Germanium oxide mono-atomic layer prepared by chemical vapor deposition method on γ-alumina: the structure and acidic property

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Received 7 November 1994; accepted 14 February 1995

An ultra thin layer of germanium oxide with mono-atomic order thickness was prepared by chemical vapor deposition (CVD) of germanium alkoxide on γ-alumina; the structure was analyzed by benzaldehyde–ammonia titration, extended X-ray absorption fine structure (EXAFS) and infrared spectroscopy. The mono-atomic layer showed Brønsted acidity, like the silica monolayer.

Keywords: mono-atomic layer; germanium oxide; CVD; EXAFS; Brønsted acidity

1. Introduction

Thin oxide layers with homogeneous structure are promising models of mixed-oxide catalysts. The ultra thin layer of silica was prepared by CVD (chemical vapor deposition) of $Si(OCH_3)_4$ (tetramethoxysilane) on γ-alumina [1,2], titania and zirconia [3,4]. It was observed that the monolayer, consisting of the 1 : 1 bonds of Si–O–M (M = Al, Ti or Zr) and the network of siloxanes (Si–O–Si), covered the surface almost completely. The silica monolayer generated Brønsted acidity [1–5]. However, few spectroscopic analyses are available for SiO_2. Germanium belongs to the same group of the periodic table as silicon, and germanium alkoxide has the same four coordinated structure as silicon alkoxide. It is therefore expected that a

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layer of germanium oxide with an atomic-order thickness can be prepared by CVD of germanium alkoxide, and that EXAFS (extended X-ray absorption fine structure) analysis, which is available for GeO_2, will give valuable information about the structure of the oxide monolayer and the origin of acidity. We have already used the CVD of germanium alkoxide on zeolite in order to study the structure of thin silica layer, which controlled the opening size of the micro pore [6,7]. Here, we report the preparation on γ-alumina of the mono-atomic layer of germanium oxide. This novel material showed Brønsted acidity.

2. Experimental

γ-alumina was supplied by Catalysis Society of Japan as a reference catalyst, JRC-ALO4 (161 $m^2\ g^{-1}$). Germanium tetramethoxide (99.999% $Ge(OCH_3)_4$) was obtained from Rare Metallic Co. Ltd. and further purified by vacuum distillation. The alumina sample was put in a basket hanged by a micro balance, and evacuated at 673 K until no change in weight was observed. The alkoxide vapor was then admitted on the sample at 473 K. The cycle of introduction of vapor and its evacuation was repeated in order to avoid vapor lock by such gaseous products as dimethyl ether and methanol. The vapor pressure of alkoxide was kept constant by chilling the reservoir in an ice bath, and the evacuation was done at a pressure of ca. 10^{-3} Torr (1 Torr = 133.3 Pa). In order to remove the organic residue, the sample was calcined at 673 K in the presence of 27 kPa of oxygen.

The BET surface area was measured by nitrogen adsorption at 77 K. The coverage by GeO_2 on the alumina surface was measured by the BAT (benzaldehyde–ammonia titration) method [8,9] as utilized for the silica layer [2]. Benzaldehyde was adsorbed in flowing helium at 523 K on the sample pretreated at 673 K until the adsorption was saturated. Ammonia was then introduced at 673 K, and the yielded benzonitrile was quantified.

Ge K-edge EXAFS was measured on a thin disk molded from the sample powder at the Beam Line 10B of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF). The synchrotron radiation from the electron storage ring (25 GeV, average current 100 mA) was monochromatized with a channel-cut Si(311) monochromator. The incident- and transmitted-beam intensities were measured by an ionization chamber filled with a gaseous mixture (15% argon and 85% nitrogen) and with 100% argon, respectively. The k^3 weighted EXAFS was extracted by the method according to Tanaka et al. [10], and Fourier transformed. As a reference, α-quartz type germanium oxide (Wako Pure Chemical Industries Ltd., 99.9999%) was used.

In order to test the acidic property, double-bond isomerization of 1-butene was carried out by the pulse method under differential conditions (conversion $< 10\%$). After pretreatment of the catalyst at 673 K, 1.3 cm^3 of 1-butene was injected at 393 K. The products were analyzed by a VZ-7 column. The activity was calculated from the amount of yielded 2-butene (mol) × flow rate of carrier gas (m^3 h^{-1})/surface area of catalyst (m^2). The infrared (IR) spectrum was recorded by a JASCO FT/IR-5300 spectrometer in an in situ cell on the disk (1 cm in diameter) molded from 7 mg of the sample powder.

3. Results and discussion

An example of the change of weight during the CVD operation is shown in fig. 1. The weight gain was observed with the introduction of germanium alkoxide vapor on alumina. This shows that the deposition readily proceeded. The reaction between the alkoxide and surface was analyzed for the CVD of silicon alkoxide [5], and the similar reaction is supposed for the germanium alkoxide, i.e. $Ge(OCH_3)_4$ + surface site → anchored alkoxide $Al–O–Ge(OCH_3)_n$ $(0<n<3)$ + such gaseous products as dimethyl ether and methanol. Since the deposited material was thus considered to contain the organic residue, the sample was calcined at 673 K in the presence of 27 kPa of oxygen in order to obtain the germanium oxide without the organic residue. The weight was almost unchanged at 673 K after the quick decrement by the contact with oxygen. This shows that the stable oxide was obtained by decomposition of the anchored alkoxide. We assumed that the calcined material had the composition of GeO_2, and the loading was determined on the basis of gravimetry.

In order to clarify the change of surface area by the CVD, fig. 2 shows the BET surface area divided by the weight of alumina support (not by the weight of the sample). The surface area was kept constant in the range of loading below 30 wt%, and a small decrement was observed above 30 wt%. This indicates that the depos-

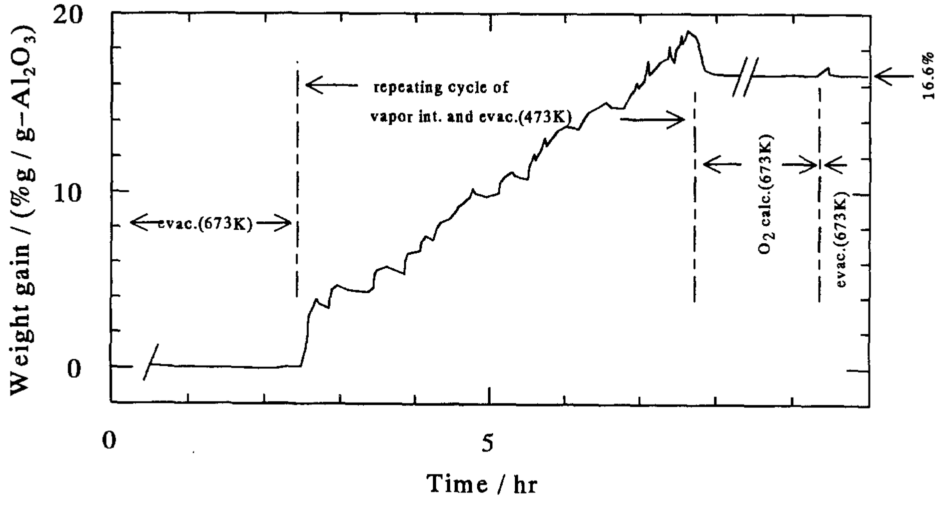

Fig. 1. Weight change during the preparation of GeO_2 (16.6 wt%)/Al_2O_3.

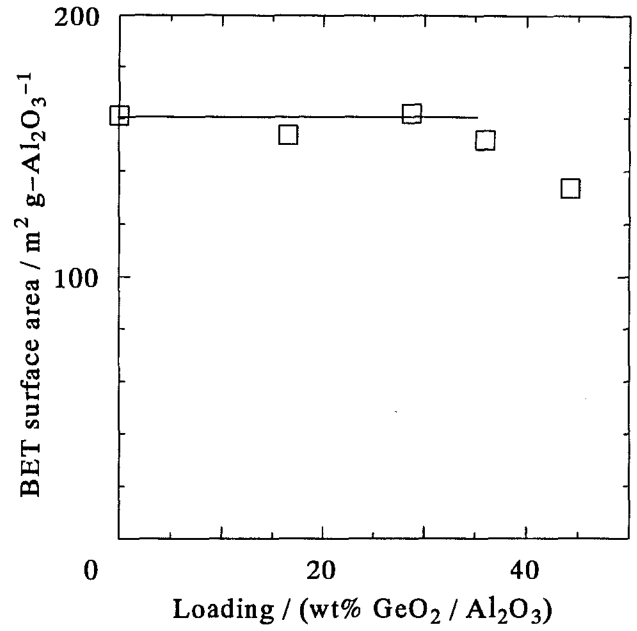

Fig. 2. BET surface area of GeO_2/Al_2O_3.

ited germanium oxide did not block the pores at the loading <30 wt%, but a small fraction of the deposited material blocked the pores at >30 wt%.

Benzaldehyde is adsorbed on alumina with high surface concentration (1.8 molecules per 1 nm^2 of surface), and readily converted into benzonitrile by the contact with ammonia. Since the saturation of surface with benzaldehyde is estimated from this concentration, it is suggested that benzaldehyde was adsorbed both on the external surface of the particle and the inner surface of the mesopores. By contrast, almost no adsorption of benzaldehyde was observed on silicon and germanium oxides [8,9]. Therefore, we defined the coverage of the alumina surface by silicon or germanium oxide as follows: coverage of modified sample = 1 − alumina exposed surface area/BET surface area (SA), where the alumina exposed surface area = yield of benzonitrile (BN) measured by the BAT method on the modified sample/BN on the unmodified alumina × SA of the unmodified alumina. We also defined the surface concentration of deposited germanium atoms as follows: germanium concentration = number of the deposited germanium atoms, calculated from the gravimetry/SA. As shown in fig. 3, the coverage by GeO_2 increased linearly with increasing germanium concentration. This linear relationship agreed well with that observed for the coverage by SiO_2 [2]. From this relationship, the deposited layer was estimated to cover 1 nm^2 of the alumina surface with 13 atoms of germanium or silicon. Because the concentration of aluminum cations on the surface of alumina was 9–15 nm^{-2} [11], ultra thin layers of germanium and silicon oxides consisting of 1 : 1 of Al–O–T (T = Ge or Si) bonds, namely the mono-

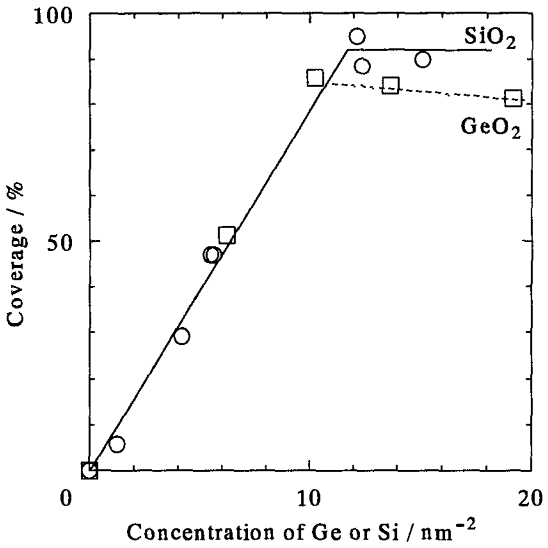

Fig. 3. Coverage by GeO_2 (□) and SiO_2 (○) on alumina surface measured by BAT method.

atomic layers, were suggested. The coverage was saturated at ca. 85% above 10 nm^{-2} of the germanium concentration. This shows that both the surfaces outside and inside the alumina particle were almost completely covered by the mono-atomic layer. The constant BET surface area at the loading below 30 wt%, which corresponded with <13 nm^{-2} of the germanium concentration, shows that the mono-atomic layer did not block the pores.

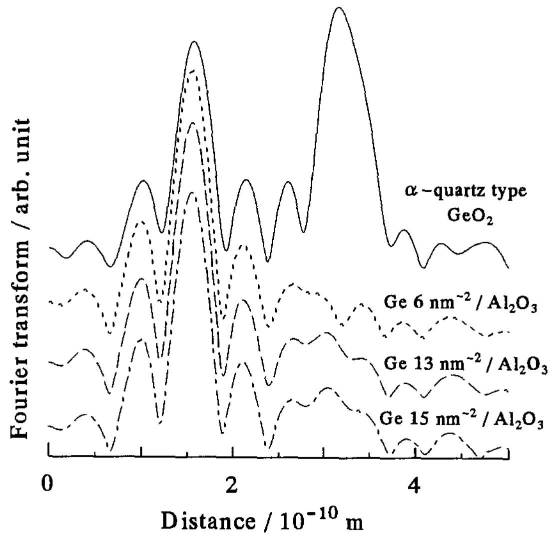

Fig. 4. Fourier transform of EXAFS. The distance was shown with the Ge–Ge distance of α-quartz type GeO_2 (3.2×10^{-10} m) as a reference.

The Fourier transform of EXAFS shows the obvious difference in the structures between the deposited GeO_2 layer and the α-quartz type GeO_2 (fig. 4). The α-quartz type GeO_2 showed both the Ge–O and Ge–O–Ge bonds, whereas the GeO_2 layer revealed only the Ge–O bond. This shows that the deposited GeO_2 formed the ultra thin layer, but not the bulk oxide.

We suppose that a strong interaction and structural similarity between the substrate surface and deposited material forms the homogeneous mono-atomic layer. In fact, the strong bonding between the silica monolayer and alumina was shown by the thermal stability of silica monolayer on alumina at a quite high temperature, 1493 K [12]. Probably, both the silicon and germanium oxide layers had strong bondings and structural similarities with the alumina surface, resulting in the formation of an ultra thin layer. However, the BAT experiments show that the saturated coverage by GeO_2 on alumina, ca. 85% was less than ca. 90–95% of coverage on SiO_2/Al_2O_3 (fig. 3). This seems to be due to the relatively low structural fitness of GeO_2 to Al_2O_3 than SiO_2.

On GeO_2/Al_2O_3, a sharp peak at 3673 cm^{-1} and a broad one at about 3600 cm^{-1} were observed in the hydroxyl region of the IR spectrum (fig. 5, A); a

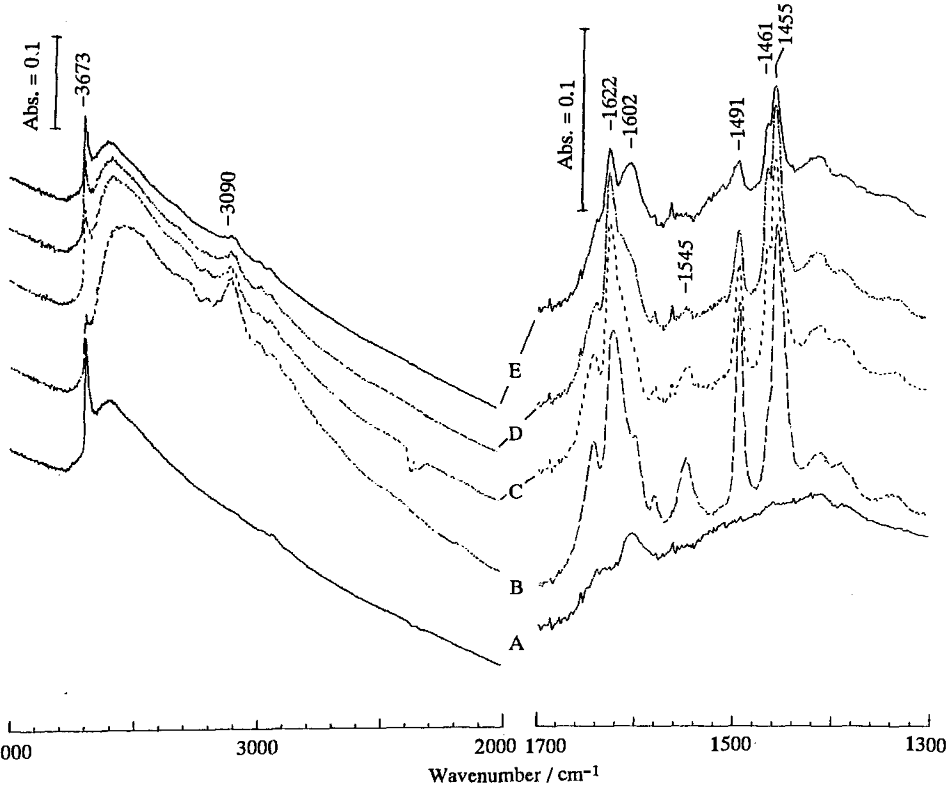

Fig. 5. IR spectra of GeO_2/Al_2O_3 (13 Ge nm^{-2}) after the evacuation at 673 K (A), after the adsorption of pyridine at 373 K followed by the evacuation at 373 (B), 473 (C), 573 (D) and 673 K (E).

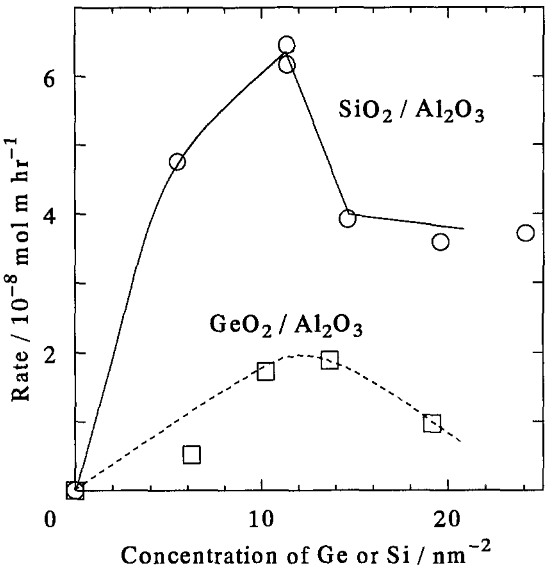

Fig. 6. Activity for double-bond isomerization of 1-butene measured by pulse technique at 393 K over GeO_2/Al_2O_3 (□) and SiO_2/Al_2O_3 (○) pretreated at 673 K.

species like Al–O–Ge–OH is suggested. No adsorptions by Al–OH (3585, 3677, 3730 and 3763 cm^{-1}) were observed, which confirms that the surface was covered almost completely by GeO_2. Neither were adsorptions due to the methoxy group (2800–3000 cm^{-1}) observed; this confirms the absence of organic residue. Alumina had only Lewis but not Brønsted acidity, whereas the spectrum of pyridine over the germanium oxide layer shows both species adsorbed on the Lewis and Brønsted acid sites at 1461 and 1545 cm^{-1}, respectively (fig. 5, B–E). The activity for the isomerization from 1- to 2-butene was generated on both oxide layers of silicon and germanium (fig. 6). The activity showed the maximum at 10–14 nm^{-2} of the concentration of germanium or silicon atoms, where the mono-atomic layers covered 80–95% of the surface. These observations indicate that the Brønsted acid sites active for the isomerization were formed on the mono-atomic layers and passivated by topping one-more layer. In the case of silica monolayer, the assumed species M–O–Si–OH (M = Al, Ti or Zr) possessed the Brønsted acidity due to the structure which was strained by the network of Si–O–Si developed on the support oxide [5]. Therefore, the assumed species Al–O–Ge–OH is also speculated to possess the Brønsted acidity.

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