), it is clearly indicated that the $CH_3{}^{16}O$ group was produced at 673 K. The conversion was quantitatively shown in Figure 2, where C-O bands in Figure 1 were deconvoluted using Gaussian line shapes. Since the total amount of methoxy species did not remain constant between 573 and 673 K probably due to the partial desorption (about 20% reduction of nC-^{16}O band from 573 to 473 K in the case of $CH_3{}^{16}OH$ adsorption), relative composition of $CH_3{}^{18}O$ and $CH_3{}^{16}O$ deduced from integrated intensities of C-^{18}O and C-^{16}O bands was plotted. Figure 2 confirms the conversion of $CH_3{}^{18}O$ to $CH_3{}^{16}O$ species on Ta-TMS1. Similar result was observed on Ta_2O_5 powder in the same temperature region. However, strong IR absorption of the oxide to slightly higher frequency region than the Ta-TMS1 and a small amount of adsorption due to its small surface area inhibited us from the quantitative analysis. In contrast, mesoporous oxides are excellent materials for the spectroscopic studies of adsorption.

The conversion of $CH_3{}^{18}O$ to $CH_3{}^{16}O$ species could be attributed to readsorption of dimethyl ether which might be formed by recombination and desorption of the methoxy groups. In such a case, however, the readsorption should result in 1:1 formation of $CH_3{}^{18}O$ and $CH_3{}^{16}O$ groups; 100% conversion to the $CH_3{}^{16}O$ group at 673 K is not explained. Thus, presently observed conversion of $CH_3{}^{18}O$ to $CH_3{}^{16}O$ species is attributed to the cleavage of C-^{18}O bond of the methoxy group and to the formation of C-^{16}O bond by a methyl group and a lattice oxygen, followed by migration of methyl group on the surface.

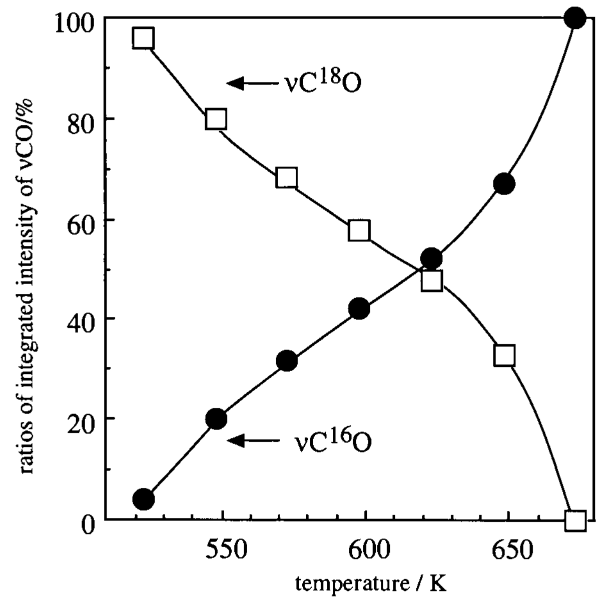

Figure 2. Ratios of integrated intensity of $C^{16}O$ and $C^{18}O$ streching bands at different temperature.

The use of a mesoporous material enabled us to observe the surface species of tantalum oxide by IR method, and its unique surface property was found for the first time. Terminal-methoxy group was formed on Ta-TMS1 from adsorption of methanol, and migrated as methyl group on the surface. The methyl migration process has been often proposed to be involved in many catalytic reactions,[13] however, this work is the first example of the direct observation of the methyl migration step on an oxide surface.

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