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Preparation of titania-impregnated silica aerogels and their application to removal of benzene in air

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Silica–titania aerogels were prepared by impregnating titanium tetraisopropoxide modified with acetylacetone into a silica alcogel followed by supercritical drying. The effects of the impregnation conditions, the supercritical drying medium (ethanol, 2-propanol or CO_2) and the calcination temperature on the homogeneity of the aerogel and the nature of the impregnated titania were investigated. Aerogels prepared in this way had large specific surface areas and maximum titanium contents of *ca.* 32 at%. Ethanol and CO_2 dried samples were homogeneous, but 2-propanol dried samples were inhomogeneous because of the extraction of impregnated titania. Ethanol and 2-propanol dried samples contained anatase particles of <10 nm agglomerated into clusters of 100–300 nm size, whereas CO_2 dried samples contained amorphous titania. Their application to the removal of benzene from air was attempted. Ethanol dried samples possessed excellent benzene adsorption capacities and the adsorbate could be decomposed to CO_2 by photocatalytic reaction.

1 Introduction

Inorganic aerogels, which are generally prepared by supercritical drying of sol–gel derived alcogels, are known as highly porous materials.[1,2] Since they have larger specific surface areas and larger porosities than conventionally dried inorganic gels, their application as catalysts, catalyst supports or adsorbents has been the subject of much recent interest.

Recently, silica–titania aerogels have received significant attention as high performance catalysts because of their larger specific surface areas and higher porosities than conventional silica–titania. Baiker and co-workers[3–7] reported a series of investigations on the preparation, characterization and application of titania–silica aerogels to olefin oxidation catalysts. They focused mainly on increasing the yield of surface Si–O–Ti bonds and studied the effects of the preparation parameters, *i.e.* titanium content, pre-hydrolysis of silicon alkoxide and supercritical drying medium, on their formation and other structural properties. They revealed that supercritical CO_2 dried (313 K) aerogels were amorphous, even after calcination at 873 K, whereas 2-propanol dried aerogels (533 K) contained anatase. The former showed a higher occurrence of surface Si–O–Ti bonds and better performance in olefin oxidation than the latter.

We have previously demonstrated the preparation of silica–titania aerogels with controlled microstructure by impregnating titanium alkoxide modified with acetylacetone (TPAA) into silica alcogels followed by alcohol supercritical drying in an earlier paper.[8] This method uses a simplified sol–gel process and has the advantage of controlling the microstructure of the silica–titania binary aerogel, because the microstructure of the resulting aerogel can be controlled by first controlling that of the silica alcogel. We demonstrated the preparation of transparent silica–titania aerogels containing 30 at% titanium with large specific surface area (over 650 $m^2 g^{-1}$) and low density (0.2 $g cm^{-3}$). Titania (anatase) aggregates were found on the surface of the silica matrix by microscopic observation. Thus, these aerogels were expected to function as both adsorbent and photocatalysts. These features could be suitable for the removal of toxic chemicals, such as volatile organic components (VOCs) in the atmosphere, by both adsorption and decomposition. If these aerogels can be used as monoliths or films, filtration of suspended particle matter (SPM) may also be expected.

In a previous paper,[8] we used only ethanol (EtOH) as the supercritical drying medium and mainly focused attention on the silica matrix of the binary aerogels. In this work, we concentrated on titania and investigated the effects of the preparation parameters, such as impregnation conditions, supercritical drying medium and calcination temperature, on the states of titania. We also evaluated the ability of the silica–titania aerogels for removal of VOCs in experiments involving benzene as a typical VOC. The adsorption capacity of aerogels for benzene and their photocatalytic activity for benzene decomposition were also measured.

2 Experimental

2.1 Preparation of silica–titania aerogels

Silica alcogels (30 mm diameter and 10 mm thickness) were generated by mixing tetramethoxysilane (TMOS), water, methanol and NH_3 catalyst in the molar ratio of 1 : 4.1 : 7.2 : 0.01. They were aged at 333 K for 2 d and then soaked for 24 h in excess 2-propanol (2-PrOH) for solvent exchange. TPAA was prepared by mixing titanium tetraisopropoxide (Tokyo Kasei) with acetylacetone (molar ratio = 1 : 1), as shown in eqn. (1), immediately prior to use and then diluted with 2-PrOH.

$$Ti(O^iPr)_4 + acacH \rightarrow Ti(O^iPr)_3(acac) + {}^iPrOH \qquad (1)$$

^{i}Pr, acacH and acac denote isopropoxyl groups, acetylacetone (enol form) and acetylacetonato groups, respectively. Silica alcogels were soaked in the TPAA solution for 24 h under inert conditions to combine TPAA on surface silanol groups of the alcogel. Although silanol groups can react with both isopropoxide and acetylacetonato groups, Sanchez *et al.* confirmed that isopropoxyl groups react first.[9]

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TPAA-impregnated alcogels were then supercritically dried using EtOH (553 K, 11.0 MPa), 2-PrOH (553 K, 7.5 MPa) and CO_2 (353 K, 16.0 MPa). The EtOH supercritical drying procedure was described in our previous work.[8] Supercritical drying with 2-PrOH was performed as with ethanol, except for the operating pressure. CO_2 supercritical drying was performed at 353 K and 16.0 MPa using a JASCO supercritical extraction system (SFC/E 201), as described elsewhere.[10] The resulting aerogels were heat treated at 773–1073 K for 2 h in air in order to remove any remaining organics.

2.2 Characterization of aerogels

The apparent density was calculated from the geometrical size and weight of the sample disk. Then the outer surface of the sample disk was carefully shaved off and the inner portion (about 10 mm diameter and 5 mm thickness) of the sample was separated. Both the inner portion and the shaved outer portion of the sample were then ground in an agate mortar. To evaluate the extent of TPAA impregnation, the titanium contents of both the outer and inner portions were determined with an X-ray fluorescence analyzer (SEIKO SEA2010). Inner samples were used for the other measurements. Mesopore size distributions (by the BJH method[11]) and BET specific surface areas were determined by nitrogen adsorption using a Coulter SA3100 analyzer (Beckmann-Coulter Co. Ltd.) after evacuating the sample for 24 h at 423 K. X-Ray diffraction analysis (XRD) was performed using a Rigaku RAX analyzer (Cu-Kα, 40 kV, 30 mA). Diffuse reflectance UV-Vis spectra were measured using a JASCO V-570 spectrometer with an ISN-470 integrating sphere reflectance attachment. Microstructures were observed by scanning electron microscopy (SEM) and transmittance electron microscopy (TEM) with an energy dispersive X-ray spectroscopic analyzer (EDS), as described in our previous work.[8,10] Infrared spectra (IR) were measured using the KBr tablet method, as described in our previous work.[10]

2.3 Adsorption and photocatalytic decomposition of benzene

Adsorption and desorption isotherms of benzene vapor on aerogel samples were measured at 303 K by the volumetric method using a BELSOAP 18 automatic vapor adsorption analyzer (Nippon Bell Co. Ltd.). The ground samples were initially evacuated at 423 K for 12 h prior to measurement. The photocatalytic activity for the decomposition of benzene in air was evaluated using the flow system illustrated in Fig. 1(a). We preferred this system since, as our samples showed high benzene adsorption capacities, it was difficult to compare their photocatalytic activity with conventional titanium oxide under the same initial concentration of benzene using a batch system. The apparatus and photoreacter (Pyrex; inner volume 18.2 cm^3) were designed with reference to the work of Yamazaki and co-workers.[12,13] A blacklight bulb of 4 W was located inside the reactor. Humidified air, prepared by bubbling air through distilled water, was mixed with 500 ppmv (parts per million by volume) benzene vapor (balanced nitrogen, Takachiho Chemical) and the benzene concentration was adjusted to 100 ppmv using a by-pass line, as shown in Fig. 1(a). Aerogel samples (0.2 g) or conventional titania (P-25, Degussa) (0.06 g) were mixed with 20 g glass beads (0.5 mm in diameter) and then placed in the photoreactor. The reactor was maintained at 333 K throughout the run using a heater and flowing air. Before irradiation, the benzene-containing air was allowed to flow through the photoreactor until the inlet and outlet concentrations became identical. During irradiation, the benzene concentration was monitored every 5 min by gas chromatography. A Shimadzu GC-9A FID model with PEG-20M column packings supplied by G-L Science was used.

The batch-type apparatus using the same photoreactor [Fig. 1(b), the volume for gas circulation without the by-pass is 91.3 cm^3] was used to demonstrate the complete removal of benzene using our samples. In this run, 50 mg of ground sample was used in the same way as the flow-type measurements. Humid air containing 1500 ppmv of benzene was introduced into the reactor (the by-pass was closed) and the benzene concentration was monitored. The concentration of CO_2 generated by the decomposition of benzene was measured gas chromatograpically (Shimadzu GC-12A TCD model with activated carbon column packings) during irradiation.

3 Results and discussion

3.1 Impregnation

The characteristics of the samples prepared in this work are listed in Table 1. Impregnations using various TPAA concentrations were performed (no. 3–6 in Table 1). The titanium contents of the inner and outer parts of the gel sample (*ca.* 10 mm diameter, 5 mm thickness in the center of the gel disk)

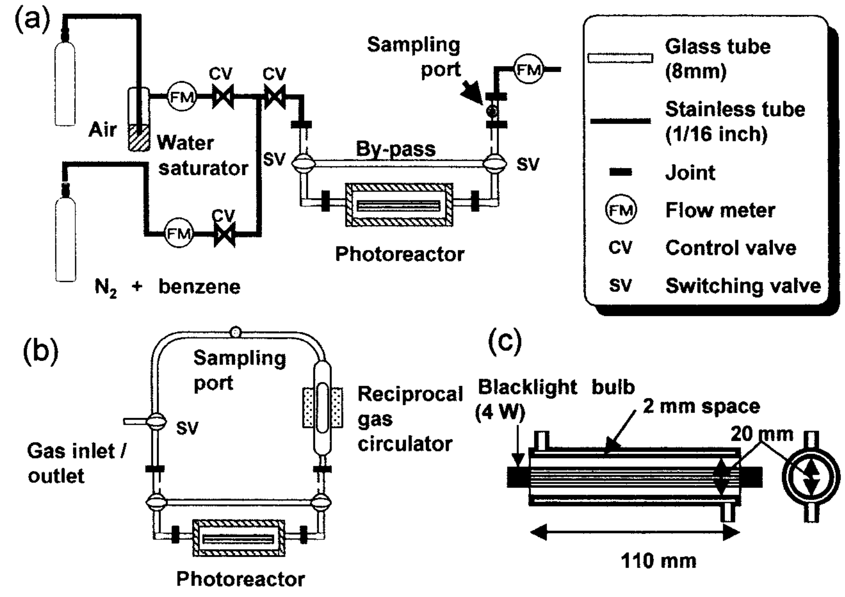

Fig. 1 Systems for evaluating photocatalytic decomposition and removal of benzene. (a) Flow system, (b) batch system and (c) details of the photoreactor.

Table 1 Characteristics of the samples prepared inthis work

Sample			Supercritical drying conditions								
No.	Name[a]	TPAA content of impregnating solution/mol dm^{-3}	Medium	P/MPa	T/K	Calcination temperature/K	Linear shrinkage (%)	Apparent density/ g cm^{-3}	Specific surface area/m^2 g^{-1}	Peak pore size/nm	Ti content[b] (outer/inner) (at%)
1	STC	1.24	CO_2	16	353	—	3.3	0.220	573	17.9	33.0/32.4
2	STCH	1.24	CO_2	16	353	773	9.7	0.199	699	19.6	34.0/32.4
3		2.56[c]	CO_2	16	353	773	18.0	0.273	702	21.6	36.0/32.5
4		0.62	CO_2	16	353	773	6.0	0.191	775	21.6	27.3/20.8
5		0.31	CO_2	16	353	773	4.0	0.162	830	19.6	23.5/8.7
6		0.155	CO_2	16	353	773	4.4	0.148	887	17.9	14.8/5.0
7		1.24	CO_2	16	353	873	15.9	0.241	615	21.6	32.7[d]
8		1.24	CO_2	16	353	973	16.6	0.260	535	21.6	29.9[d]
9		1.24	CO_2	16	353	1073	16.7	0.274	452	21.6	29.9[d]
10	STEt[e]	1.24	Ethanol	11	553	773	2.4	0.213	649	11.0	23.4[d]
11	STEtH	1.24	Ethanol	11	553	773	9.7	0.210	757	17.9	27.4/30.1
12	STiPr	1.24	2-Propanol	8	553	773	0.1	0.186	530	11.3	23.8/31.8
13	STiPrH	1.24	2-Propanol	8	553	773	3.3	0.183	717	15.4	24.0/34.7
Ref.	SCH	—	CO_2	16	353	773	6.6	0.143	967	15.7	—

[a]S and ST denote silica and silica–titania, respectively. C, Et and iPr indicate the supercritical drying medium: CO_2, ethanol or 2-propanol, respectively. H is used to indicate samples calcined at 773 K. [b][Ti]/([Si]+[Ti]). [c]Without dilution. [d]Evaluated without dividing the gel sample into inner and outer parts. [e]Prepared in our previous work.[8]

were different, especially at lower concentrations of TPAA impregnation (no. 4–6). This indicates that impregnation is not complete in the inner section of the sample. These results were independent of the amount of TPAA solution. Therefore, the driving force for penetration seems to depend on the concentration of TPAA. Impregnation was almost completed at higher concentrations of TPAA, but severe shrinkage by syneresis was observed when neat TPAA was used (sample no. 3). A TPAA solution of 1.24 mol dm^{-3} was therefore used for the remainder of the study. At this concentration, homogeneous impregnation was achieved without shrinkage.

3.2 Drying media and heat treatment

The supercritical drying medium has a significant effect on the microstructure of impregnated titania. STCH, STEtH and STiPrH (Table 1) were made from the same TPAA-impregnated alcogels using CO_2, EtOH and 2-PrOH, respectively. Extraction of the impregnated titanium component from the gel was observed when an alcohol was used as the drying medium, and a non-uniform surface appeared, especially in STiPr and STiPrH. We previously confirmed that dissolution of the silica matrix was low during supercritical drying when EtOH, 1-propanol, 2-PrOH or CO_2 were used as the drying medium (shown in ref. 10, except for the case of 2-PrOH). The differences between EtOH and 2-PrOH dried samples would depend on the affinity for TPAA bound to silica matrix. The lower titanium content of STEt samples prepared in our previous work,[8] compared to that of STEtH, may be caused by exceptional extraction. Titanium depletion was hardly observed with CO_2 dried samples. Their titanium contents were a little higher than those of alcohol dried samples.

XRD patterns of aerogel samples [Fig. 2(a)] indicated the existence of anatase in both STEtH and STiPrH, but STCH was amorphous. Uncalcined samples showed similar diffraction patterns. The influence of the calcination temperature on the XRD patterns was evaluated for CO_2 dried samples (no. 2, 7, 8 and 9 in Table 1). Even after heat treatment at 1073 K, the CO_2 dried sample retained amorphous states as revealed by XRD analysis [Fig. 2(b)]. These results are similar to those of Baiker *et al.*,[3] even though the titanium content of our aerogels was much higher than theirs (*ca.* 20 at%) and titanium aggregation could be expected. Using our impregnation method, we anticipated that titania would be so highly dispersed in the silica matrix as to overcome the aggregation and crystallization problems during calcination.

3.3 Microstructure and spectroscopic analysis

Fig. 3 shows diffuse reflectance UV-Vis spectra of STEtH, STiPrH, STCH and conventional pure anatase (TP-2, Fuji Titan Corporation; mean particle size 44 nm). The SCH sample was highly transparent and showed no absorbance in this wavelength region. STEtH, STiPrH and STCH samples

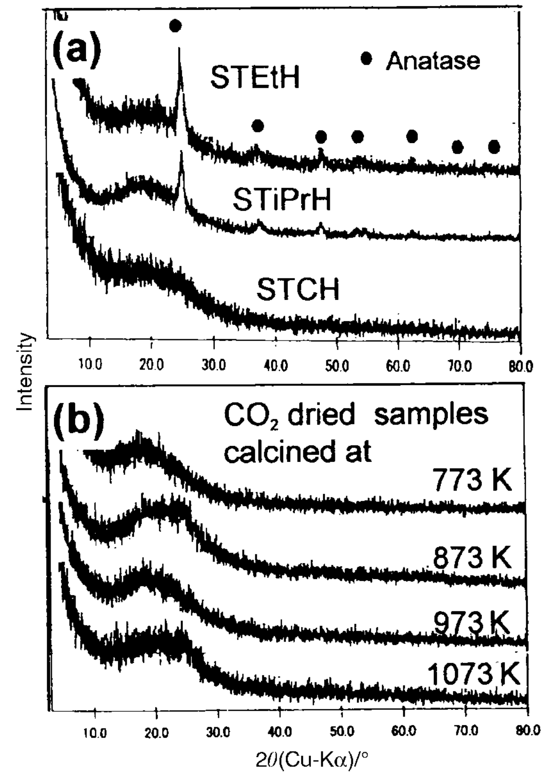

Fig. 2 XRD patterns of silica–titania aerogels: (a) effect of the supercritical drying medium and (b) effect of the calcination temperature on CO_2 dried samples.

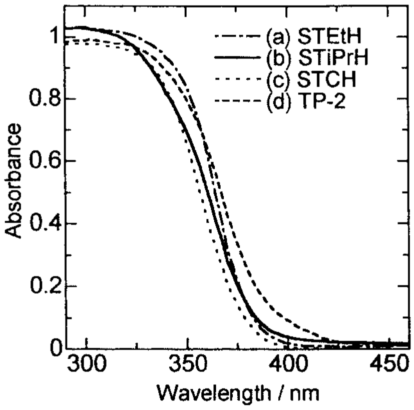

Fig. 3 Diffuse reflectance UV-Vis spectra of (a) STEtH, (b) STiPrH, (c) STCH and (c) conventional anatase powder (Fujititan TP-2, mean crystalline size 44.2 nm). Baselines were corrected for comparison.

showed similar spectra to TP-2, but the absorption band edge position was slightly different in each case (approximately 385 nm for STEtH and STiPrH, 380 nm for STCH, 390 nm for TP-2). Bulk crystalline anatase TiO_2 showed the absorption band edge at 390 nm corresponding to the bandgap (3.18 eV) in its semiconductor properties, and a spectral blue shift was observed for fine anatase (*ca.* 20 nm) due to size quantization effects.[14] The spectral band edges of the STEtH and STiPrH samples, which contained anatase (see Fig. 2), corresponded to that of anatase with a mean particle size of 8.5 nm.[14] Thus, the size quantization effect in these spectra helps provide strong evidence for the existence of fine anatase particles in the silica matrix.

SEM micrographs of STiPr, STC and STCH samples are shown in Fig. 4. STiPrH, STEt and STEtH exhibit similar microstructures to STiPr (STEt micrographs were shown in our previous work[8]). The microstructure of the silica matrix of these samples is similar to that of the STCH samples (not shown). Aggregates (100–300 nm) were found on the surface of the silica matrix for both STiPr and STCH samples, but the surface of the STC sample is comparable to those of SCH samples.

TEM observations were performed on both STiPrH and STCH samples. Aggregates with a different appearance from the matrix were found in STiPrH samples and their size was similar to the aggregates seen in the SEM micrographs. These aggregates consisted of fine particles about 10 nm in size. Elemental analysis of these aggregates by EDS indicated that they contained more titanium than the matrix [see Fig. 5(a)]. Similar aggregates were observed in STEt samples.[8] The aggregates were also observed in CO_2 dried samples, and their titanium content was a little higher than the matrix, but the difference between the aggregates and the matrix was much smaller than for the alcohol dried samples [Fig. 5(b)].

IR measurements were performed to estimate the extent of Si–O–Ti bonding in the aerogels. An absorption shoulder at 945 cm^{-1}, which overlapped with the absorption band due to Si–OH stretching[16] around 970 cm^{-1}, was seen for STC samples. The adsorption band was assigned to the ν(Si–O–Ti) vibration which was reported to appear at 940–950 cm^{-1} for silica–titania binary gels.[3,15] This shoulder almost disappeared for the calcined samples (STCH). The spectra of other samples were similar to that of SCH, indicating that there was little Si–O–Ti bonding.

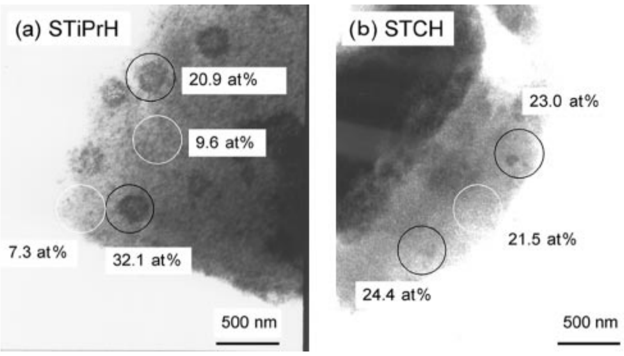

Fig. 5 TEM photographs with local titanium content analysis ([Ti]/[Si+Ti], at%) by EDS. (a) STiPrH and (b) STCH. Samples were grained and directly sputtered onto carbon-supported copper mesh. Black and white circles denote estimated titanium rich regions and the silica matrix, respectively.

We conclude from our microscopic observations and spectroscopic results that titanium compounds impregnated into alcogels disperse in such a way that the number of Si–O–Ti bonds might be increased. During alcohol supercritical drying, the titanium compounds bound to the silica matrix were extracted from the matrix and rearranged into titania aggregates. There was no remarkable difference between STEt and STiPr from the viewpoint of microstructure. Because supercritical CO_2 drying is performed at lower temperature and because CO_2 scarcely reacts with titanium compounds, their extraction from the silica matrix did not progress so efficiently. Titania tends to aggregate and crystallize upon heat treatment because of its poor glass-forming properties. Aggregation might occur during heat treatment *via* surface or volumetric diffusion but silica matrices, in general, seem to retard the aggregation of titania. The titanium content in the aggregates on the surface of CO_2 dried samples was lower than that of alcohol dried samples. These results might be attributed to the difference in the rate of the dissolution–reprecipitation process during supercritical drying using CO_2 and alcohol.

3.4 Adsorption and photocatalytic decomposition of benzene

Adsorption/desorption isotherms of STEtH, STCH and SCH and of conventional crystalline titanium (P-25, Degussa) were determined by a volumetric method, as shown in Fig. 6. Aerogel samples showed larger adsorbtion capacities than

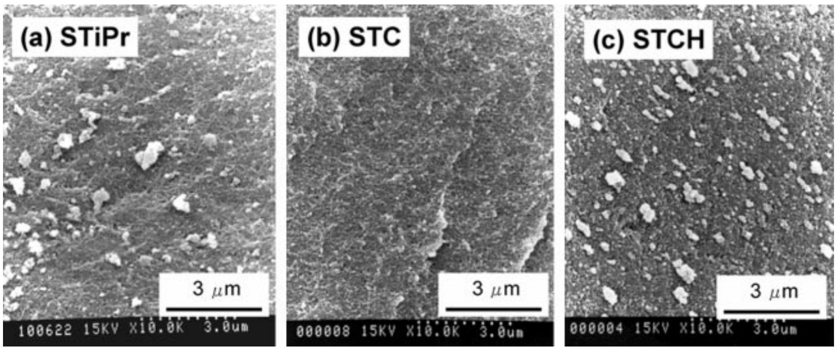

Fig. 4 SEM micrographs of (a) STiPr, (b) STC and (c) STCH. Samples were platinum coated by ion sputtering. Magnification is 10 000.

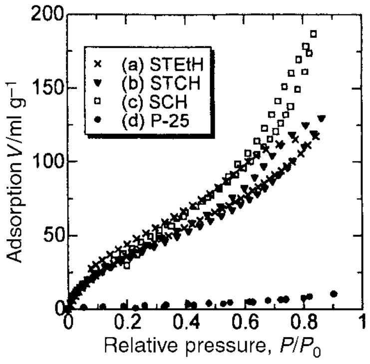

Fig. 6 Adsorption/desorption isotherms of benzene vapor on (a) STEtH, (b) STCH, (c) SCH and (d) conventional crystalline titania (P-25 Degussa) at 303 K measured by a volumetric method. P_0 is the saturated vapor pressure of benzene at this temperature (119.3 mmHg).

P-25. The adsorption isotherms were characterized as type II according to the IUPAC classification, which indicates BET-type multilayer adsorption of benzene. A small hysteresis effect was observed in these isotherms. Silica aerogel (SCH) shows the largest adsorbtion capacity. This may be a result of SCH having the largest specific surface area and the most porous structure of all the samples studied here. The adsorption capacities of STEtH and STCH were comparable, and the contribution of solid acidity originating from Si–O–Ti bonds expected for STCH samples was was not clear.

The photocatalytic activity was evaluated by conversion of benzene (100 ppmv) contained in humid air in a flow (non-circulating) system. In order to eliminate adsorption effects, the photocatalytic reaction was started only after the adsorption of benzene had reached its equilibrium state (see Experimental section). Fig. 7 shows the relationship between the gas flow rate and conversion of benzene. We had anticipated deactivation of the catalysts, since calcined silica aerogels are known to shrink under humid conditions. However, the catalytic performances of the samples used were stable under the present reaction conditions. The STEtH sample containing anatase showed higher activity than the amorphous STCH sample. This result is in agreement with the observed trend on the decomposition of toxic chemicals by titania: it is widely known that anatase has the best performance, while amorphous titania is practically inert.[17] However, although our samples contained highly dispersed fine anatase, the performance did not reach that of P-25 when STEtH containing the same amount of titania was used. The limited diffusion of benzene vapor into the small pores in the aerogel probably influences the performance efficiency. Tanaka *et al.* reported that, upon comparing the photocatalytic performance *versus* specific surface area in the decomposition of trichloroethylene and monochloroacetic acid, anatase with larger crystallites was superior to smaller crystallites.[17] This effect might be antagonistic to the increase in surface area and size quantization effect induced by high dispersion of titania.

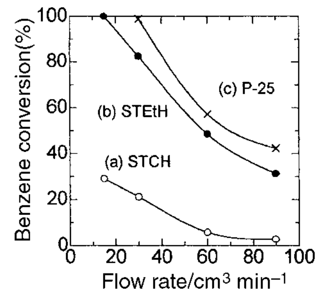

Fig. 7 Photocatalytic conversion of benzene *versus* flow rate of air containing 100 ppmv of benzene at 333 K by (a) STCH (0.2 g), (b) STEtH (0.2 g) and (c) P-25 (Degussa) (0.06 g).

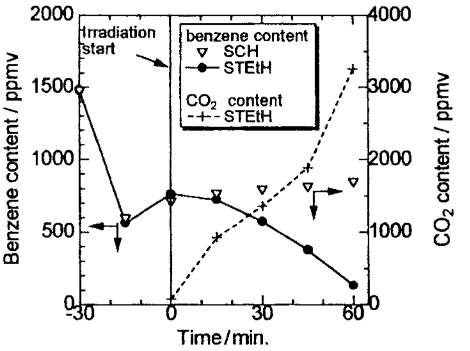

Fig. 8 Removal of benzene from air containing 1500 ppmv of benzene in a 91.3 cm³ glass reactor by STEtH and STC samples. The content of CO_2 produced by photocatalytic decomposition of benzene was monitored in the case of STEtH.

At present, TiO_2-impregnated SiO_2 aerogels appear suitable for use as adsorbents with photocatalytic properties. In Fig. 8, the adsorption of benzene on STEtH aerogels in the absence of irradiation followed by photocatalytic decomposition of the adsorbates is demonstrated using a circulating system [see Fig. 1(b)]. The same measurement was performed using SCH aerogels for comparison. After irradiation, the degree of removal of benzene by the STEtH sample was continuously increased and benzene adsorbed on the silica–titania aerogels was confirmed to be decomposed to CO_2. On the other hand, no formation of CO_2 was observed with SCH samples.

5 Conclusions

The preparations of silica–titania aerogels using an impregnation method was investigated under various impregnation conditions, supercritical drying media and calcination temperatures. The aerogels so-prepared had large specific surface areas and high titanium contents. From the point of view of aerogel homogeneity, ethanol was more appropriate than 2-PrOH. Both EtOH and 2-PrOH dried samples contained crystalline anatase (under 10 nm), whereas CO_2 dried samples were amorphous. These trends are concordant with the work of Baiker *et al.*[3] EtOH dried samples showed excellent capacities for the adsorption of benzene. Furthermore, these samples are able to photocatalytically decompose benzene to CO_2.

STEtH functions as both an adsorbent and a photocatalyst. Thus, it has the potential to be used as an adsorbent with a self-cleaning function. It can adsorb VOCs in the dark and decompose them in the presence of light without the necessity of supplying power. Improvement of the photocatalytic performance and gas diffusion should be investigated in future studies.

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