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Photocatalytic degradation of gaseous benzene in air streams by using an optical fiber photoreactor

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Abstract

A batch-type photoreactor contains a bundle of TiO_2-coated quartz fiber was employed for the photocatalytic oxidation of gaseous benzene in air stream. For experiments conducted with initial benzene concentration of 20 ppmv, about 80% of benzene was decomposed in the optical fiber photoreactor after 4 h of ultraviolet (UV) irradiation with the presence of 5% relative humidity. The reaction order of light intensity to the decomposition rate is varied with longitudinal position of optical fiber and the calculated overall order was calculated to be 0.74. A maximum quantum yield (Φ) of 0.5 was achieved for experiments operated in the optical fiber photoreactor, comparing to a maximum quantum yield of 3.55×10^{-3} for those conducted in an annular fixed-film photoreactor under similar operational conditions. The reaction products adhered on the fiber were sampled at various longitudinal positions and identified by the FTIR spectrum. The gaseous reaction intermediates were detected using a GCD/MS. Phenol was identified to be the major intermediate generated at the early stage of benzene decomposition, and the final products were found to be CO_2, CO and H_2O. Deactivation of TiO_2 photocatalyst coated on the optical fiber reactor was found to be much slower than those coated on annular photoreactor.

Keywords: Optical fiber; Photoreactor; Photocatalysis; TiO_2; Benzene; Quantum yield

1. Introduction

Volatile organic compounds (VOCs) are extensively used in numerous industrial processes as clean solvents or diluents for specific purposes. Many of the VOCs in common use are toxic and some are considered to be carcinogenic, mutagenic, or teratogenic [1]. The environmental impacts of VOCs emission, hence, have become a major air pollution problem since last decade. Current industrial-scale technologies on the removal of VOCs from various gaseous streams are treatment processes such as scrubbing, absorption and incineration. Recently, a variety of photocatalytic processes has been studied for treating gaseous streams containing lower concentrations of VOCs. Among the photocatalysts studied, titanium dioxide (TiO_2) is considered to be relatively inexpensive, chemically stable and has been extensively studied for the ultraviolet (UV)-induced photocatalytic reactions. The UV-irradiated TiO_2 surface can generate highly oxidative electrical holes to decompose various organic compounds present in aqueous and gaseous streams at ambient temperature and pressure conditions. Previous studies were usually conducted in fixed-bed photoreactors such as annular photoreactor [1], packed-bed photoreactor [2] and thin-film reactor [3]. The efficiency of traditional fixed-bed photoreactor, however, is relatively low because of the light depreciation within the reactor and the limited irradiated surface area restricted by the reactor configuration.

The employment of optical fibers for the photocatalytic decomposition of organic pollutants was studied by several research groups [4–12]. Instead of using a single UV light lamp, a bundle of optical fibers were utilized as the media for delivering UV within a photoreactor. The optical fiber photoreactors possess two apparent advantages over the conventional fixed-bed photoreactors: the optical fibers provide fairly high specific surface area for immobilizing photocatalyst; and the relatively uniform distribution of UV light within the reactor. Both may contribute to higher quantum yields for the photocatalytic decomposition of various organic compounds [7,8]. In addition, Kribus et al. [13] mentioned the application of optical fiber for remote UV light delivery without significant light depreciation, which makes it possible to treat pollutants present in places difficult to access, such as groundwater, hazardous and dangerous areas. In this study, an optical fiber photoreactor has been employed

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Nomenclature

C_A	concentration of gaseous benzene (ppmv)
$C_{A,0}$	initial concentration of gaseous benzene in the photoreactor (ppmv)
C_w	concentration of gaseous water (ppmv)
h	Planck constant (J s)
I	UV light intensity (W/m^2)
I_{abs}	UV light intensity absorbed by TiO_2 (W/m^2)
k	intrinsic photocatalytic reaction rate constant (ppmv/(min l))
K_{ads}	adsorption equilibrium constant of benzene on TiO_2 particle (ppmv^{-1})
K_w	adsorption equilibrium constant of water on TiO_2 particle (ppmv^{-1})
L	the length of optical fiber in the photoreactor (cm)
m	reaction order of UV light intensity
N_{mol}	number of molecules reacted
N_{photon}	number of photons absorbed by TiO_2
r_A	photocatalytic decomposition rate of gaseous benzene (ppmv/min)
S	area of photon entering to reactor (cm^2)
t	time (min)
$U_{\lambda=365\,nm}$	the energy of 1 einstein of light at 365 nm (J/einstein)
V	volume of reactor (cm^3)
x	the position of the optical fiber in axial direction (cm)

Greek symbols

ν	frequency of UV light at 365 nm (m^{-1})
ϕ_{AP}	apparent quantum yield used in this study
Φ	quantum yield for the photocatalytic reaction

to investigate the effect of various operational parameters on the photocatalytic decomposition of benzene in the gaseous stream. Instead of general optical fiber for communication field employed by Sun et al. [10], the large core of optical fiber with diameter of 1.0 mm was used in this study in order to construct a pilot-liked photoreactor, which is more strong and easy to be composed uniformly in the reactor. The UV light intensity distribution along the TiO_2-coated fibers was characterized with the model developed in our previous study [14]. The photocatalytic degradation pathway of benzene was studied by identifying the intermediates and the by-products during the reaction. Combining the UV light distribution with the kinetic results obtained from experiments, the photocatalytic decomposition behavior of gaseous benzene in the optical fiber photoreactor was described.

2. Experimental

Reagent-grade chemicals used in this study were purchased from major chemical companies and utilized without any further purification. The schematic diagram of the reactor system used in this study is shown in Fig. 1, which consists of an optical fiber photoreactor, a VOC generation unit, a humidity-tuning unit and an UV light source. A bundle of 48 pieces of fused silica fibers (Shanghai Optical Communication, Q4-1.0N; 1 mm diameter, 6 cm length) coated with TiO_2 were arranged uniformly and coaxially with interval of 2.0 mm in a 195 ml cylindrical reactor (55 mm diameter and 80 mm length) made of Pyrex glass. The total geometrical surface area of fibers was determined to be about 9.0×10^3 mm^2. The nude fibers (fused silica optical fibers without acrylic cladding and rubber protective layer) were pretreated with sulfuric acid and rinsed with pure water to remove the organic contaminants and fine particles. The roughness of fiber surface was observed by scanning electron microscope (SEM; Cambridge model S-360) and could be regarded as level and smooth. TiO_2 photocatalyst was coated on the surface of the nude fibers by dipping the fibers in a 10 wt.% TiO_2 slurry solution (Degussa P-25), and the coated fibers were then dried at 80 °C for about 80 min. A GTE model F15T8 UV lamp with approximately 40 W maximum output (primarily at 365 nm wavelength) was placed above the reactor. The UV light from the lamp was irritated vertically on the tips of optical fibers and transmitted through the fibers. A tiny electrical blower was operated at the bottom of the reactor vessel to ensure the well mixing within the reactor.

The benzene-laden gas stream was prepared by extracting the vapor from the benzene-containing aqueous solution with dehydrated compressed air. The initial benzene

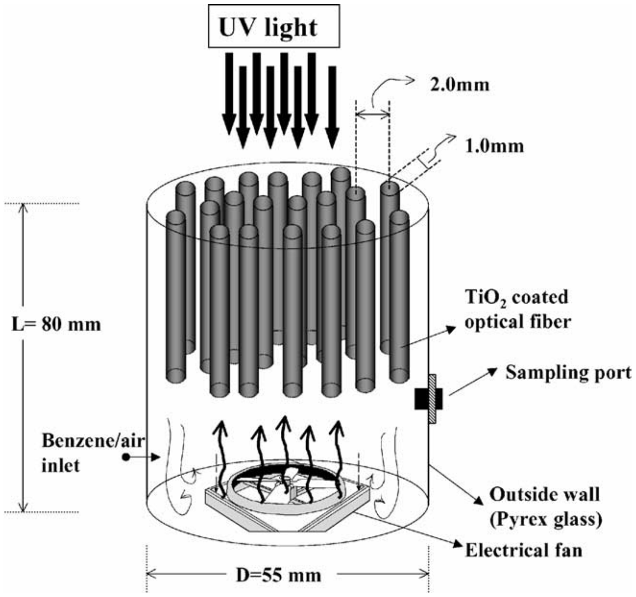

Fig. 1. The schematic diagram of the optical fiber photocatalytic reactor.

concentration and humidity in the gas streams were controlled by adjusting the solution temperature. The benzene-laden air stream was flown through the reactor for about 20 min until the adsorption of benzene on TiO_2 layer coated on the optical fibers was assumed to reach equilibrium. The UV light source was warmed up for about 10 min before it was located above the reactor to warrant a steady light output. Adjustment of UV light intensity was controlled by variable voltage transformer (FT-Voltec-140). A plano-convex lens (JML-PPX12910) made by quartz was set in front of light source in order to achieve an consistent light intensity on each fiber tip. The benzene-laden gas stream in the pipeline was kept at 40 °C by wrapping a flexible electric heating tape (Omegalux, USA) around the pipeline to avoid condensation of benzene and humidity. The temperature of the reactor was maintained constant at 22.0 °C to control the diffusion and adsorption behaviors of reactants on TiO_2. At desired time intervals, aliquots of 0.5 ml gaseous sample were withdrawn from the sampling port, which was located at the middle part of the reactor. Each experimental run in this study was replicated at least twice.

A gas chromatograph (China Chromatography 9800F) equipped with a RTX-624 capillary column (30 m length and 0.53 mm i.d.) and a flame ionization detector (FID) was used for the analysis of benzene. An external standard of benzene was injected into gas chromatograph for calibration. The reaction intermediates retained on the surface of TiO_2 coated on optical fiber was collected and analyzed by a FTIR (BIO-RAD 1420) coupled to an attenuated total reflectance (ATR) detector, the spectrums were identified by a spectrum database (BIO-RAD IR Search Master v6.5). The FTIR/ATR was set up in an isolated cabinet and purged by pure nitrogen to prevent from the background interference of moisture and CO_2 in the air. The gaseous reaction intermediates in the outlet gas stream were detected using a HP-G1800A GCD/MS equipped with a HP-5 capillary column (30 m length, 0.25 mm i.d., 2.5 μm film thickness) and an electron captured detector (ECD). The MS spectrums were identified with the NIST MS Chem Station Library v1.0 chemical structure analytical software.

3. Result and discussion

Kinetic models of benzene decomposition in the batch-type optical fiber photoreactor are presented in this section. The examined reaction system was considered to be heterogeneous assuming that the reaction takes place only on the external surface of catalyst. The photocatalytic decomposition of gaseous benzene under various initial concentrations of benzene, illumination UV light intensities and humidities was performed to calculate the kinetic parameters in kinetic models. For the modeling of the isothermal photocatalytic reactor system employed in this research, the bi-molecular Langmuir–Hinshelwood kinetic model was used and shown as follows:

$$-\frac{\partial C_A}{\partial t} = -r_A = kI^m \left(\frac{K_{ads}C_A}{1+K_{ads}C_A}\right)\left(\frac{K_w C_w}{1+K_w C_w}\right), \quad (1)$$

where C_A is the concentration of benzene (ppmv), C_w the concentration of water molecule (ppmv), r_A the photocatalytic rate of benzene (ppmv/min), t the reaction time (min), I the incident UV light intensity (W/m^2), m the reaction order of UV light intensity, k the intrinsic reaction rate constant (ppmv/(min l)), K_{ads} the adsorption rate coefficient of benzene (ppmv^{-1}) and K_w the adsorption rate coefficient of water (ppmv^{-1}).

The differential light intensity absorbed by coated fiber, $I'_{abs}(x)$, as a function of axial position along the fiber can be described by the following equation developed in our previous study [14]:

$$I'_{abs}(x) = \frac{-\mathrm{d}I_{fiber}(x)}{\mathrm{d}x} = \alpha I\, e^{-\alpha x}, \quad (2)$$

where $I_{fiber}(x)$ is the light intensity on the surface of optical fiber at axial position x and α the attenuation coefficient of the TiO_2 layer. Integrating the $I'_{abs}(x)$ of Eq. (2) and substituting into Eq. (1) for I gives:

$$-\frac{\mathrm{d}C_A}{\mathrm{d}t} = k\left(\int_0^L \alpha I\, e^{-\alpha x}\,\mathrm{d}x\right)^m \left(\frac{K_{ads}C_A}{1+K_{ads}C_A}\right) \times \left(\frac{K_w C_w}{1+K_w C_w}\right). \quad (3)$$

In this study, the variance of humidity in the reactor was monitored as ignorable although the limited surface site may consume the adsorbed water molecules. Hence, the C_w was act as a driving force to mass transfer but not depended on reaction time. The C_w during the reactions with operation conditions of this study could be set as a constant value and the adsorption term of humidity in Eq. (3) was treated as a pseudo-constant of K^*. Integrating and rearranging Eq. (3) gives:

$$\frac{\ln(C_{A,0}/C_A)}{C_{A,0}-C_A} = -K_{abs} + \frac{kI^m(1-e^{-\alpha L})^m K^* K_{ads} t}{C_{A,0}-C_A} \quad (4)$$

where $K^* = K_w C_w/(1+K_w C_w)$ and $C_{A,0}$ is the initial concentration of benzene (ppmv).

With the results for experiments conducted at various initial benzene concentrations, the adsorption equilibrium constant of benzene (K_{ads}) can be determined to be 0.0139 ppmv^{-1}. Our previous study [14] indicated that about 90% of UV light was refracted out of the optical fiber within 6.0 cm of delivery distance. The exponential decay of the light intensity in the axial direction may affect the photocatalytic reaction rate. After taking the natural logarithm of Eq. (4):

$$\ln\left(-\left(\ln\left(\frac{C_A}{C_{A,0}}\right) + (C_A - C_{A,0})K_{ads}\right)\right) = m\ln(I) + \ln(kK^*(1-e^{-\alpha L})^m K_{ads} t). \quad (5)$$

It can be seen that a plot of $\ln(-(\ln(C_{\mathrm{A}}/C_{\mathrm{A},0}) + (C_{\mathrm{A}} - C_{\mathrm{A},0})K_{\mathrm{ads}}))$ versus $\ln(I)$ is a straight line with a slope of 0.74, which is the reaction order of UV light intensity (m), for experiments conducted in the range of 10–40 W/m^2. The calculated results could be comparable to those reported by previous researchers [2,15–18] that the reaction order of light intensity lies between 0.5 and 1.0 for experiments conducted with lower light intensities (less than 80 W/m^2). The intrinsic reaction rate constant (k) and adsorption coefficient of water (K_{w}) are determined to be 0.0541 ppmv/(min l) and 6.01×10^{-3} ppmv^{-1}, respectively, for the decomposition of benzene in the optical fiber photoreactor with the presence of various humidity. Hence, the experimental results can be correlated by the bi-molecular Langmuir–Hinshelwood rate equation:

$$-r_{\mathrm{A}} = 0.0541 I^{0.74}(1 - \mathrm{e}^{-\alpha L})^{0.74}\left(\frac{0.0139C_{\mathrm{A}}}{1 + 0.0139C_{\mathrm{A}}}\right) \times \left(\frac{0.006C_{\mathrm{w}}}{1 + 0.006C_{\mathrm{w}}}\right). \tag{6}$$

A series of adsorption experiments on the removal of gaseous benzene due to TiO$_2$ particles was carried out; experimental results indicate that the adsorption of gaseous benzene by TiO$_2$ is minimal. Experiments conducted with 20 ppmv initial gaseous benzene concentration illustrate that more than 80% of benzene was decomposed after 4 h of UV irradiation in the optical fiber photoreactor with the presence of 5.0% of humidity. The effect of reactant concentration on the benzene decomposition for this reactor was studied and modeled by the kinetics developed above. The increased reaction rate of benzene decomposition at higher benzene concentration is tended to moderate although the increasing concentration of benzene provides more opportunities for surface reaction possibly due to the limited active sites of photocatalyst on the fiber. Similar results were reported by Obee [18], d'Hennezel et al. [19], and Lichtin and Sadeghi [20] and usually attributed to the limited amount of active sites available for the adsorption of benzene. As shown in Fig. 2, fairly good agreements were found between the experimental results and the calculated reaction rates based on Eq. (6) indicating the proposed approach is reasonable on describing the decomposition of gaseous benzene. The calculated reaction rates by Eq. (6) were found to be somewhat less than the experimental data at higher concentration (300 ppmv) possibly because of the adsorption of benzene on TiO$_2$ may not obey the assumptions for Langmuir isotherm. Moreover, the kinetic terms of benzene and humidity in Eq. (6) tended to be unity when experiments conducted with higher than 700 ppmv initial gaseous benzene and 5.6% relative humidity (1500 ppmv), respectively. Hence, the application of the proposed kinetic equation is limited for experimental conditions of low humidity or higher benzene concentration.

Previous works [21–24] revealed different results about the effect of UV light intensity on the decomposition of

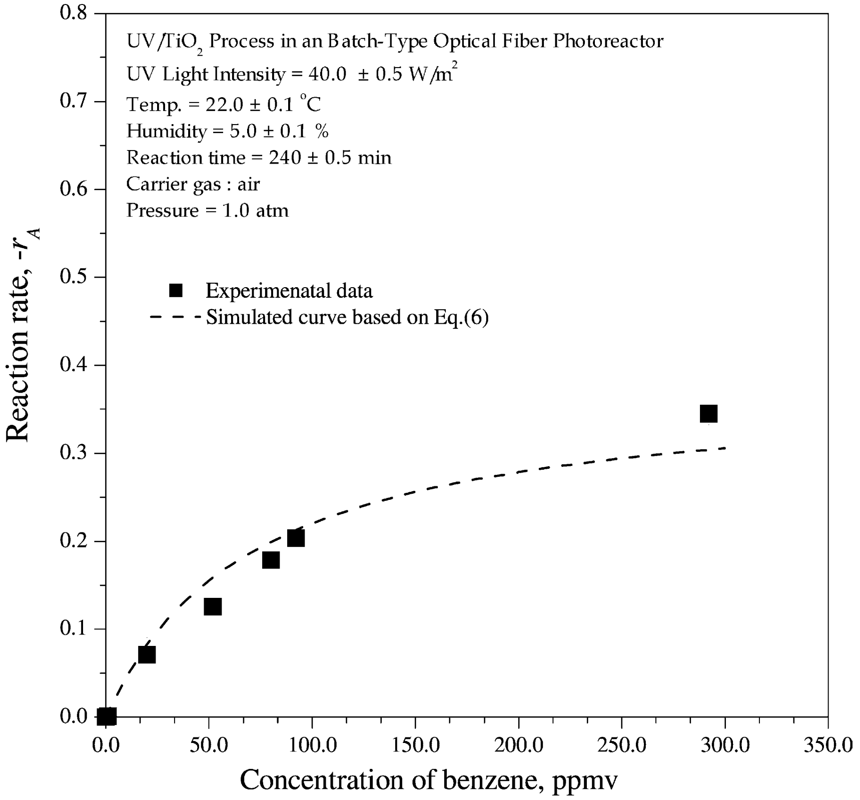

Fig. 2. The effect of initial benzene concentration on the reaction rates for the photocatalytic oxidation of gaseous benzene by UV/TiO$_2$ process in an optical fiber reactor.

various organic species. In this study, the photocatalytic decomposition of benzene was increased with increasing light intensity applied. The highest decomposition of benzene can approach about 80% in this study, although the conversion of isopropanol was claimed to be greater than 99% under lower level of UV light and uncertain humidity by Sun et al. [10] using optical fiber photoreactor. However, the light intensity applied by them was approximately 17–256 times higher than those applied in our experiment; and the characteristics of target reactants (benzene and isopropanol) may be responsible for the large difference on decomposition efficiency. In addition, their radiation source, reactor size and diameter of optical fiber differed widely from our reaction conditions. The quantum yields (Φ) had been addressed precisely by Serpone [25] as the number of molecules N_{mol} undergoing an event (conversion of reactants or formation of products) relative to the number of quanta N_{photon} absorbed by the reactants or by the photocatalyst:

$$\Phi \equiv \frac{N_{\mathrm{mol}}\ (\mathrm{mol/s})}{N_{\mathrm{photon}}\ (\mathrm{einstein/s})} = \frac{\text{rate of reaction}}{\text{rate of photon absorption}}. \quad (7)$$

Because the number of absorbed photons is hard to access owing to the optical effects, such as reflection, scattering, transmission and absorption, on photocatalyst and support, the usage of the term apparent quantum yield referenced to incident photons in heterogeneous photocatalysis has been proposed at 365 nm for phenol [26]. In this study, the apparent quantum yield was adequately employed due to the novel configuration of optical fiber photoreactor. All of the incident photons entering fiber tips were treat as absorbed photons on photocatalyst coated on fiber surface without attenuation owing to the unique light delivery mechanism. The apparent quantum yield (ϕ_{AP}) could be defined as the change of benzene concentration (ΔC_{A}) in a constant volume (V) divided by the incident light intensity (I_{int}) of 365 nm entered fibers during a certain time interval (Δt):

$$\phi_{\mathrm{AP}} = \frac{\text{mole of reactant disappeared}}{\text{mole of photons absorbed}} \cong \frac{\Delta C_{\mathrm{A}} V}{(I_{\mathrm{abs}}/U_{\lambda=365\,\mathrm{nm}})\Delta t}, \quad (8)$$

where $U_{\lambda=365\,\mathrm{nm}} = 3.28 \times 10^5$ J/einstein is the energy of 1 einstein of light at 365 nm, and $I_{\mathrm{int}} \cong I_{\mathrm{abs}}$ because the incident photons were absorbed by TiO_2 photocatalyst via reflection/refraction behavior reported in our previous study [14]. As shown in Fig. 3, the calculated apparent quantum yield decreased from 0.501 to 0.218, for experiments conducted with the applied incident UV light intensity increased from 10 to 40 W/m^2. The decrease of apparent quantum yield with increasing incident light intensity was possibly attributed to the limited surface area of the TiO_2-coated optical fibers which can not absorb excess light energy; however, the faster electron–hole recombination occurred until

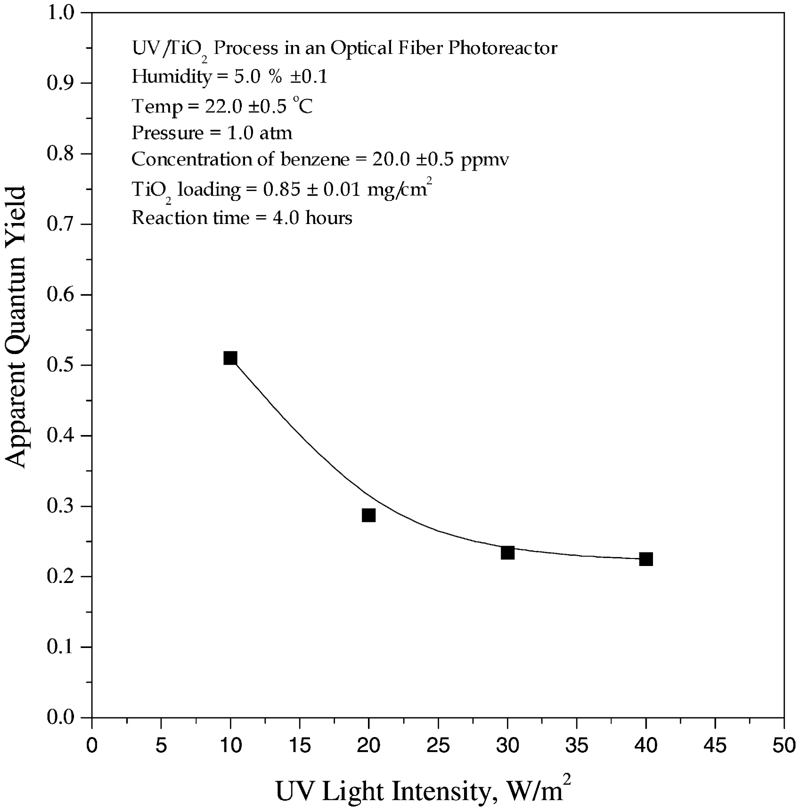

Fig. 3. The effect of irradiation UV intensity on the apparent quantum yield for the photocatalytic oxidation of gaseous benzene by UV/TiO_2 process in an optical fiber reactor.

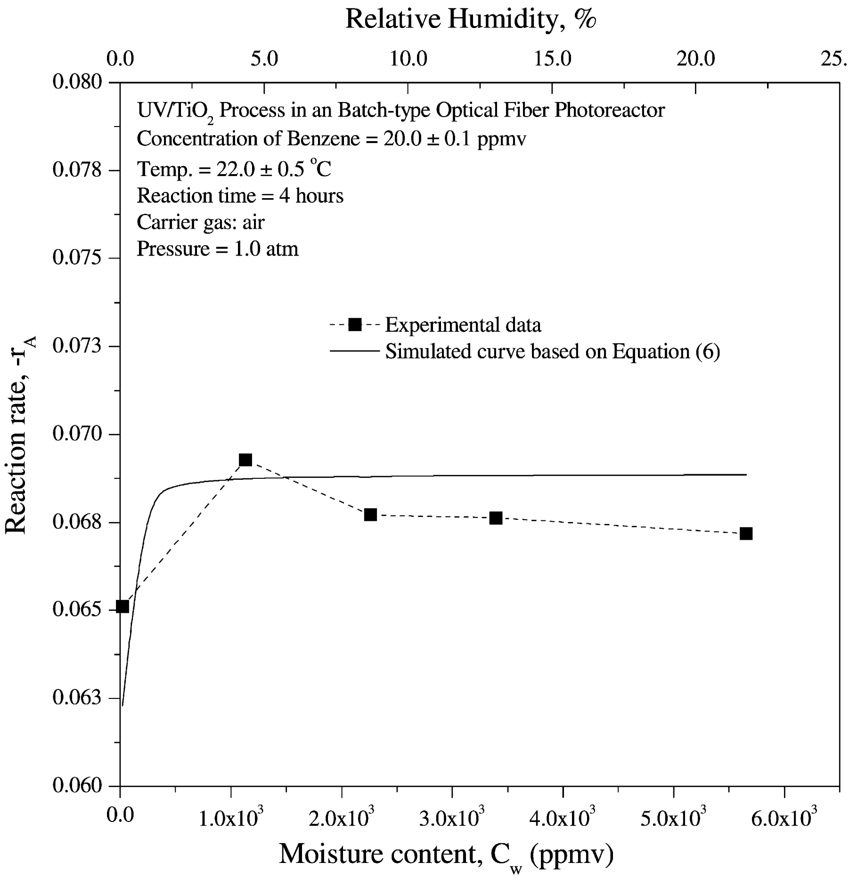

Fig. 4. The effect of humidity on the reaction rates for the photocatalytic oxidation of gaseous benzene by UV/TiO_2 process in an optical fiber reactor.

the surface sites were light-saturated was also proposed by previous studies [8,12].

According to the studies reported by several researchers [19,20,27,28], the humidity revealed a significant influence on the photocatalytic oxidation of organic compounds. The effect of humidity on the reaction rate of benzene decomposition in optical fiber photoreactor was modeled by Eq. (6) and shown in Fig. 4. The experiment results reveals that water can enhance the reaction rate for air streams with humidity less than 5.0%; further addition of water content may result in the inhibition of benzene decomposition. It is generally believed the photocatalysis of water molecules leads to the generation of hydroxyl radicals ($OH^\bullet$); however, the decomposition of organic compounds may also be inhibited when excessive water molecules occupy the active sites on the surface of TiO_2 [3,18,22,29,30]. In this study, about 80% of benzene decomposition was achieved in the optical fiber reactor for experiments conducted with relative humidity between 5.0 and 25.0%. Compare to other reports about benzene photodecomposition, the humidity is much lower than optimum humidity (about 41.0–92.0%) observed for experiments conducted in traditional fixed-bed reactor [19,20]. Although the distribution of light intensity is not well uniform along the length of fiber, the distribution of surface light intensity on the radial direction of the 48 optical fibers at radial position contained in the reactor used in this study is comparably uniform than the traditional annular reactor containing only one light source. Hence, the mass transfer resistance could be minimized for better conversion possibly due to the well-distributed optical fibers providing much more and uniform surface sites inside the space of reactor. Moreover, the enhancement of the light energy utilization was suggested to be attributed to the more efficient absorption of incident photons by photocatalyst fiber surface referring to annular photoreactor. The higher processing capacities of multi-fiber configuration have also been identified for isopropanol decomposition [10].

The chemical species adsorbed on the reacted surface of TiO_2 photocatalyst before and after reaction were scanned by a FTIR/ATR spectroscopy in the range of 1250–4000 cm^{-1} for 20 times, and the results are shown in Fig. 5. The band at 1480 cm^{-1} and that in the region of 1500–1600 cm^{-1} in the spectrum (b) are related to C–H bonding and C=C bonding, respectively, and could be assigned to be the signals of benzene derivatives and possibly oxidized aromatic intermediates, the latter being overlapped with those for the adsorbed water and hydroxyl groups [28]. A weak absorbance shown in the spectrum (b) between 1690 and 1760 cm^{-1} indicates the formation of C=O bonding, implying that the occurrence of the attack by the activated oxygen species or hydroxyl

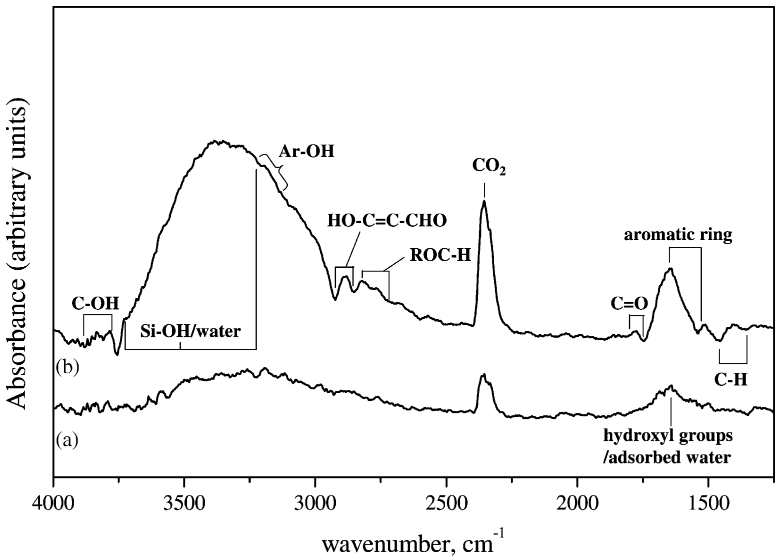

Fig. 5. FTIR spectra of the residues on TiO_2: (a) the fresh TiO_2 sample as a reference; (b) the residues on TiO_2 after 240 min of reaction time.

radical ($OH^{\bullet}$) upon the carbon structures. The band due to C=O stretching of CO_2 (at 2348 cm^{-1}) were observed in both spectra (a) and (b), the absorbance was found to be increased during the photocatalytic mineralization of benzene. The narrow band of 2900 cm^{-1} indicates the presence of C–H bonding of –HO–C=C–CHO– alkenes. During the region of higher wave number, the bands in the region of 3200–3250 and 3590–3650 cm^{-1} could also be assigned to the OH bonding of phenols and alcohols, respectively, which were believed to be intermediates formed in various stages of reaction. However, the quantity of organic compounds adsorbed on TiO_2-coated fibers was very little and hard to be collected for further GC/MS analysis. Functional groups observed from the FTIR spectra was comparable to the intermediates (hydroquinone, 1,4-benzoquinone and catechol) identified by d'Hennezel et al. [19] and Einaga et al. [31] with GC/MS.

Because the batch-type photoreactor used in this study was well mixed; the concentrations of benzene and other products in air stream were supposed to be uniform in the bulk phase. Only the composition of the thin layer close to TiO_2 coating might be varied because of the occurrence of the photocatalytic reaction. The reaction products adhered on the fiber were sampled at various longitudinal positions

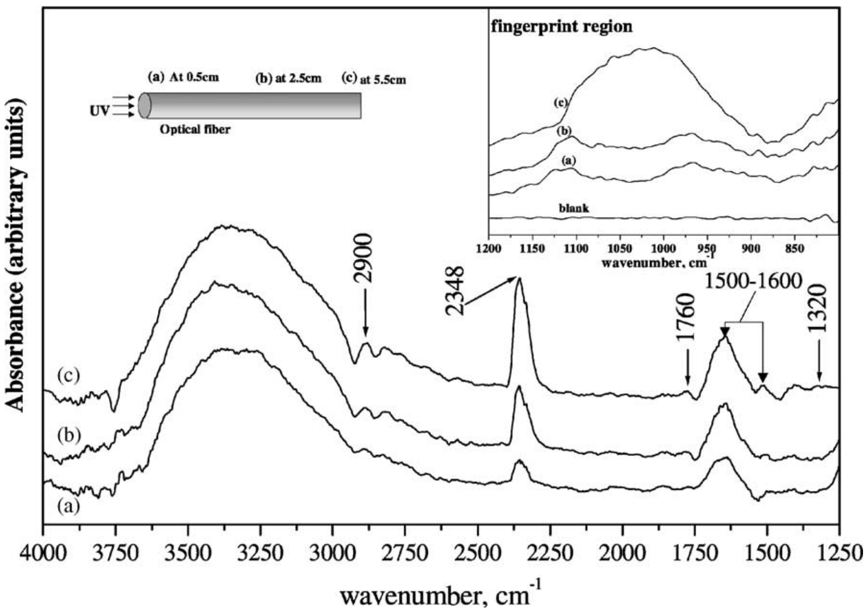

Fig. 6. FTIR spectra of the residues on TiO_2 sampled at: (a) the position of 0.5 cm near the light incident tip of optical fiber; (b) the position of 2.5 cm in the middle part of fiber; (c) the position of 5.5 cm far away from the light incident tip.

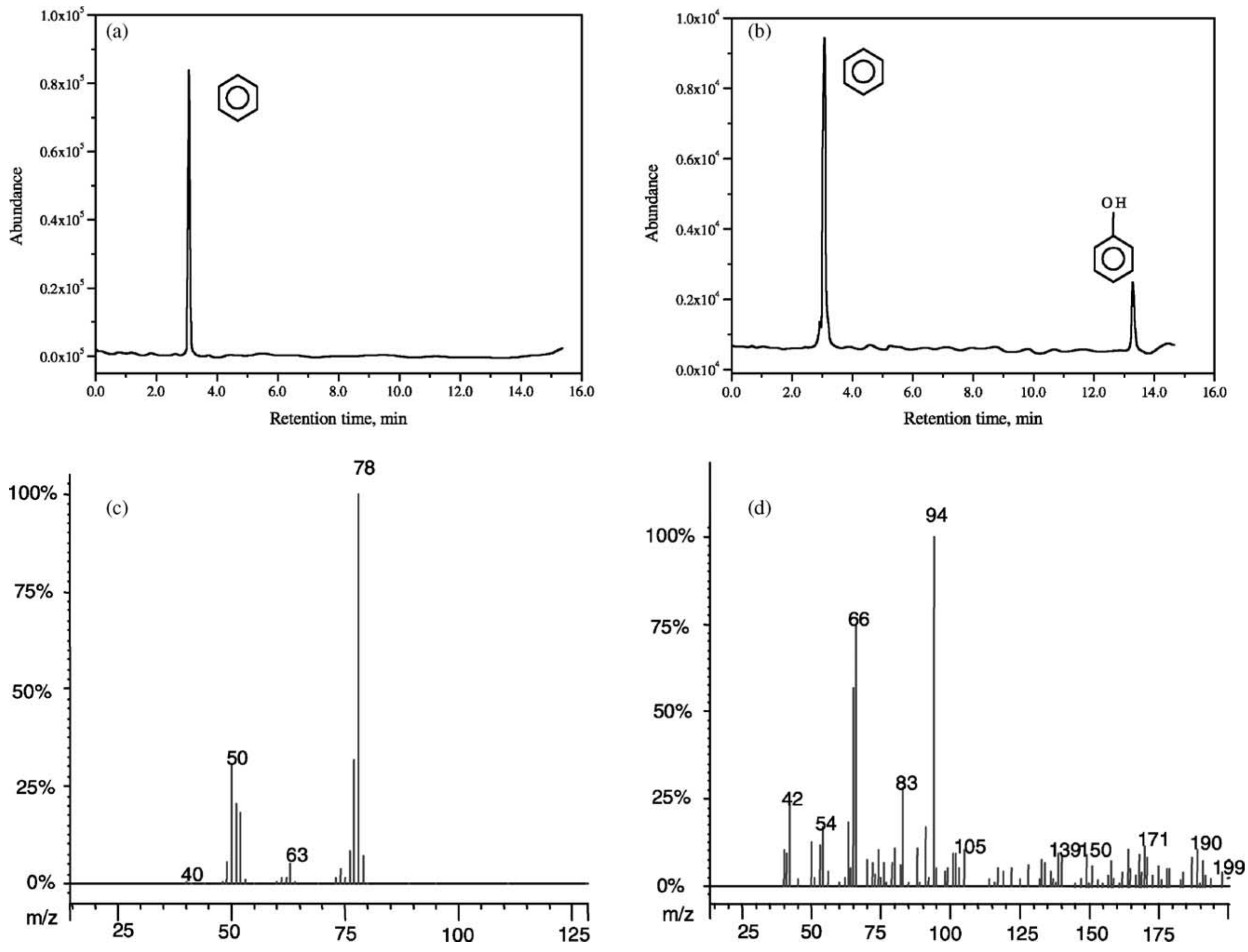

Fig. 7. The GC chromatograms and mass spectra of outlet gas streams during the photodecomposition of benzene by optical fiber photoreactor: (a) the GC chromatogram at very early stage of reaction around 5 min; (b) the GC chromatogram after 40 min of reaction time; (c) the mass spectrum at very early stage of reaction around 5 min; (d) the mass spectrum after 40 min of reaction time.

and identified by the FTIR spectrum as shown in Fig. 6 indicating that the extent of reaction varied at different locations along the fiber. Small amounts of CO_2 were detected for positions near the light source possibly due to the unfavorable adsorption of non-polar CO_2 on the hydrophilic surface of irradiated TiO_2 [32]. In addition, the interferences of background CO_2 and H_2O in the air have been overcome by purging N_2 during the analysis. The intensified signals of spectra increased with longitudinal distance demonstrate that organics were accumulated during the reaction. It reveals that UV intensities at the ends of tips are too weak to decompose efficiently the adsorbed organics deposited on optical fiber. In the fingerprint region shown in Fig. 6, the spectra of compounds adhered on the TiO_2 surface at various positions of optical fiber were compared to the blank experiment. The band of 1100 cm^{-1} detected at (a) and (b) positions ascribes to the aliphatic ketones ($–CH_2–CO–CH_2–$). The band intensity due to the COOH stretching (in the region of 800–900 cm^{-1}) increased with the length of the optical fiber. Three-band weak signals appeared in the region of 800–1200 cm^{-1} (around 1080, 1050 and 970 cm^{-1}) with two-band signals at 1500 and 1600 cm^{-1} were attributed to the mono-substituted benzene. For the broad band of position (c) at around 1050 cm^{-1}, the ether structure ($–CH_2–O–CH_2–$) was identified and ascribed to the oxidized intermediates. According to the spectra confirmation in fingerprint region, the adsorbed materials on TiO_2 coating was could be classified as aromatics, aliphatic oxides and residual benzene.

The gaseous reaction intermediates of effluent gas stream were identified by on-line GC/MS spectroscopy during the photocatalytic oxidation of benzene. The GC chromatograms of reacted gas stream for experiments conducted at very early stage around 5 min and with 40 min of reaction time are shown, respectively, in Fig. 7(a) and (b) which reveals that benzene molecule has been degraded into other derivatives. The mass spectra of GC chromatogram at retention time of 3.1 and 13.3 min was shown in Fig. 7(c) and (d), respectively. Via the comparison of mass spectra, phenol was supposed to be the major by-product at the

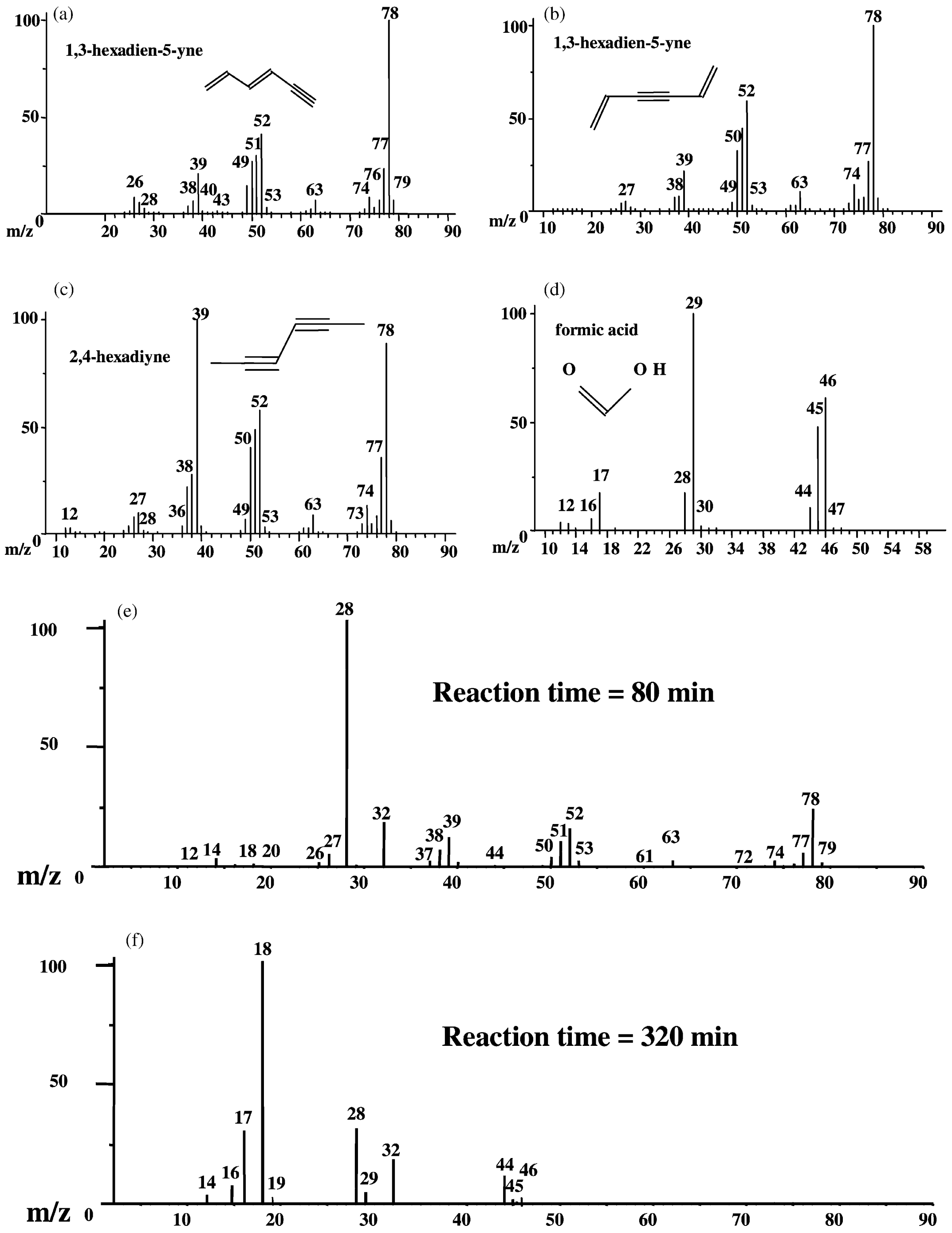

Fig. 8. The mass spectra of the intermediates and referenced compounds for decomposition of benzene in optical fiber photoreactor by UV/TiO_2 process.

early stage (around 40 min) of benzene degradation, and its mass spectra was shown in Fig. 7(d); similar to the observation reported by Einaga et al. [31]. However, the possible intermediates such as 1,5-hexadien-3-yne, 2,4-hexadiyne, 1,3-hexadien-5-yne and formic acid have also been identified in this study subsequently after the rupture of the aromatic ring. It was quite different from the results reported by previous researchers [19,31] that no gaseous organics were detected in the exhaust gas by GC/FID. The mass spectra of gaseous species in photoreactor after 80 and 320 min of reaction were properly matched the compared spectra proposed in this study and shown in Fig. 8. The mass spectra of Fig. 8(f) did not match the referenced formic acid of Fig. 8(d) very well possibly due to the very low level of production. The intermediates with alkene's and alkyne's structure were hydrophobic and hard to condensed [33] on TiO_2 surface; hence, it is difficult to find the gaseous intermediates of low concentrations by FTIR spectra. The more

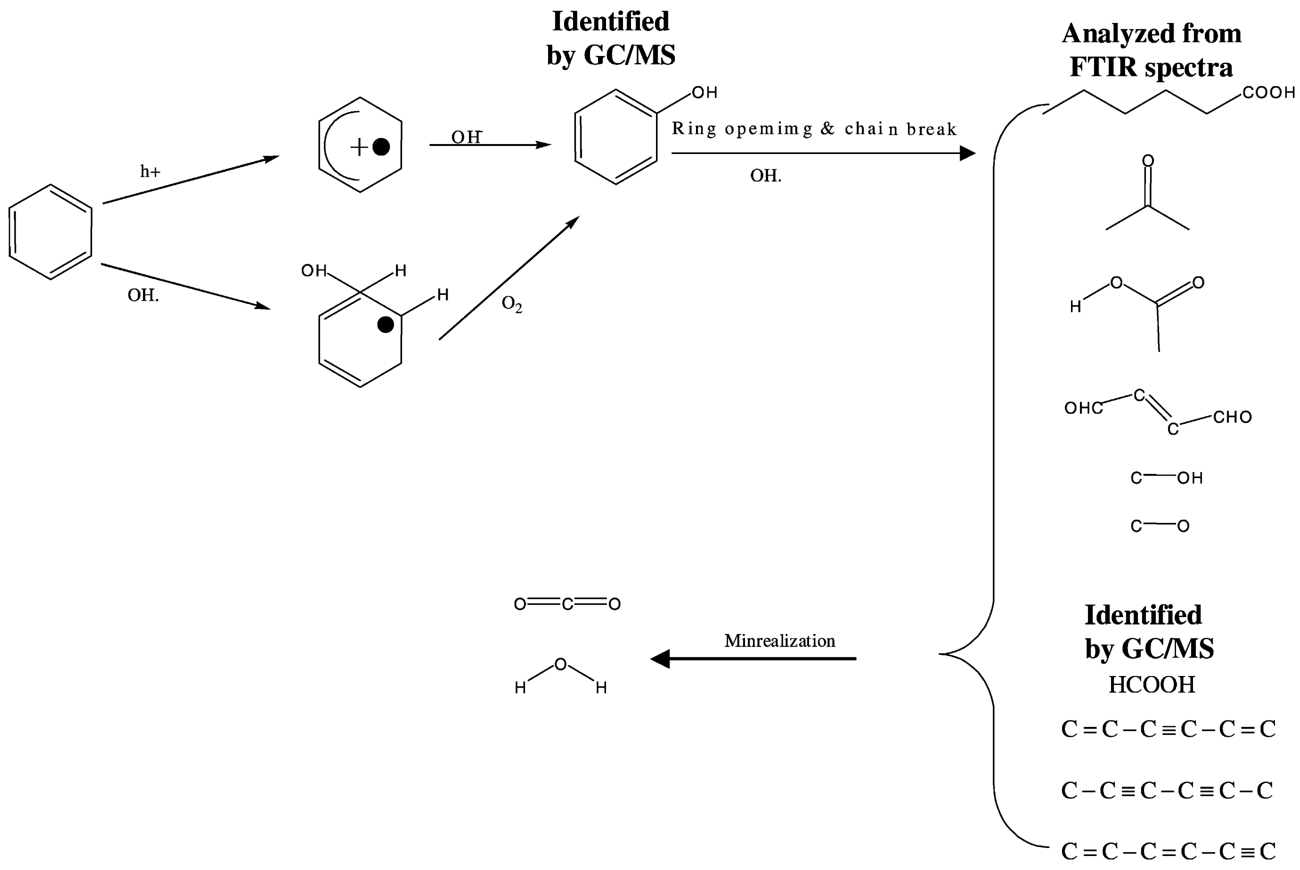

Fig. 9. Functional groups of organic intermediates identified by FTIR and GC/MS and the proposed degradation mechanism for the photocatalytic oxidation of gaseous benzene by UV/TiO_2 process.

efficient utilization of UV light due to the unique configuration possibly contributes to the rapid ring-opening of benzene derivatives, so that aromatic organic intermediates (such as catechol and hydroquinone) were not found except for phenol. Nearly no any organic intermediates but trace level of formic acid was detected for gaseous stream sampled at 320 min of reaction time, only CO_2, N_2 and H_2O were obviously found as shown in Fig. 8(f). Based on the reaction products identified, the photocatalytic oxidation pathway of benzene in gaseous stream was proposed in this study and depicted in Fig. 9. The hydroxyl radical ($OH^\bullet$) attack was believed to be the predominant mechanism for benzene degradation. In this study, some brown matter was observed on the TiO_2 surface after long-term operation and was difficult to be identified. However, previous studies supposed that the brown material was due to the co-polymerization of aromatic structures [19,34] or carbon deposits due to the uncompleted oxidation of the organic species [35].

Decomposition of benzene in an annular photoreactor coated with TiO_2 on the inner wall was proposed as

Table 1
The design criteria for the annular photoreactor and optical fiber reactor

Properties	Reactor type	
	Annular photoreactor	Optical fiber reactor
Geometric characteristics		
TiO_2-coated area in photoreactor (A, cm^2)	691	90.5
Volume of photoreactor (V, cm^3)	1276	180
Area of photon entering (S, cm^2)	691	0.377
The quotient value of TiO_2-coated surface to reactor volume (A/V, cm^{-1})	0.542	0.503
The quotient value of TiO_2-coated surface to photon entering area (A/S)	1	240.1
Photon characteristics		
Rate of incident photon to photocatalyst at UV source of 20 W/m^2 (quanta/s)	5.37×10^{13}	5.23×10^{10}
Conversion of benzene (%)	44.3	48.2
Apparent quantum yield (ϕ_{AP})	0.00355	0.5023

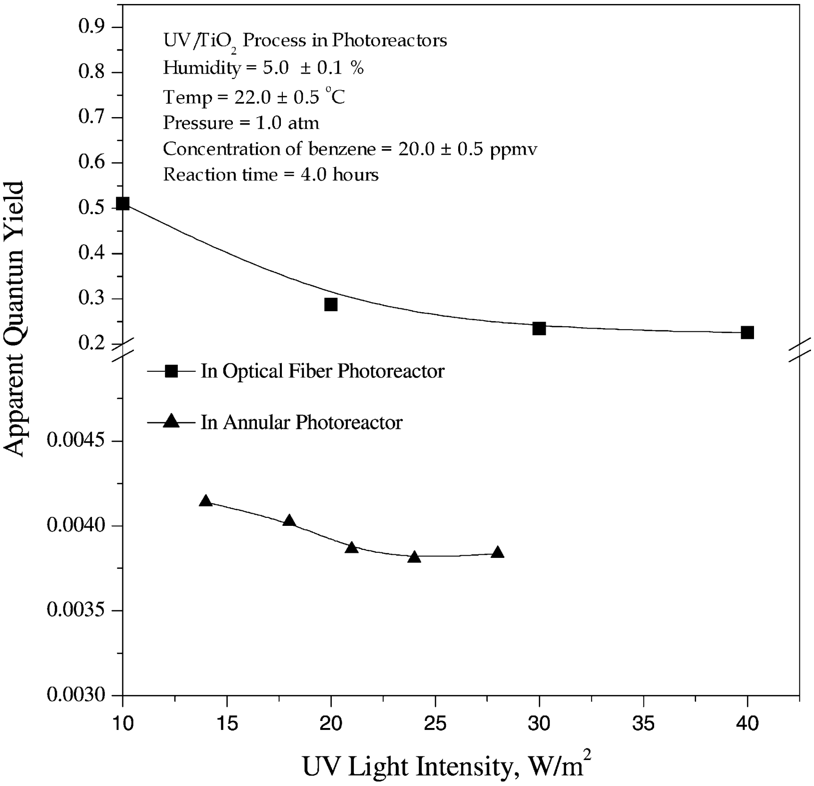

Fig. 10. Calculated quantum yields for the photocatalytic oxidation of gaseous benzene by UV/TiO2 process in various photoreactor.

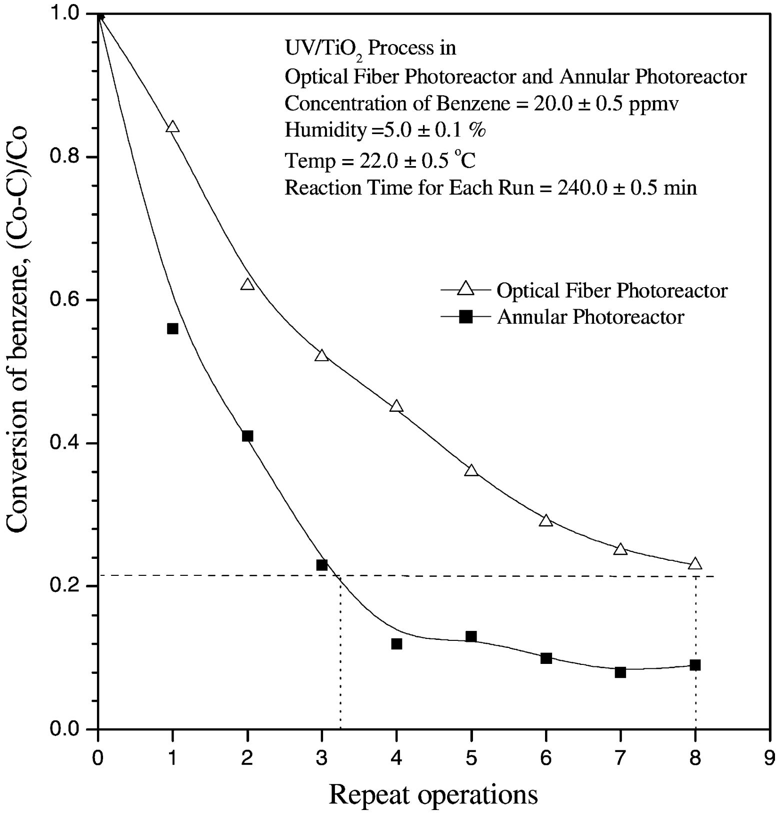

Fig. 11. Deactivation of coated TiO2 photocatalyst in various photoreactor under eight repeated operations for the photocatalytic oxidation of gaseous benzene by UV/TiO2 process.

control experiment in order to evaluate the performance of the optical fiber photoreactor conducted under similar reaction conditions. However, the design criteria for the optical fiber reactor and annular reactor in this study were summarized in Table 1. Via the calculation result related to the geometric natures of reactors, the area of photon receiving in annular reactor was 1833 times in optical fiber reactor; however, optical fiber reactor was 240 times the quotient value of TiO_2-coated surface to photon entering area (A/S) for annular photoreactor. It is supposed that optical fiber reactor can suffer from higher UV intensity input and distribute it to lower level for each fiber because of the unique light delivery mechanism [10,14]. Table 1 also represented that two orders of apparent quantum yield was achieved by optical fiber refers to annular photoreactor under similar conversion of benzene, although the incident rate of photon on photocatalyst (5.28×10^{10} quanta/s) was only 1/1000 lower than in annular reactor (5.37×10^{13} quanta/s). With similar loadings of TiO_2 (defined as the quotient value of coated areas of TiO_2 divided by the reactor volume, A/V), the quantum yields for the optical fiber and annular photoreactors under various UV light intensity were depicted in Fig. 10. The experimental results conducted for Table 1 show that optical fiber photoreactor is superior in the quantum yield possibly due to the more efficient utilization of incident photons and minimized mass transfer resistance by well-distributed activated sites inside the space of reactor. Similar comparison was also addressed that the quantum yields for experiments conducted in the optical fiber photoreactor were reported to be much higher (about 100–130 times) than those conducted in the conventional fixed-film photoreactor for VOC photocatalytic destruction [10,20].

According to the intermediates identification mentioned above, some of hydrophilic compounds (such as phenol, alcohol, aldehyde, organic acid and water presumed by FTIR and GC/MS) were easily attached to the TiO_2 surface by hydrogen bonding which was turned from hydrophobic into hydrophilic after UV illumination [32]. It is concluded that the deactivation of TiO_2 photocatalyst might be resulted from the competitive adsorption of these organic intermediate. The photocatalytic activity of TiO_2 coated on the two different photoreactors was compared for duplicate experiments under similar operational conditions, and the experimental results are shown in Fig. 11. The decomposition of benzene was rapidly decreased from 55 to 20% for experiments conducted in the annular photoreactor after three operation cycles (each batch cycle lasts for 240 min), while the conversions were decreased from 85 to 20% for experiments conducted in the optical fiber photoreactor after eight operation cycles.

4. Conclusion

The unique mechanism of light delivery and less mass transfer resistance of optical fiber photoreactors in this study possibly enhanced the photoreaction due to efficient utilization UV light and well-dispersed surface sites of TiO_2. It is found that the use of bi-molecular Langmuir–Hinshelwood kinetic model with moderated modification of UV light intensity attenuation can describe the decomposition of benzene properly in optical fiber photoreactor. Excess UV light intensity may cause the decreasing of apparent quantum yield in benzene decomposition possibly because limited surface sites in the reactor can not make good use of overloaded light energy, or the faster electron–hole recombination might occurred simultaneously. The apparent quantum yields for the photocatalysis of gaseous benzene in an optical fiber TiO_2-coated reactor were much higher than those operated in an annular fixed-bed photoreactor under similar conditions; the comparisons of reactor geometry and photon incidents were also considered and evaluated. Due to the unique light intensity distribution along the optical fiber, the intermediates generated on the fiber surface was supposed to be varied with longitudinal positions on the fiber. The FTIR spectrum reveals that oxidation at positions near the light source was more completed than other positions away from the light-incident tips. The possible intermediates identified and pathway of benzene decomposition was merely determined by GC/MS and FTIR according to the m/z fragment distribution of chemical structure and function groups represented in the spectra, respectively. It was difficult to completely and precisely identify the exact mechanisms of benzene photodecomposition. The characteristics of the intermediates were also mentioned in this study for explain the adsorption behavior of intermediates. The deactivation behavior of photocatalyst could be possibly referred to the adhesion by the organic intermediates generated during the decomposition of benzene. The deactivation of photocatalyst in an annular photoreactor is more noticeable than in an optical fiber photoreactor.

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