The adsorption, thermal reactions, and photochemistry of benzene on powdered TiO$_2$ have been investigated using Fourier-transform infrared spectroscopy. Benzene is adsorbed with its $\pi$ electrons interacting with the surface Ti$^{4+}$ ions, and is stable even when the TiO$_2$ temperature is increased to 400 $^\circ$C. However, it is subject to thermal decomposition to H$_2$O(g), CO(g) and CO$_2$(g) in the presence of O$_2$ and the dissociation occurs below $\sim$225 $^\circ$C. With the aid of an adsorption study of phenol and iodobenzene, it is found that phenoxy groups are generated on the surface in the photooxidation of benzene on TiO$_2$ and the amount greatly increases in the presence of H$_2$O or O$_2$. Other surface products containing carbonyl or carboxylate groups are produced as well for benzene photoreaction in O$_2$. The present in situ study shows that the products extracted using solvents from TiO$_2$ catalysts after photooxidation of benzene in previous investigations may not reveal the real products formed on the surface during photolillumination processes.

Introduction

The use of TiO$_2$ as a photocatalyst has been widely investigated for the degradation of a large number of organic molecules. As TiO$_2$ absorbs photons with energy larger than its band gap ($\sim$3.2 eV), the electrons in the valence band can be excited to the conduction band, leaving holes behind in the valence band. The photogenerated electron–hole pairs may diffuse to the surface where they can initiate oxidation and/or reduction reactions of organic molecules.

Benzene is one of the most widely used solvents and may be carcinogenic. Its breakdown to environmentally innocuous compounds by a photochemical process using TiO$_2$ has been extensively studied. These studies were performed with the catalyst in benzene-containing solutions or in contact with benzene vapor. Fujihira et al. conducted, after photoirradiation of aqueous benzene solutions under air, GC (gas chromatography) analysis of the products obtained by acidifying the photoirradiated solutions, then extracting with ether, and finally concentrating under a reduced pressure. They observed phenol and biphenyl. However in a GC/MS (mass spectrometry) analysis of the products obtained from acidification and extraction with CH$_3$Cl$_2$ of photoirradiated aqueous benzene solution in the presence of O$_2$, Turchi et al. observed the formation of phenol and benzoquinone. In the photooxidation of a deaerated aqueous solution of benzene in the presence of Ag$^+$ ion as an electron acceptor, Hashimoto et al. observed the products phenol, biphenyl, hydroquinone, catechol and muconic acid in the gas phase and liquid phase by MS and GC/LC after consuming 1 mmol of Ag$^+$. On the other hand, after photooxidation catalyzed by TiO$_2$ in contact with a gaseous mixture of benzene, oxygen and water, Jacoby et al. observed, using high performance liquid chromatography (HPLC), phenol, malonic acid and hydroquinone/benzoquinone in the water extract solution of the catalyst. In a similar extraction procedure using HPLC as well, d’Hennezel et al. observed phenol, hydroquinone and benzoquinone. Meanwhile they suspected the formation of a polymer product having chains of several aromatic rings, similar to the suggestion in Sitkiewitz et al.’s study of benzene photodegradation.

In addition to the exploration of reaction products and intermediates in benzene photodegradation, parameters including the effects of photon flux, temperature and concentrations of benzene, water and O$_2$ on the benzene conversion and reaction rate have been investigated. In the present paper, we study the adsorption, thermal reaction, and photooxidation of benzene on TiO$_2$ by Fourier-transform infrared spectroscopy (FTIR). Since, in the previous studies of the photooxidation of benzene vapor over TiO$_2$, the reaction intermediates or products on the surface were characterized through solvent extraction after the photoprocess, it may not reveal the real adsorbates formed on the surface during the photoreactions. Therefore in the present study of the photooxidation of benzene on TiO$_2$, we focus on the identification of reaction intermediates or products adsorbed on the surface and on the effect of the addition of O$_2$ or H$_2$O by using “in situ” measurements of infrared spectroscopy.

Experimental

The sample preparation of TiO$_2$ powder supported on a tungsten fine mesh ($\sim$6 cm$^2$) has been described previously. In brief, TiO$_2$ powder (Degussa P25, $\sim$50 m$^2$ g$^{-1}$, anatase 70%, rutile 30%) was dispersed in water/acetone solution to form a uniform mixture which was then sprayed onto a tungsten mesh. After that, the TiO$_2$ sample was mounted inside the IR cell for simultaneous photochemistry and FTIR spectroscopy. The IR cell with two CaF$_2$ windows for IR transmission down to 1000 cm$^{-1}$ was connected to a gas manifold which was pumped by a 60 L s$^{-1}$ turbomolecular pump with a base pressure of $\sim$1 $\times$ 10$^{-7}$ Torr. The TiO$_2$ sample in the cell was heated to 450 $^\circ$C under vacuum for 24 h by resistive heating. The temperature of the TiO$_2$ sample was measured by a K-type thermocouple spotwelded on the tungsten mesh. Before each run of the experiment, the TiO$_2$ sample was
heated to 450 °C in vacuum for 2 h. After the heating, 10 Torr O₂ was introduced into the cell as the sample was cooled to 70 °C. When the TiO₂ temperature reached 35 °C, the cell was evacuated for gas dosing. O₂ (99.998%) was purchased from Matheson. Benzene (99.8%, Merck), iodobenzene (99%, TCI) and phenol (98%, Osaka) were purified by several freeze-pump-thaw cycles before introduction into the cell. Pressure was monitored with a Baratron capacitance manometer and an ion gauge. In the photochemistry study, both the UV and IR beams were set at 45° to the normal of the TiO₂ sample. The UV light source used was a combination of a 350 W Hg arc lamp (Oriel Corp.), a water filter, and a bandpass filter with a band width of ~100 nm centered at ~320 nm (Oriel 51650). The photon power at the position of the TiO₂ sample was ~0.24 W/cm² measured in air by a power meter (Molecron, PM10V1). Infrared spectra were obtained with 4 cm⁻¹ resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with dry air. CO₂ resolution by a Bruker FTIR spectrometer with a MCT detector.

Results and discussion

Adsorption of benzene on TiO₂

Fig. 1 shows the infrared spectrum of a TiO₂ surface exposed to 5 Torr of benzene and then evacuated at 35 °C. Absorption bands appear at 1256, 1335, 1478, 1832, 1977, 3032, 3068 and 3089 cm⁻¹. Among them, the three high-frequency peaks are assigned to C–H stretching of adsorbed benzene. The 1478 cm⁻¹ band is related to C–C stretching and C–H rocking; 1335 cm⁻¹ to C–H rocking; and 1256 cm⁻¹ to C–C–C bending and C–H rocking. The 1832 and 1977 cm⁻¹ bands are due to γ₁₀ + γ₁₇ and γ₅ + γ₁₇, respectively in Wilson’s numbering; γ₁₅ and γ₁₀ are related to the torsion mode about the C–C bonds and C–H out-of-plane bending. The sharp band at 1478 cm⁻¹ is the same as the previous observation of benzene on rutile TiO₂ and is ~5 cm⁻¹ lower than the corresponding vibrational mode of gaseous benzene. Suda attributed this red-shift to the interaction of a surface Ti⁴⁺ ion with the benzene ring through the π system. This argument was supported by the NMR study of C₆D₆ adsorbed on monolayer coverage on rutile TiO₂. The values of the effective quadrupole coupling constants suggested that the benzene molecules were adsorbed flat on the surface. In addition to the 1478 cm⁻¹ band revealing the interaction and adsorption configuration of benzene on the surface, the frequencies of γ₁₅ + γ₁₇ and γ₁₀ + γ₁₇, can serve a similar role. In the study of benzene adsorption on zeolites, it was found that the γ₁₀ + γ₁₇ and γ₁₀ + γ₁₇ of adsorbed benzene had frequencies ~20–40 cm⁻¹ higher than those of liquid benzene at 1960 and 1816 cm⁻¹ (ref. 16–18). The blue-shift is attributed to the interaction of benzene with metal cations through the π-electron cloud. In the present study the γ₁₀ + γ₁₇ and γ₁₀ + γ₁₇ of benzene on TiO₂ have frequencies ~17 cm⁻¹ higher than those of liquid benzene, further supporting the type of interaction between the benzene π system and the surface Ti⁺⁺ ions. Similar blue-shifts for ν₁ + ν₁₇ and ν₁₀ + ν₁₇ of benzene on TiO₂ were also observed by Ramis et al. After brief annealing at 500 °C under vacuum for 1 min, it is found that ~10% of benzene still remained on the surface (not shown). The surface hydroxyl stretching range between 3400 and 3800 cm⁻¹ was also checked but the change is small after exposure of benzene to TiO₂ followed by evacuation. However, prior to evacuation, i.e. the TiO₂ was in contact with benzene vapor (more adsorbed benzene in this case), the OH(a) stretching peak intensities decreased noticeably, suggesting that, at higher benzene concentration on the surface, benzene does interact with surface hydroxyl groups.

Thermal reaction of benzene on TiO₂

Figs. (a)–(c) show the infrared spectra taken in the course of heating TiO₂ initially in contact with a mixture of ~30 Torr benzene and ~60 Torr O₂ in a closed cell. Comparing Fig. 2(a) with the gaseous benzene spectrum of Fig. 2(e) obtained by using the same optical conditions of the infrared spectrometer in a separate measurement, it is found that adsorbed benzene contributes significant absorption for the 1479 cm⁻¹ band. All the infrared bands in Fig. 2(a) can be attributed to adsorbed and gaseous benzene in the cell. The amount of surface benzene decreases with temperature, leading to a change of the spectral features. As shown in Fig. 2(b) at 300 °C, the peak at 1479 cm⁻¹ due to adsorbed benzene is no longer observed; instead, gaseous benzene absorption features at 1474, 1482, 1495, 3047 and 3056 cm⁻¹ become more obvious. Furthermore, absorptions at 1574 and 2349 cm⁻¹ grow. Increasing the temperature to 400 °C for 3 min, the 2349 cm⁻¹ band increases significantly in intensity, accompanied by new bands at 2143 and 1413 cm⁻¹ and narrow peaks represented by the 1558 cm⁻¹ band in the region of 1400–1750 cm⁻¹. The 1558, 2143 and 2349 cm⁻¹ bands are identified as H₂O(g), CO(g) and CO₂(g) formed in the gas phase respectively. As the temperature is cooled down to ~35 °C after surface annealing, residual gaseous benzene is adsorbed back on the surface as indicated by the 1479 cm⁻¹ band in Fig. 2(d). Likewise, gaseous water also decreases and is adsorbed on the surface with its characteristic absorption at 1605 cm⁻¹. There are two unidentified absorption bands located at 1413 and 1567 cm⁻¹ in Fig. 2(d) which do not belong to adsorbed water and benzene and are tentatively assigned to carboxylates.

Fig. 1 Infrared spectrum of a TiO₂ surface exposed to 5 Torr of benzene and then evacuated at 35 °C. The spectrum was recorded with 50 scans. The TiO₂ powder used was ~84 mg.
carboxylic acid, implying that benzene may decompose, through carboxylic acid or carboxylate groups, to CO$_2$(g).\textsuperscript{20}

Fig. 4 shows the infrared spectra taken at 35°C before and after annealing at 400°C for 3 min for a TiO$_2$ surface initially in contact with ~30 Torr benzene. The two spectra in Fig. 4 are almost the same, showing that benzene remains intact without O$_2$ at 400°C.

**Photoreaction of benzene on TiO$_2$**

Fig. 5(a) is the infrared spectrum taken after photoillumination of a TiO$_2$ surface initially in contact with 2 Torr benzene, followed by evacuation to show the adsorbed species on the surface. Fig. 5(b) and (c) are infrared spectra taken after the same photolrradiation procedure, but with the TiO$_2$ initially in contact with a mixture of 2 Torr benzene and ~10 Torr O$_2$, and a mixture of 2 Torr benzene and ~0.2 Torr O$_2$. This spectrum has been multiplied by a factor of 0.25. The TiO$_2$ powder used was ~94 mg. All the spectra were recorded with 50 scans at ~35°C.
H$_2$O, respectively. The characteristic benzene peak at 1480 cm$^{-1}$ is present in the three spectra of Fig. 5. In addition, another three common bands appear at 1254, 1488 and 1587 cm$^{-1}$, of which the 1254 cm$^{-1}$ band falls in the C-O stretching frequency range. We thus follow this clue to identify the species responsible for these three bands by investigation of the adsorption of phenol.

The reason to study the adsorption of phenol is that this compound contains a C-O bond and is one of the photo-products in previous benzene photoreaction studies. Fig. 6 shows the infrared spectra taken after phenol adsorption at 35 °C followed by evacuation at the indicated temperatures for 1 min. Peaks appear at 1152, 1164, 1216, 1276, 1288, 1491, 1592, 3033, 3065 and 3616 cm$^{-1}$ in the 35 °C spectrum. The 3616 cm$^{-1}$ band is assigned to the O-H stretching of adsorbed phenol molecules. The 3033 and 3065 cm$^{-1}$ bands are assigned to C-H stretching. All the peaks in the range 1100–1650 cm$^{-1}$ are related to C-C stretching and C-H rocking, but with different extents of contribution of these two modes. Particularly among them, the bands at 1216 and 1288 cm$^{-1}$ also have an O-H rocking component and the band at 1276 cm$^{-1}$ has a C-O stretching contribution.

The band at 1491 cm$^{-1}$ is 6–13 cm$^{-1}$ lower than the corresponding mode of gas-phase phenol molecules, suggesting the type of interaction of the benzene ring with surface Ti$^{4+}$ ions as in the case of adsorbed benzene. However, the broad feature in the range ~3400–3600 cm$^{-1}$ due to the absorption of associated hydroxy groups shows another type of interaction, namely hydrogen bonding. The negative bands between ~3600 and 3800 cm$^{-1}$ indicate that the surface hydroxy groups are involved in the hydrogen bonding to adsorbed phenol. In Fig. 6, the bands at 1288 and 3616 cm$^{-1}$ assigned to absorbed phenol decrease in intensity with increasing temperature. After further heating to 500 °C, absorption bands show their positions at 1255, 1479, 1589 and 3072 cm$^{-1}$. Adsorbed phenol is not present on the surface at this high temperature, as shown by the disappearance of the 3616 cm$^{-1}$ band due to the O-H stretching of phenol. The bands in the 500 °C spectrum are assigned to the modes of surface phenoxy: 1255 cm$^{-1}$ to C-O stretching, 1479 and 1589 cm$^{-1}$ to C-C stretching and C-H rocking, and 3072 cm$^{-1}$ to C-H stretching. Phenol is adsorbed similar to the case of aliphatic alcohols on the surface.

Previous aliphatic alcohol adsorption studies have shown two adsorption forms of molecular alcohol and dissociative alkoxy groups on TiO$_2$ at 35 °C and only alkoxy groups remain on the surface at temperature above 200 °C. There is a common feature in the infrared absorptions of aliphatic alkoxy and phenoxy groups on TiO$_2$, i.e., the peak width of C-O stretching is much larger than those of other vibrational modes, probably due to the two forms of monodentate and bidentate adsorption configurations. However, phenoxy is more stable than aliphatic alkoxy, which is completely removed from TiO$_2$ surface by 350 °C. To further support that phenoxy is present on the surface in the photooxidation of benzene, we continue by investigating the adsorption of iodobenzene, because in previous studies, alkyl iodides are dissociatively adsorbed, forming alkoxy groups on a TiO$_2$ surface.

Fig. 7 shows the infrared spectra taken after iodobenzene adsorption on a TiO$_2$ surface at 35 °C followed by evacuation and annealing at 425 °C for 1 min. All the bands in the 35 °C spectrum involve excitation of vibrational modes of C-C stretching and C-H rocking. After heating to 425 °C, these bands decrease in intensity, but enhanced absorptions grow at 1249, 1490 and 1588 cm$^{-1}$. Further experiments to study the dissociation of iodobenzene to form phenoxy on TiO$_2$ in different conditions were carried out. Fig. 8 shows the infrared spectra taken after iodobenzene adsorption followed by annealing at 150 °C for 2 h in the presence of water as indicated by the 1615 cm$^{-1}$ band (a), in 10 Torr of O$_2$ (b), and with neither both water nor O$_2$ (c). In all these cases, three new bands appear at 1260, 1490 and 1590 cm$^{-1}$. These three bands are attributed to the formation of phenoxy groups on the surface based on two reasons. First, their positions are very close to those bands in the 500 °C spectrum in Fig. 6, which is assigned to adsorbed phenoxy. Second, previous studies of alkyl iodide adsorption on TiO$_2$ have shown alkoxy formation on the surface as the C-I bond breaks. Iodobenzene...
processes include: (1) a reagent which reacts, with benzene
roles of adsorbed water in the semiconductor photochemical
only surface product observed and its amount is greatly
oxidation of benzene in the presence of phenoxy is the
or surface hydroxy groups to produce phenoxy. In the photo-
absorbed benzene, forming benzene radical cation (~C
that the photoreaction can be initiated by the hole capture of
1618 cm
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1640 cm
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al

First conclusion in the present study, the most important
reÑect the actual species that are formed on the surface during
from surface phenoxy groups instead of adsorbed phenol, as
A: Chem.

radicals which may add to the benzene ring and then turn
into phenoxy; and (3) solvation for benzene radical cations
after hole capture of benzene. The latter effect may increase
the efficiency of hole capture energetically and/or may cause
misalignment of the orbital energy levels involved in the
charge transfer between the TiO
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in vacuum after iodoben-
(a), in 10 Torr of O
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in 10 Torr of (b) and with neither water nor O
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(c). All the spectra were obtained with 50 scans. The TiO
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powder used was ~80 mg.

is not important for the growth of the adsorbed phenoxy
groups by comparison of Figs. 8(b) and (c). However, phenoxy
is enhanced in the presence of adsorbed water. Similar
bands at 1358,O
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1384,1439 and 1564 cm
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suggest the formation of carboxylates; and the
1618 cm
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suggests carbonyl-containing adsorbates.
However, we are not able to identify exactly the molecules
that contain these three functional groups. Recently, Einaga
have taken an ex situ diffuse reflectance IR spectrum of a
TiO
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sample after benzene photooxidation in dry air. Based
on the IR absorptions, they suggested the formation of water,
benzene derivatives, and carbonyl-containing species.

The three common peaks observed in the photoirradiation
of benzene on TiO
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in the different conditions in Fig. 5 are
therefore attributed to the phenoxy group according to the
similar peak positions and broad peak features of the C–O
stretching bands obtained in the adsorption of phenol and
iodobenzene. In Fig. 5, it is found that the amount of phenoxy
formed on the surface is much less in the case without O
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or H
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O, and only phenoxy groups are observed in the presence
of H
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O. However, other surface species are generated in the
presence of O
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. For example, the strong, broad bands at 1358,
1439 and 1564 cm
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suggest the formation of carboxylates; the
1618 cm
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band suggests the formation of water; and the
1640 cm
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band suggests carbonyl-containing adsorbates.

Conclusion
As a brief conclusion in the present study, the most important
finding in the photoirradiation of benzene on TiO
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is the in
situ detection of the photoproduct, phenoxy, on the surface.
This finding shows that, in the previous photoreaction studies
of benzene vapor over TiO
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6,7 the photoproducts extracted
from the TiO
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catalyst after the photoprocesses may not
reflect the actual species that are formed on the surface during
the photoillumination. For example, the phenoxy identified
from the extract solutions of benzene photoreaction on TiO
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, especially in an acidic condition, may very likely be derived
from surface phenoxy groups instead of adsorbed phenol, as
suggested by our experiments. Likewise, solvents functioning
in this respect cannot be ignored for photoreactions occurring
in solution phase.

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