IR Characterization of Mesoporous Tantalum Oxide, Ta-TMS-1

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By IR observation, Lewis acid sites of medium strength were found by CO adsorption on a mesoporous Ta-TMS-1 while no basic sites were detected by CO_2 adsorption. Methyl migration of methoxy species and formation of methoxy species from adsorbed dimethyl ether were quantitatively demonstrated.

Since the discovery of a family of mesoporous molecular sieves of silica,[1,2] attempts to extend the synthetic strategy to oxides other than silica have been made. The objectives can be classified into: 1) incorporation of some other component such as B[3], Al[4–7], Ti[7–9], Fe[10], V[11], Cu[12], and Zn[12] into the silica-based mesoporous MCM-41, and 2) preparation of oxides of transition metals such as W[13], Sb[13], Fe[13,14], Pb[13], Ti[15], Mn[13,16], Nb[17], Zr[18], and Ta[19] with mesoporous structures. When one considers the use of them as catalysts or supports, especially for the latter group, complete elimination of the templates and suitable thermal stability are required. Successful examples are reported for oxides of Ti[15], Mn[16], Nb[17], Zr[18], and Ta[19]. These materials are expected to provide a new reaction field and to be used as supports taking advantage of their extremely high surface areas.[20] Such high surface area would enable the infrared (IR) spectroscopic characterization of adsorbed species on oxides.

The acid-base character and adsorption of molecules on any Ta_2O_5 powder have not been well investigated. Recently, we reported on a mesoporous tantalum oxide (Ta-TMS-1) and Ta_2O_5 that methoxy (CH_3O) groups migrated on the surface by cleaving C–O bond, exchanging the O atom with that of the lattice.[21] Detailed characterizations of Ta-TMS-1 and Ta_2O_5 by IR spectroscopy are reported in this paper.

Experimental

Ta-TMS-1 was synthesized according to the following procedure, which is similar to the one described by Antonelli and Ying:[19] 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 d. 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-TMS-1 with stoichiometric quantities of trifluoromethanesulfonic acid (triflic acid) in 1, 2-dimethoxyethane at 195 K, followed by extensive washing with 2-propanol at room temperature. The XRD pattern for the trifluoromethanesulfonic acid-treated sample had a peak at 3.8±0.1 nm. The N_2 adsorption isotherm shown in Fig. 1 reproduced the original result on the synthesis of Ta-TMS-1.[19] The

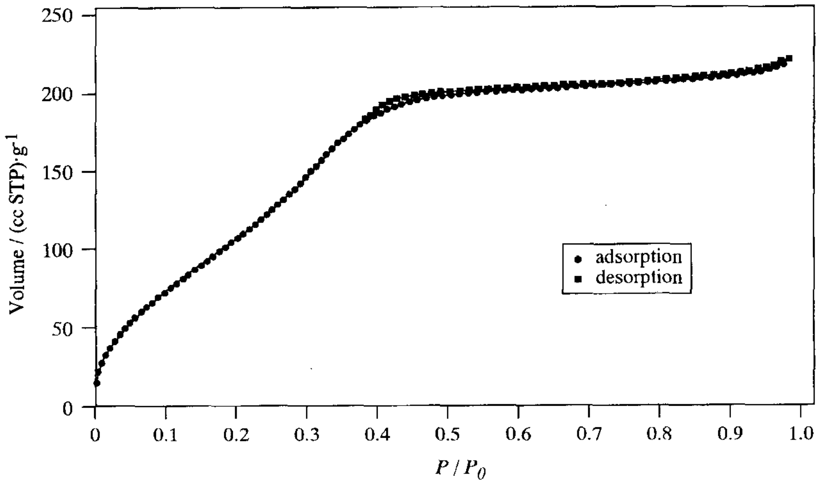

Fig. 1. Nitrogen adsorption isotherm of the template-removed Ta-TMS-1.

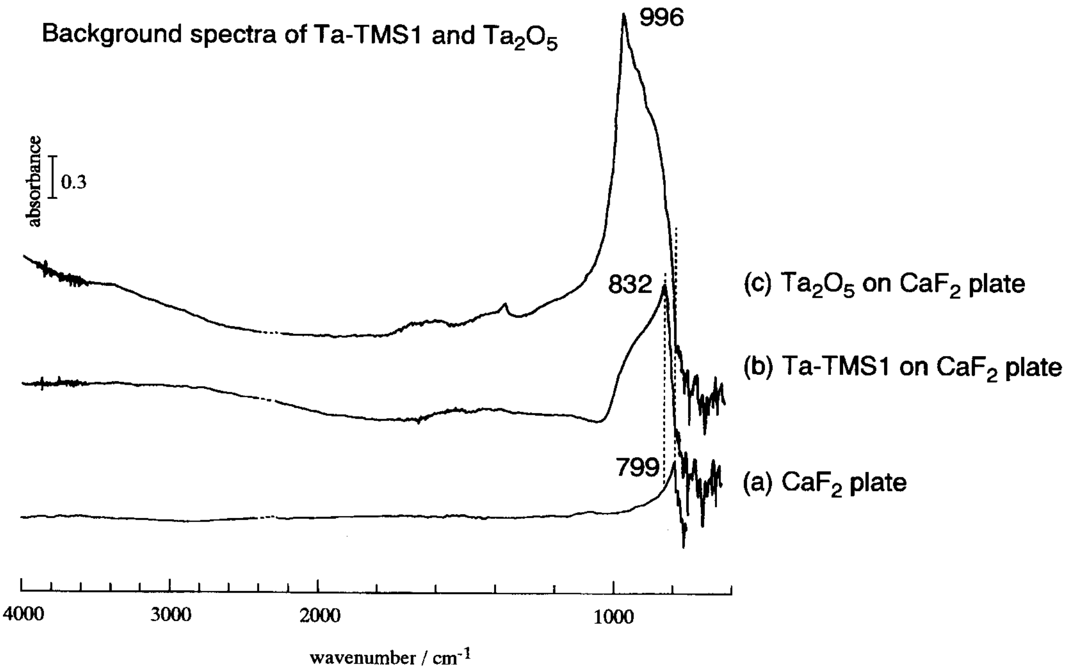

Fig. 2. Background spectra at room temperature of (a) CaF_2 plate, (b) Ta-TMS-1 on CaF_2 plate and (c) Ta_2O_5 on CaF_2 plate.

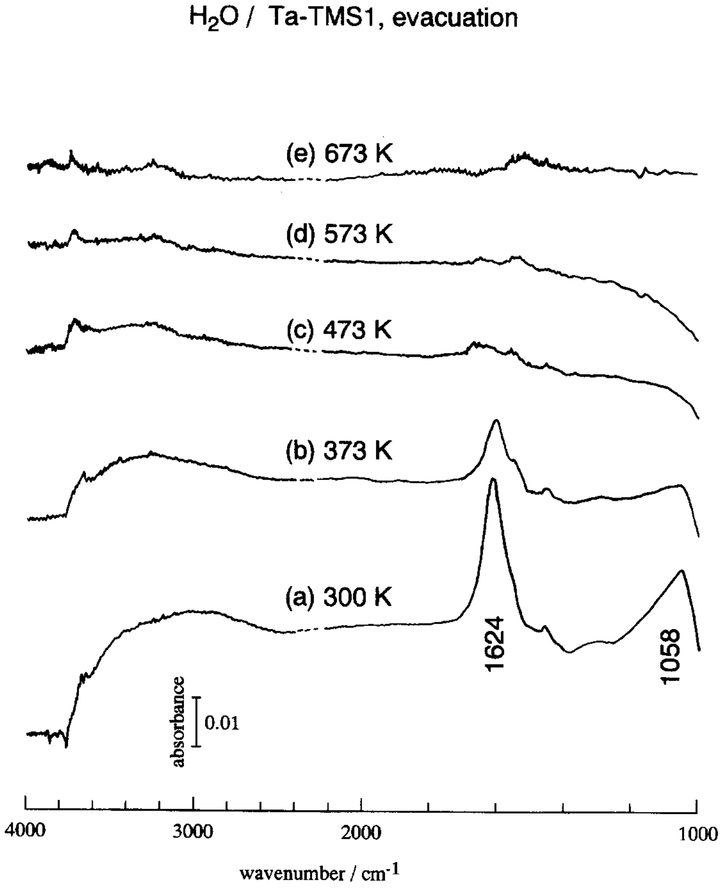

Fig. 3. H_2O adsorbed Ta-TMS-1 in evacuation (a) at 300 K, heated to (b) 373 K, (c) 473 K, (d) 573 K, and (e) 673 K.

BET surface area was estimated by some data acquisitions between $P/P_0 = 0.05$ and 0.30, which resulted in 450±50 $m^2\,g^{-1}$. This corresponds to more than 1800 $m^2\,g^{-1}$ by a molar evaluation to SiO_2. The pore size distribution was situated at around 2.5 nm after calcination in vacuo at 373 K for 1 h.

Less than 5 mg of the sample was dispersed on a CaF_2 plate for IR measurements instead of the use of a self-supporting disk, in order to avoid the sample collapse by pressing. Since a small amount of the surfactant still remained in the as-prepared sample (observed by IR), it was calcined in O_2 at 673 K for 1 h, followed by evacuation at the same temperature. This pretreatment condition was chosen because a gradual decrease of the bands due to the surfactant could be observed at 673 K when the sample disk was warmed in the atmosphere of O_2. The complete disappearance of the surfactant was confirmed after 1 h at 673 K by IR observation. Although the BET surface area of Ta-TMS-1 after O_2 treatment at 673 K decreased to ca. 60% of the original one (ca. 300 $m^2\,g^{-1}$), N_2 adsorption and desorption isotherms still showed some porosity, while the BET surface area of amorphous Ta_2O_5 prepared from the same starting material without adding the surfactant was less than 100 $m^2\,g^{-1}$. Details of the improvement of the synthetic approach as well as the structural characterization of Ta-TMS-1 will be shown elsewhere, together with its photocatalytic activity.[22] D_2O treatment was performed by exposing Ta-TMS-1 to D_2O vapor at room temperature followed by heating in evacuation to 673 K. This procedure was cycled three times before observation of adsorbed D_2O. Ta_2O_5 (Wako, purity > 99.8%) with 1.8 $m^2\,g^{-1}$ of surface area was used as a reference by being dispersed on a CaF_2 plate for the background comparison or by being pressed into a disk for adsorption study. The crystal structures of the Ta_2O_5 and Ta-TMS-1 were confirmed by XRD as orthorhombic and amorphous, respectively. 64 scans were collected for a spectrum at 4 cm^{-1} resolution with an MCT detector. Background spectra were measured at various temperatures in evacuation after pretreatment. One of the background spectra was subtracted from a spectrum measured after adsorption of probe molecules.

Results and Discussion

1. Background Spectra. The dispersed Ta-TMS-1 on a CaF_2 plate showed an IR spectrum at 293 K after O_2 pretreatment, as shown in Fig. 2(b). A broad band due to lattice vibrations was observed below 1000 cm^{-1} with a sharp peak at 832 cm^{-1}, which is well above the cut-off frequency for CaF_2 substrate (799 cm^{-1}, Fig. 2(a)). The band at 832 cm^{-1} which is assigned to the Ta=O stretching[23] shifted to 996 cm^{-1} on Ta_2O_5 (Fig. 2(c)), while a broad band between 800 and 1000 cm^{-1} appeared almost the same. The difference of the Ta=O stretching frequency between Ta-TMS-1 and Ta_2O_5 can probably be attributed to the difference in the crystal structure: amorphous and orthorhombic, respectively. The dispersed Ta_2O_5 was not suitable for observation of adsorbed species due to its small surface area (1.8 $m^2\,g^{-1}$), and a disk of Ta_2O_5 was used for adsorption study. The strong lattice absorption of Ta_2O_5 at higher frequency greatly inhibited observation and quantification of IR spectra below 1000 cm^{-1}. On the other hand, the appearance of it at lower frequency on the mesoporous Ta-TMS-1 is of advantage as shown below.

It is noted that no characteristic surface OH groups were observed, which might appear between 3500 and 3800 cm^{-1}

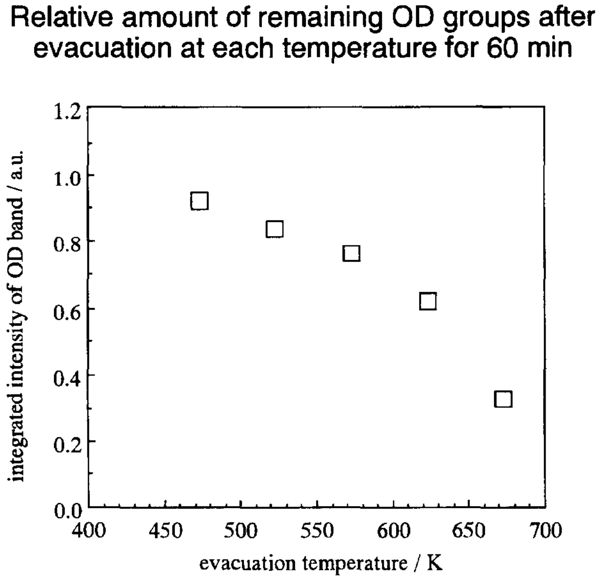

Fig. 4. Relative amount of terminal OD groups formed by D_2O adsorption on D_2O-treated Ta-TMS-1. D_2O-adsorbed Ta-TMS-1 was maintained in evacuation at each temperature for 60 min before spectrum measurement.

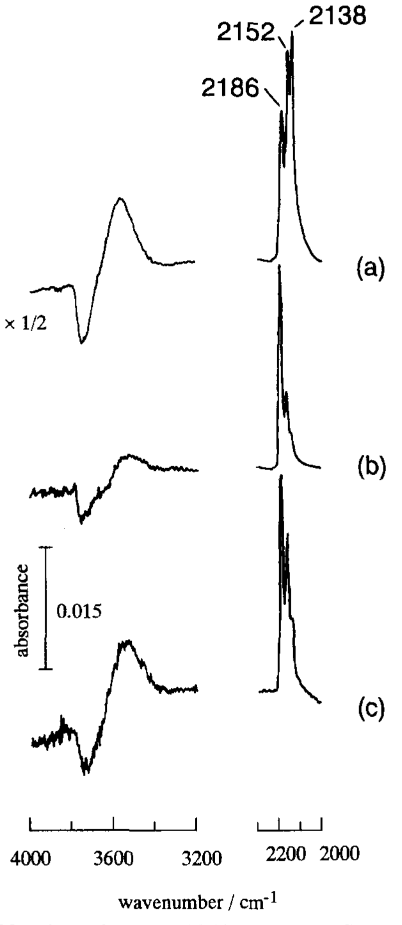

Fig. 5. CO adsorption at 156 K on Ta-TMS-1 evacuated at 673 K (a) in the presence of 4 Torr of CO, (b) after evacuation, and (c) after evacuation of CO at 156 K on Ta-TMS-1 evacuated at 473 K.

on oxide surfaces.[23—25] although a small negative peak of OH stretching band was observed at ca. 3740 cm^{-1} after subtraction of a background from spectra measured after adsorption (see below). Therefore, a very small amount of OH groups was found to exist on Ta-TMS-1.

Since no OH groups were clearly observed after pretreatment, water adsorption and heating in evacuation, which generate surface OH groups on oxide surfaces, were attempted. Thr IR spectrum of adsorbed water on Ta-TMS-1 at 300 K is shown in Fig. 3(a). H_2O (0.5 Torr, 1 Torr = 133.322 Pa) was introduced and maintained at 300 K for 30 min, followed by evacuation at the sample temperature for 60 min. A broad OH stretching band and a bending band attributed to adsorbed H_2O were observed at 2600—3800 cm^{-1} and 1624 cm^{-1}, respectively. The integrated intensities of the stretching band of water adsorbed on oxides are known to appear several times larger than that of the bending mode.[24] On Ta-TMS-1, however, the bending mode was observed as an unusually intense band. A raise of the baseline from 3800 to 1400 cm^{-1} and an absorption at 1058 cm^{-1} appeared upon water adsorption, and simultaneously decreased with water desorption. Similarly to the cases of CO, ethylene, pyridine, dimethyl ether and methanol, a change of the baseline at 3800—1400 cm^{-1} and an absorption at ca. 1050 cm^{-1} were reversibly and concurrently observed with adsorption and desorption. This phenomenon was not observed on Ta_2O_5 and is regarded as particular to the amorphous or mesoporous structure of Ta-TMS-1. However, the origin of it is not yet clear. (This would be established by some reference data on non-mesoporous Ta_2O_5.) During the stepwise heating in evacuation at 100 K intervals to 673 K (spectra were measured after 60 min maintenance at the indicated temperatures), the desorption of water was confirmed by the decrease of the bending band at 1624 cm^{-1}, which almost disappeared at 473 K. In general, dissociation of adsorbed water produces OH groups on oxides, and IR bands of isolated OH groups are observed between 3500 and 3800 cm^{-1} when oxides are evacuated at high temperatures.[24] On Ta-TMS-1, a weak band was observed at ca. 3740 cm^{-1} at 473 K (Fig. 3(c)) but decreased in intensity at 673 K (Fig. 3(e)). The stretching frequencies of surface OH groups are known to reflect the coordination number of O atom to metal ions and can be classified into terminal (mono-coordinated), bridged (di-coordinated), three fold (tri-coordinated) and so on.[25] The OH groups on Ta-TMS-1 are regarded as terminal ones from its high frequency. Since the amount of OH groups was not exactly quantified due to the poor signal-to-noise ratio and interference by IR absorption of gaseous water, similar ex-

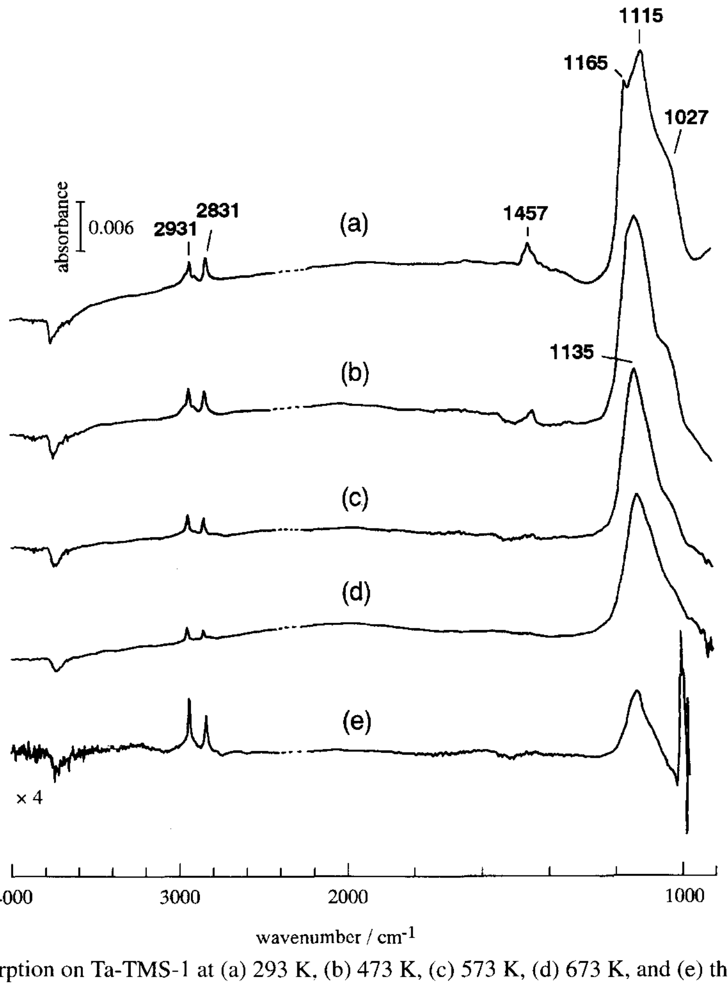

Fig. 6. Methanol adsorption on Ta-TMS-1 at (a) 293 K, (b) 473 K, (c) 573 K, (d) 673 K, and (e) that on Ta_2O_5 at 573 K.

periments using D_2O were performed. D_2O was adsorbed at room temperature and the sample was evacuated and heated to each temperature. The spectra were measured after evacuation at the temperatures for 60 min. The corresponding OD band appeared at 2757 cm^{-1} (ω_{OH}/ω_{OD} = 1.36). Intensity of OD band was integrated in as-observed spectra without subtraction of the background spectrum. As plotted in Fig. 4, the amount of OD groups remaining after evacuation at 673 K decreased to one-third of that evacuated at 473 K, in contrast to other oxides[24,25] where evident removal of isolated OH (OD) groups occurs above 673 K. This indicates that the OH (OD) groups are only weakly held on Ta-TMS-1, which was the same for the orthorhombic Ta_2O_5.

2. Acid-Base Properties. The terminal OH groups and cation sites (coordination-unsaturated metal ions) generated by dehydration may be regarded as Brønsted and Lewis acid sites, respectively. For the estimation of the strength of acidic property, CO was used as a probe; the higher the C–O stretching frequency appears, the stronger the acid site is.[26] The adsorbed CO was observed at 156 K, as shown in Fig. 5, on Ta-TMS-1 after water adsorption followed by evacuation at 473 and 673 K. In the presence of gaseous CO, three CO stretching bands at 2186, 2152, and 2138 cm^{-1} were observed on Ta-TMS-1 evacuated at 673 K (Fig. 5(a)). These bands are assigned to the CO adsorbed on Lewis and Brønsted acid sites, and to physically adsorbed CO, respectively.[27] As listed in Table 1, the strength of the Lewis acid site on Ta-TMS-1 is comparable with those of TiO_2, ZrO_2, and Cr_2O_3 but much weaker than that of the typical acid catalysts. The shift of OH band in Fig. 5(a) from ca. 3640 to ca. 3500 cm^{-1} in background spectrum is attributed to the CO adsorption on OH groups; the corresponding CO band was observed at 2152 cm^{-1}. The interaction of CO with acidic OH groups on oxides is weaker than that with cation sites, and as a result, CO bands are only observed at low temperatures in the presence of gaseous CO. The terminal OH group on Ta-TMS-1 behaved as a very weak acid site from its frequency (Table 2) and decreased after evacuation together with the pairing OH band at ca. 3500 cm^{-1} (Fig. 5(b)). When gaseous CO was evacuated, physically adsorbed CO disappeared, and CO dominantly existed on Lewis acid sites. On Ta-TMS-1 evacuated at 473 K, more amount of CO on OH groups remained after evacuation due to the surface hydroxylation. However, CO on Lewis acid sites still exists on the Ta-TMS-1 even on the hydroxylated surface. Therefore, we concluded from Figs. 4 and 5 that cation sites are easily formed, and that a considerable amount of Lewis acid sites with medium strength exist on the surface of Ta-TMS-1. When the same experiments were performed on Ta_2O_5, similar results were obtained, indicating that acid property is identical to tantalum oxide.

Table 1. CO Stretching Frequency of CO Adsorbed on Lewis Acid Sites of Oxides

Cation	Frequency/cm^{-1}	Reference
Mg^{2+} (MgO)	2153	28
Ce^{4+} (CeO_2)	2169	28
Ti^{4+} (TiO_2)	2182	28
Cr^{3+} (Cr_2O_3)	2182	28
Ta^{5+} (Ta-TMS-1)	2186	Present study
Zr^{4+} (ZrO_2)	2184, 2192	29
Mo^{5+} (MO_xO_y)	2194	30
Al^{3+} (SiO_2–Al_2O_3)	2195	28
Al^{3+} (H-ZSM-5)	2227	31

Table 2. CO Stretching Frequency of CO Adsorbed on OH Groups (Brønsted Acid Sites) of Oxides

Oxide	Frequency/cm^{-1}	Reference
Ta-TMS-1	2152	Present study
γ-Al_2O_3	2152	32
SiO_2	2158	33
H-ZSM-5	2177	31

The basic property of Ta-TMS-1 was probed by CO_2 adsorption. CO_2 adsorption results in forming carbonate (CO_3^{2-}) species on basic O atoms on oxides, and $H_2CO_2^-$ or $HOCO_2^-$ species on basic OH groups.[34] The analogous species were observed on various oxides such as ZrO_2, ThO_2, CeO_2, La_2O_3, and ZnO.[34] In the case of Ta-TMS-1, a sharp peak due to OCO asymmetric stretching due to physically adsorbed CO_2 was observed at 2342 cm^{-1} (7 cm^{-1} lower than that of free molecule) only below ca. 200 K. Adsorption of CO_2 at the temperature as high as 473 K did not form any chemisorbed species. Therefore, no basic sites were found to exist on Ta-TMS-1 surface.

3. Methanol and Dimethyl Ether Adsorption. Ta-TMS-1 was exposed to 4 Torr of methanol at 293 K, followed by evacuation and heating to 673 K. Molecularly adsorbed methanol was confirmed by a shoulder band at 1030 cm^{-1} up to 473 K, but disappeared at 573 K (Fig. 6(c)). On the other hand, methoxy groups were already formed at 293 K, and remained on the surface even at 673 K. The methoxy groups showed the C–O stretching band at 1135 cm^{-1} and were classified into the terminal (mono-coordinated) groups.[21] In spectrum (e) in Fig. 6, methoxy groups on Ta_2O_5 are shown. Terminal methoxy groups were also produced, but the C–O stretching band was distorted by the strong lattice absorption of Ta_2O_5 below 1000 cm^{-1}. The intensity ratios of CH stretching and of C–O stretching bands greatly differed; they were comparable on Ta_2O_5, while the CH stretching band was much weaker than the C–O stretching band on Ta-TMS-1. The enhancement of the low frequency bands or reduction of intensity of high frequency bands on Ta-TMS-1 was also observed for water (Fig. 3), dimethyl ether (Fig. 8), pyridine, and ethylene (not shown).

As we have reported in the previous paper,[21] the methyl groups of methoxy species migrated on the surfaces of both Ta-TMS-1 and Ta_2O_5 as methyl groups by cleaving C–O bonds. This was evidenced by an isotope shift of $C^{18}O$ band of methoxy groups at 573 K to $C^{16}O$ band at 673 K, indicating the isotope exchange of O atoms in methoxy groups with those in the lattice. The results are summarized in Fig. 7. The band at 1098 cm^{-1} due to C–^{18}O stretching shifted to

1134 cm^{-1} (C–^{16}O stretching) on increasing the temperature from 573 to 673 K on Ta-TMS-1 (spectra (c) and (d)). In the similar manner, ^{18}O-labeled methoxy groups on Ta_2O_5 were converted to ^{16}O-methoxy groups on Ta_2O_5, although the strong background absorption distorted the spectra of Ta_2O_5 (spectra (a) and (b)). Therefore, the methyl migration was correlated to the property of tantalum oxide itself, but good transmittance of the mesoporous material enabled us to quantitatively demonstrate the gradual conversion of C–^{18}O band to C–^{16}O.[21]

From the above results on the behavior of methoxy species, we expected that active surface sites for C-O bond cleavage would exist on Ta-TMS-1. Next, dimethyl ether adsorption and formation of methoxy species were studied in the light of C–O bond cleavage. IR spectra of dimethyl ether adsorbed on Ta_2O_5 and Ta-TMS-1 at 298 K are shown in Figs. 8(a) and 8(b), respectively. All the observed bands are assigned to dimethyl ether molecule (Table 3). The change of spectra by increasing temperature in evacuation is only shown for Ta-TMS-1 due to the clarity of spectra at the low frequency region where changes of the structure of adsorbates evidently appear. The molecularly adsorbed dimethyl ether simply desorbed up to 423 K, but conversion of the adsorbed dimeth-

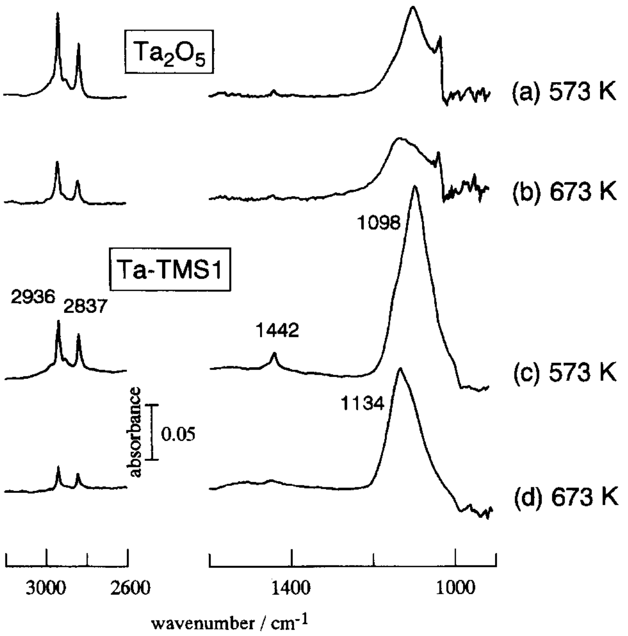

Fig. 7. Change of IR spectra of ^{18}O-labeled methoxy groups at 573 K and 673 K. (a) 573 K, (b) 673 K on Ta_2O_5, and (c) 573 K, (d) 673 K on Ta-TMS-1.

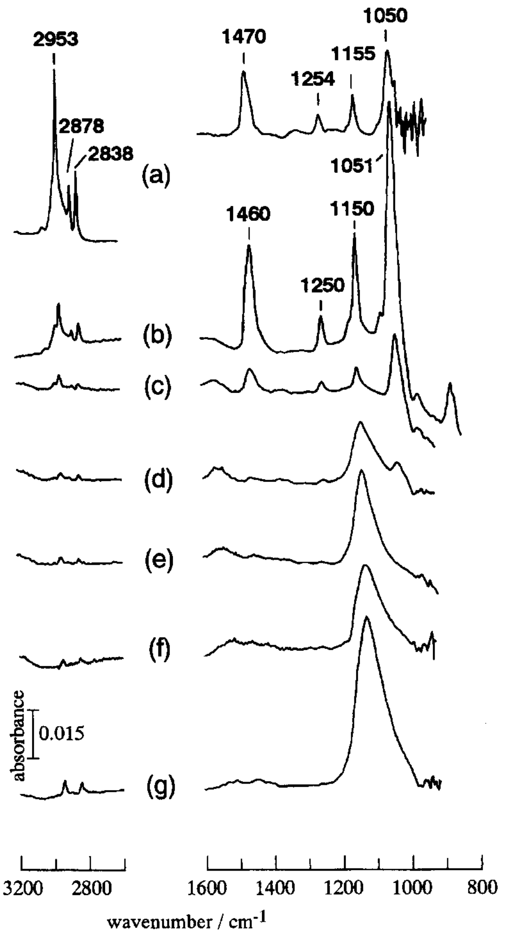

Fig. 8. Dimethyl ether adsorption on (a) Ta_2O_5 at 298 K, Ta-TMS-1 at (b) 298 K, (c) 423 K, (d) 473 K, (e) 523 K, (f) 673, and (g) readsorption of dimethylether at 673 K.

Table 3. Observed Frequencies of Dimethyl Ether Adsorbed on Ta-TMS-1

Assignment	Free molecule[a)]	on Ta-TMS-1[b)]	
CH_3 d-str.	2996 S	2953	(−43)
CH_3 d-str.	2952 i.a.	—	
CH_3 d-str.	2925 S	2878	(−47)
CH_3 s-str.	2817 S	2838	(+21)
CH_3 d-def.	1464 M	1460	(−4)
CH_3 s-def.	1452 M	—	
CH_3 rock.	1244 W	1250	(+6)
CH_3 rock.	1179 VS	1150	(−29)
C–O str.	1102 VS	1051	(−51)

a) Ref. 35. M, medium; W, weak; VS, very strong; i.a., IR inactive.
b) present study. Numbers in parenthesis are the defference from those of free molecules.

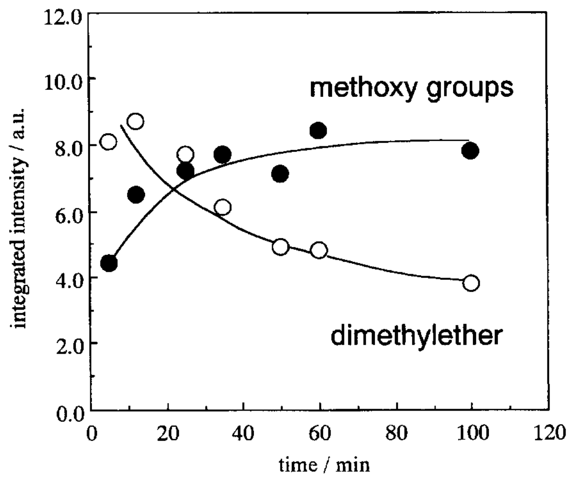

Fig. 9. Time course of conversion of dimethyl ether to methoxy species on Ta-TMS-1 at 473 K.

yl ether into methoxy species was observed from 423 to 523 K (Figs. 8(c) and 8(e)). Desorption or decomposition of methoxy species was observed at 673 K, similarly to the case of methanol adsorption (Fig. 7). The time course of the methoxy formation from dimethyl ether at 473 K is shown in Fig. 9 by peak deconvolution into bands at 1051 and 1140 cm^{-1} as key bands of dimethyl ether and methoxy species, respectively, assuming Gaussian line shapes. Good correlation between decrease of adsorbed dimethyl ether and increase of methoxy groups was observed. Therefore, methoxy formation from dimethyl ether also confirmed that active sites for C–O bond cleavage exist on Ta-TMS-1 surface (and also on Ta_2O_5). When dimethyl ether was readsorbed at 673 K to the surface of Fig. 8(f), the amount of methoxy groups greatly increased to about 4 times more (Fig. 8(g)). Therefore, the amount of methoxy groups formed by adsorption of dimethyl ether at 298 K, followed by evacuation to 673 K, is estimated as about one fourth of full coverage at 673 K.

Conclusion

The surface properties of Ta-TMS-1 as well as Ta_2O_5 were studied. The good transmittance of the former sample at low frequency region enabled quantitative analysis of the adsorbed species. OH groups were found to be easily removed by evacuation at 673 K, and CO adsorption indicated that relatively weak Lewis acid sites existed on the surface. Existence of active sites for methyl–oxygen bond cleavage was proposed by methoxy migration in our previous paper, and was confirmed by methoxy formation from adsorbed dimethyl ether in this study.

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