Soft Chemical Synthesis of Mesoporous Metal Oxides and Their IR Characterization

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A mesoporous tantalum oxide, Ta-TMS-1, was characterized by FT-IR. Terminal-OH groups (ca. 3740 cm⁻¹) was formed by water adsorption and evacuation at 473 K, which decreased to one third by evacuation to 673 K. Lewis acid sites of medium strength was found by CO adsorption to dominate the surface, while no basic sites were detected by CO_2 adsorption. The lattice vibrations of Ta-TMS-1 appeared at lower frequency region than those of Ta_2O_5 powder. Ta-TMS-1 was applied for IR study of quantitative analysis of conversion of surface species possessing C-O bonds; migration of methyl groups of methoxy species, and formation of methoxy species from adsorbed dimethylether.

1. INTRODUCTION

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 The objectives are classified into; 1) been made. incorporation of other component such as B³, Al⁴⁻⁷ Ti ⁷⁻⁹, Fe ¹⁰, V¹¹, Cu ¹² and Zn ¹² into the silica based mesoporous MCM-41, and 2) preparation of oxides of transition metals such as W¹³, Sb¹³, Fe^{13, 14}, Pb¹³, Ti¹⁵, Mn^{13, 16}, Nb¹⁷, Zr¹⁸ and Ta¹⁹ with mesoporous structures. When considering the use of them as catalysts or supports, especially for the latter group, complete elimination of the templates and the thermal stability are required. Successful examples are reported for oxides of Ti 15 , Mn 16 , Nb 17 , Zr 18 and Ta¹⁹. These materials are expected to provide new reaction field and to be used as supports taking advantage of their extremely high surface areas ²⁰. The high surface area of them would as well, enable the infrared (IR) spectroscopic characterization of adsorbed species on oxides.

The acid-base character and adsorption of molecules on Ta_2O_5 have not been well investigated. Recently, we reported that on a mesoporous tantalum oxide (Ta-TMS-1) and Ta_2O_5 methoxy (CH₃O) groups migrated on the surface by cleaving C-O bond, exchanging the O atom with that of the lattice ²¹. Detailed characterization of Ta-TMS-1 and Ta_2O_5 by IR spectroscopy is reported in this paper.

2. EXPERIMENTAL

Ta-TMS-1 was synthesized according to the following procedure 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 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-TMS-1 with stoichiometric quantities of trifluoromethanesulfonic acid (triflic acid) in dimethoxy ethane at 195 K followed by extensive washing with 2-propanol at room temperature. The XRD pattern for the trifluoromethanesulfonic acid

treated sample had a very strong peak at 3.82 nm and its BET surface area was measured as 320 m²·g⁻¹ with a sharp pore size distribution at 2.5 nm after calcination in vacuo at 573 K for 30 min. Less than 5 mg of the sample was dispersed on a CaF₂ 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 hr followed by evacuation at the same temperature. D2O treatment was performed by exposing Ta-TMS-1 to D₂Ovapor 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 m²·g⁻¹ of surface area was used as a reference, being dispersed on CaF2 plate for the background comparison or pressed into a disk for adsorption study. The crystal structure 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.

3. RESULTS AND DISOCUSSION

3.1 Background Spectra

The dispersed Ta-TMS-1 on a CaF₂ plate showed an IR spectrum at 293 K after O₂ pretreatment A broad band due to lattice as shown in Fig. 1(b). vibrations was observed below 1000 cm⁻¹ with a sharp peak at 832 cm⁻¹ which is well above the cut-off frequency by CaF₂ substrate (799 cm⁻¹, Fig. 1(a)). The band at 832 cm⁻¹ is assigned to the Ta=O stretching ²² shifted to 996 cm⁻¹ on Ta₂O₅ (Fig. 1(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 Ta₂O₅ is probably attributed to the difference in the crystal structure. The dispersed Ta₂O₅ was not suitable for observation of adsorbed species due to its small surface area (1.8 $m^2 \cdot g^{-1}$), and a disk of Ta₂O₅ was used for adsorption study. The strong lattice absorption of Ta₂O₅ 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.



Fig. 1 Background spectra of Ta-TMS-1 and Ta₂O₅

It is noted that any surface OH groups which were expected to appear between 3500 and 3800 cm⁻¹ were not observed. This is not due to the insufficient amount of the sample as will be shown below. Therefore, very small amount of OH groups exist on Ta-TMS-1, 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).

Since any OH groups were not clearly observed after pretreatment, water adsorption and heating in evacuation, which generate surface OH groups on the surface, were attempted. IR spectrum of adsorbed water on Ta-TMS-1 at 300 K is shown in Fig. 2(a).



Fig. 2 IR spectra of H₂O adsorbed on Ta-TMS-1

A broad OH stretching and a bending bands 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 is known to appear several times larger than that of the bending mode 23 . 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. In the case of CO, ethylene, pyridine, dimethyl ether and methanol, a similar change of the baseline at $3800-1400 \text{ cm}^{-1}$ and the absorption at ca. 1050 cm⁻¹ were reversibly and concurrently observed

This phenomenon with adsorption and desorption. was not observed on Ta₂O₅ and is regarded as particular However, the origin of it is not yet to Ta-TMS-1. The desorption of water by heating in clear. evacuation was confirmed by decrease of the bending band, which almost disappeared at 473 K. In general, adsorption and dissociation of water produce 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 ²³. On Ta-TMS-1, a weak band was observed at ca. 3740 cm⁻¹ at 473 K (Fig. 2(c)) but decreased in intensity at 673 K (Fig. 1(e)). The stretching frequency of surface OH groups are known to reflect the coordination number of O atom to metal ions and classified into terminal (monocoordinated), bridged (di-coordinated), three fold (tricoordinated) and so on ²⁴. 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 experiments using D_2O was performed. 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 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 is common to the surface of Ta_2O_5 (not shown).

3.2 Acid-Base Property



The terminal OH group and cation sites 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; at the higher the C-O stretching frequency appears, the stronger the acid site is 25 . The adsorbed CO was observed at 156 K as shown in Fig. 3 on Ta-TMS-1 of both pretreatment of evacuation at 473 and 673 K after water adsorption. 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. 3(a)). These bands are assigned to the CO adsorbed on Lewis and Brønsted acid sites, and physically adsorbed CO, respectively 26 .

The strength of the Lewis acid site on Ta-TMS-1 is comparable with those of TiO₂, ²⁷ ZrO₂ ²⁸ and Cr₂O₃ ²⁷ but much weaker than typical acid catalysts. The shift of OH band in Fig. 3(a) from ca. 3940 cm⁻¹ in background spectrum to ca. 3500 cm^{-1} 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 also behaved as very weak acid sites from its frequency $^{30-32}$ and decrease after evacuation together with the pairing OH band at ca. 3500 cm⁻¹ (Fig. 43(b)). When gaseous CO was evacuated, physically adsorbed CO disappeared, and CO on Lewis acid sites dominantly existed. 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 exist on the Ta-TMS-1 with more OH groups. Therefore, it is concluded from Figs. 2 and 3 that cation sites are easily formed, and considerable amount of Lewis acid sited with medium strength exist on the surface of Ta-TMS-1. When the same experiments were performed on Ta₂O₅, similar results were obtained, indicating that acid property is identical to tantalum oxide.

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 HOCO₂⁻ species on basic OH groups ³³. The analogous species were observed on various oxides as ZrO_2 , ThO_2 , CeO_{24}/La_2O_3 , ZnO and so on ³³. 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.

3.3 Methanol and Dimethyl ether Adsorption

As we have reported in the previous paper ²¹ that methyl group of methoxy species migrated on the surfaces of both Ta-TMS-1 and Ta₂O₅ as methyl groups by cleaving C-O bond. This was evidenced by isotope shift of $C^{18}O$ band of methoxy groups at 573 K to C¹⁶O 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. 4. The band at 1098 cm⁻¹ due to C-¹⁸O stretching shifted to 1134 cm⁻¹ (C-¹⁶O stretching) by increasing the temperature from 573 to 673 K on Ta-TMS-1 (spectra In the similar manner, ¹⁸O-labeled (c) and (d)). methoxy groups on Ta_2O_5 were converted to $^{16}O_$ methoxy groups on Ta₂O₅. However, the strong background absorption distorted the spectra of Ta₂O₅ (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 $C^{-16}O^{21}$.



Fig. 4 Change of IR spectra of ¹⁸O-labeled methoxy groups at 573 K and 673 K

By observation of methoxy species, it was found that there exist active surface sites for C-O bond cleavage 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 Ta₂O₅ and Ta-TMS-1 at 298 K are shown in Fig. 5(a) and (b), respectively. All the observed bands are assigned to dimethyl ether molecule. ³⁴



Fig. 5 Dimethylether adsorption

The change of spectra by increasing temperature in evacuation is only shown for Ta-TMS-1 for the clarity of spectra at low frequency region where change of the structure of adsorbates evidently appear. The molecularly adsorbed dimethyl ether simply desorbed up to 423 K, but conversion of the adsorbed dimethyl ether into methoxy species was observed from 423 to 523 K (Fig. 5(c)-(e)). Desorption or decomposition of methoxy species was observed at 673 K similarly to the case of methanol adsorption. The time course of the methoxy formation from dimethyl ether at 473 K is shown in Fig. 6 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.



Fig. 6 Time course of conversion of dimethylether to methoxy species on Ta-TMS-1 at 473 K

Good correlation between decrease of adsorbed dimethyl ether and increase of methoxy groups was observed. Therefore, it is also confirmed by methoxy formation from dimethyl ether that active sites for C-O bond cleavage exist on Ta-TMS-1 surface (and also on Ta₂O₅). When dimethyl ether was readsorbed at 673 K to the surface of Fig. 5(f) (Fig. 5(g)), the amount of methoxy groups greatly increased to about 4 times more. 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 forth of full coverage at 673 K.

4. CONCLUSION

The surface property of Ta-TMS-1 as well as Ta_2O_5 was 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 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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