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Photodegradation of phenol and 4-chlorophenol by $BaO–Li_2O–TiO_2$ catalysts

E. Leyva[a], E. Moctezuma[a,*], M.G. Ruíz[a], L. Torres-Martínez[b]

[a]*Universidad Autónoma de San Luis Potosí, San Luis Potosí (SLP) 78210, México*
[b]*Universidad Autónoma de Nuevo León, Nuevo León (NL), México*

Abstract

The catalytic photodegradation of phenol and 4-chlorophenol with white and UV light over TiO_2, $BaTi_4O_9$ and Hollandite catalysts has been studied in our laboratories. $BaTi_4O_9$ and Hollandite catalysts were prepared by solid state reaction at 900°C and 1200°C, respectively. All the catalysts were characterized by different techniques such as surface area measurements by the BET method, atomic absorption spectroscopy and XRD. Photodegradation reaction experiments were monitored by HPLC analysis. The reaction intermediates: hydroquinone and 1,4-benzoquinone were identified by GC–MS analysis. The photocatalytic activities of these catalysts in the degradation of phenol and 4-chlorophenol were evaluated in comparison with titanium oxide. Experimental results showed that $BaTi_4O_9$ and Hollandite catalysts exhibit small photocatalytic activity as compared with TiO_2. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Phenol; 4-Chlorophenol; Hollandite; Barium-titanate

1. Introduction

Phenol and chlorophenols represent an important class of environmental water pollutants. These organic compounds have been considered on the EPA's priority pollutants list since 1976 [1]. Most phenolic compounds are present in waste waters from petrochemical, coal tar, plastic and pesticidal chemical industries [2–4], which produce them as chemical intermediates or generate them during chlorination of effluents containing phenolic compounds. Furthermore, pentachlorophenol is widely used as pesticide in the wood preservation industry [5]. These organic compounds can be oxidized by chemical, photochemical and microbiological processes [2,3]. But, biological treatment of waste waters containing chlorinated phenols requires longer retention times and in the case of higher concentrations, the activated sludge formation can be substantially intoxicated and suppressed [3,6]. Phenol and chlorophenols can also be degraded by photocatalytic processes [2,7–11], in which photo-induced holes in semiconductor particles oxidize hydroxide ions or water molecules adsorbed on the surface of the particles to produce •OH radicals which subsequently attack adsorbed organic molecules [12,13].

Several research groups have reported the reaction mechanisms and the reaction rate equations for the photocatalytic degradation of phenol and different chlorophenols [2,3,7–11,13]. Photocatalytic degradation reaction pathways, product yield and reaction rates depend on the reaction conditions [14,15].

*Corresponding author.

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Photocatalytic degradation of 4-chlorophenol [4,14–16] can be described by three parallel reaction pathways resulting in stable intermediates including hydroquinone, benzoquinone and 4-chlorocatechol that are decomposed to water and CO_2. In the case of phenol oxidation, Okamoto [17,18] suggested that phenol also undergoes complete mineralization by three different pathways and identified hydroquinone, catechol, 1,2,4-benzenetriol, 2-hydroxybenzoquinone and benzoquinone. The photocatalytic degradation of phenol and 4-chlorophenol can be described by Langmuir–Hinshelwood rate expressions [16,19,20] with two independent adsorption parameters that depend on the reaction conditions.

Most of the research groups have used fine powders of semiconductor oxides [21,22] as photocatalysts, e.g. TiO_2, ZnO and WO_3. Others have modified the catalyst surface structure with another metal oxide. It has been reported that chromium [23] and molybdenum oxides [24] enhance the photocatalytic activity of TiO_2 for phenol degradation. But, it was reported that iron oxides have a negative effect on the photocatalytic activity of TiO_2. Recently, Ahuja and Kutty [25] have demonstrated that strontium titanates ($SrTiO_3$), which has a band gap near 3.2 eV corresponding to an adsorption of 387 nm approximately, also exhibit photocatalytic activity in the degradation of phenol. Inoue and Khono have shown that the combination of either barium titanate or sodium hexatitanate with ruthenium oxide leads to active photocatalysts for water decomposition [26–28]. These type of catalysts present a UV diffuse reflectance spectra with absorption between 320 and 410 nm [27]. In this paper, we report the synthesis and characterization of several barium–lithium titanates with similar structure to the barium titanates prepared by Inoue and Khono [26,27]. We also report their photocatalytic activity for the degradation of phenol and 4-chlorophenol and compare them against the photocatalytic activity of TiO_2 under the same reaction conditions.

2. Experimental

2.1. Materials

Starting materials for catalyst preparation were $LiCO_3$, $BaCO_3$ (reagent grade, Aldrich) and TiO_2 (Degussa P25). The organic compounds used in the photocatalytic experiments were phenol and 4-chlorophenol (99.9% purity, Aldrich). All the solutions were prepared with deionized water. Mobile phase for HPLC analysis was prepared with methanol (HPLC grade, Fisher Scientific), citric acid (99.9% purity, Aldrich) and EDTA (Mallinckrodt).

2.2. Catalyst preparation

We prepared four catalysts of the $BaTiO_3$–Li_2TiO_3–TiO_2 system [29,30] with different chemical composition (Table 1) and a general formula $Ba_{3x}Li_{2x+4y}Ti_{8-2x-y}O_{16}$. The x values are between 0.32 and 0.42. The y values are between 0.01 and 0.20. This chemical composition corresponds to the stoichiometry usually accepted for Hollandites, where the barium cations occupy the channels in the framework of TiO_6 octahedra [29]. We also prepared barium tetratitanate ($BaTi_4O_9$) catalyst, which also has a tunnel structure [26,29].

To prepare Hollandite catalysts, lithium and barium carbonates were dried at 200°C, and the TiO_2 was dried at 900°C. These starting materials were stored in a desiccator after the drying step. Stoichiometric amounts of each reactant were mixed into a paste with acetone, using an agate mortar and pestle, dried and placed in a Pt crucible. The paste of the solids and acetone was heated from 200°C to 900°C at a heating

Table 1
Catalyst chemical composition

Composition	Formulae	BaO (% mol)	Li_2O (% mol)	TiO_2 (% mol)	Sample ID
x=0.35, y=0.08	$Ba_{1.05}Li_{1.02}Ti_{7.22}O_{16}$	11.96	5.808	82.023	Hollandite I
x=0.36, y=0.06	$Ba_{1.08}Li_{0.96}Ti_{7.22}O_{16}$	12.30	5.467	82.230	Hollandite II
x=0.34, y=0.14	$Ba_{1.02}Li_{1.24}Ti_{7.18}O_{16}$	11.56	7.029	81.400	Hollandite III
x=0.34, y=0.12	$Ba_{1.02}Li_{1.16}Ti_{7.20}O_{16}$	11.59	6.591	81.810	Hollandite IV

rate of 3°C/min. This final temperature was kept for 3 h to expel CO_2. Finally, the mixture was calcined at 1200°C for 48 h, with intermediate regrindings to achieve complete reaction. Barium tetratitanate ($BaTi_4O_9$) was prepared using the same experimental method, but the final calcination step was carried out at 900°C.

2.3. Catalysts characterization

All the catalysts were characterized by various characterization techniques. Surface areas were measured by the BET method with a Micromeritics ASAP 2000 instrument using Krypton or Nitrogen as adsorbate. X-ray diffraction patterns were obtained using a Rigaku Dmaxb diffractometer with a Cu K_α radiation (λ=1.5432 Å) incident X-ray source. The chemical composition of each catalyst was determined by atomic absorption analysis with a Varian, Spectra A5.

2.4. Reaction experiments

Photodegradation experiments can be carried out in a vertical glass flask (125 cm^3) illuminated by either four 8 W white light lamps (Hitachi model 8T5/D, 300<λ<800 nm) or four 15 W UV light lamps (Cole Palmer E-09815-55, λ_{max}=365 nm). The reactor has a gas-tight cover with four ports for gas inlet and outlet, sampling, and pH measurements. A water condenser filled with glass beads, which is cooled with water from a constant temperature bath, is connected to the gas outlet port to condense and reflux water, reactants and degradation products. This photoreactor system can be placed in a water bath to control the reaction temperature.

We carried out three different sets of experiments. First, we investigated the effect of pH on the photocatalytic degradation of phenol under white light illumination using TiO_2 as catalysts. For these experiments, 0.6 g of TiO_2 were mixed with 100 cm^3 of phenol solution (100 ppm). The pH was adjusted with H_2SO_4 or KOH [17] to different values from 3 to 8. The slurry was agitated with a magnetic stirrer. Saturated air was bubbled through the slurry at a rate of approximately 100 cm^3/min. Samples for analysis were withdrawn after 1 h of reaction. Each sample was filtered with a Millipore membrane (0.22 μm of pore diameter) and analyzed by HPLC. On the second set of experiments, we determined the photocatalytic activity of barium-titanate and Hollandite catalysts for phenol and 4-chlorophenol degradation under white light illumination. For each reaction experiment, a small amount of the catalyst was mixed with a volume (100 cm^3) of phenol or 4-chlorophenol solution (100 ppm). In this case, the pH was adjusted with H_2SO_4 or KOH solutions to a constant value of 3 [17]. Samples for analysis were withdrawn at different reaction times for HPLC analysis. Some of the samples were also analyzed by GC–MS. On the last set of experiments, we repeated some of the photocatalytic degradation experiments using UV light lamps.

2.5. Chromatographic analysis

Each of the reaction samples was analyzed by HPLC using a Waters Cromatographer model 600E equipped with a UV detector Waters 490 tuned at 280 nm and a NovaPak Phenyl column (60 Å 4 mm, 100×3.9 mm). The mobile phase was 11 mM citric acid/0.055 mM EDTA/45% methanol and the flow rate was 0.8 cm^3/min.

As mentioned before, some of the samples were analyzed by GC with MS detector in order to identify the reaction intermediate products. The organic compounds in the reaction samples were extracted with ethyl acetate and concentrated in a rotary evaporator. Then, this solution was analyzed in a Hewlett Packard gas cromatographer Model 5890 series II equipped with a quadrupole mass detector Hewlett Packard model 5972. The chromatographic separation was performed by a capillary column (Crosslinked 5% Me-Phenyl-silicone, 0.2 mm i.d., 0.33 mm×25 m) using Helium as carrier gas.

3. Results and discussion

X-ray diffraction patterns of all the catalysts are presented in Fig. 1, where we can see that the Hollandite catalysts prepared in our laboratories have a crystalline structure. All the Hollandite catalysts have very similar diffraction patterns to the crystallographic data reported before [29,30]. Hollandite I and Hollandite II are pure phases. However, Hollandite III and Hollandite IV diffraction patterns (lines d and e) show

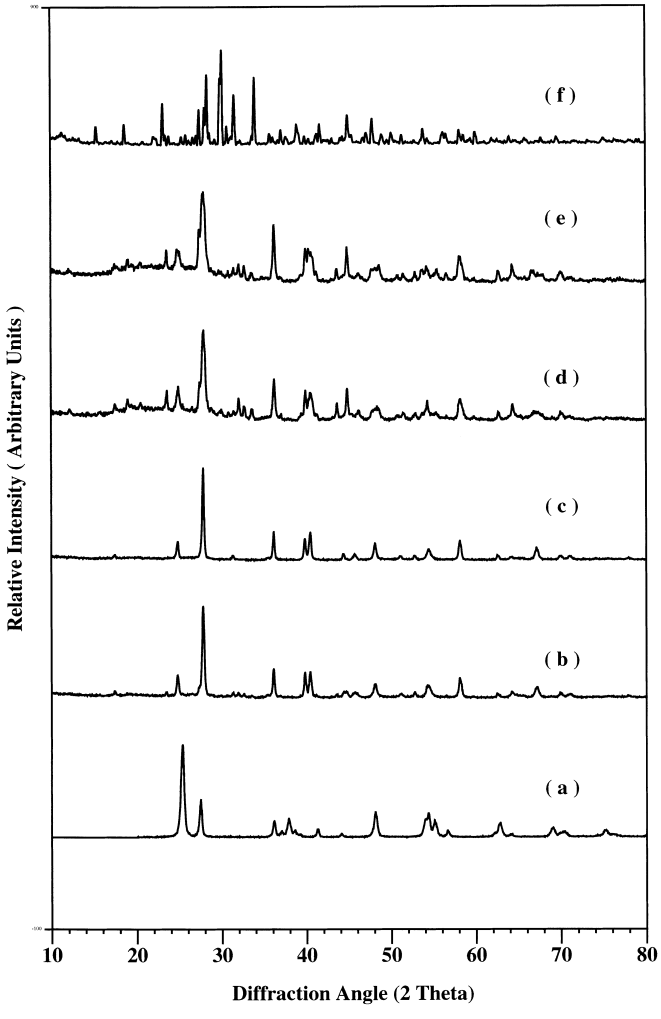

Fig. 1. Catalyst X-ray diffraction patterns: (a) TiO_2; (b) Hollandite I; (c) Hollandite II; (d) Hollandite III; (e) Hollandite IV; and (f) $BaTi_4O_9$.

some important differences. Two peaks located at 39.95° and 40.6° are not well resolved indicating incomplete reaction during catalyst preparation. Furthermore, lines d and e also present small peaks at 2Θ angle of 23.42°, 62.75° and 64.35° that are characteristic of TiO_2, Li_2O and BaO. Lithium and barium oxides are formed during the initial heating of the corresponding carbonates. These results clearly indicate that the calcination time at 1200°C should be longer than 48 h in order to eliminate those impurities. The diffraction pattern of barium tetratitanate ($BaTi_4O_9$) prepared in our laboratories, line f, shows the main features of the pure phase. However, it also shows several peaks that correspond to TiO_2 and $BaTiO_3$.

The results of the chemical analysis by atomic absorption spectroscopy confirmed the stoichiometric composition of all barium–lithium catalysts as shown in Table 1. Since these catalysts were prepared by solid state reactions at very high temperature, they have very low surface area in the order of 0.5 m^2/g measured by krypton adsorption. Pure TiO_2 has a surface area of 51.47 m^2/g measured by nitrogen adsorption.

Fig. 2 shows the effect of pH on the photocatalytic degradation of phenol. It indicates that higher conver-

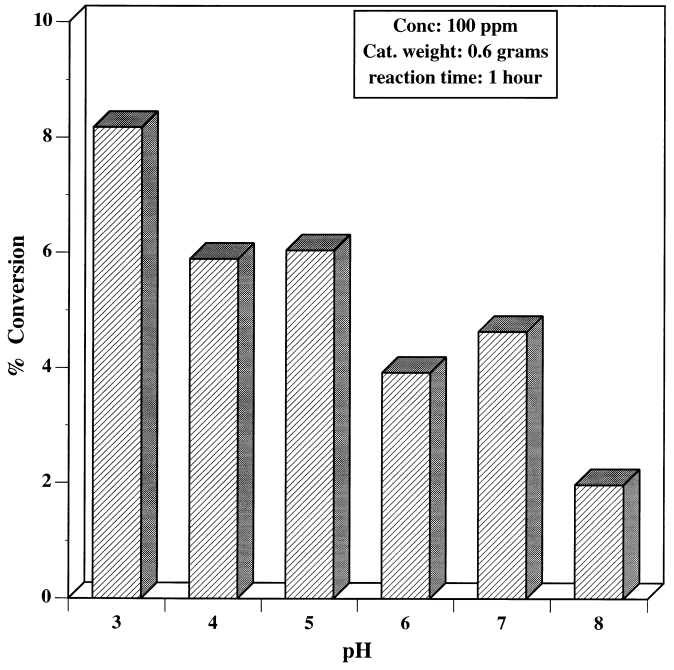

Fig. 2. Effect of pH on the photocatalytic degradation of phenol using TiO_2 as catalyst.

sions are obtained at pH 3. Okamoto [17] has reported that pH 3.5 is the optimum for the photocatalytic decomposition of phenol. Yung-Hsu [3] reported that pH 3 is the optimum for the photocatalytic decomposition of 2,4-dichlorophenol. They suggested that low pH values facilitated the adsorption of the organic molecule and promoted better photocatalytic degradation. They also indicated that higher pH retarded the formation of •OH radicals and decreased the photocatalytic reaction rate. Besides, TiO_2 coagulates at pH 9 and the samples of the reaction slurry could not be filtrated and analyzed.

The results of the photocatalytic degradation of phenol reaction experiments with different catalysts irradiated with white light lamps at 40°C in the presence of oxygen are shown in Fig. 3. These results indicate that Hollandites I and II, barium tetratitanate and TiO_2 exhibit similar photocatalytic activity for phenol degradation. In these experiments, TiO_2 had the higher activity and the catalyst identified as Hollandite III had the lowest activity. It may be possible that impurities had a negative effect on the photocatalytic activity.

Even though the reactor system was equipped with a water condenser, some of the reactants and degradation products can be lost by bubbling air through the system. Therefore, a cold finger trap was connected to the outlet of the system to trap the water and any of the organic chemical species. In the worst of the cases, 15 cm^3 of an aqueous solution with a concentration of 48 ppm of phenol were condensed inside the cold trap after 24 h of reaction of phenol solution with no catalyst. Since the reaction was carried out bubbling saturated air, 92 cm^3 of solution remained in the reaction flask. The overall material balance indicates that 15.79 mg of phenol were consumed after 24 h of reaction and the real conversion was 15.8 instead of 16.3 as reported in Fig. 3. Since this difference is considered rather small, all the results on the conversion plots are reported uncorrected.

After these observations, Fig. 3 still shows that phenol can be oxidized under these reaction conditions in the absence of any catalyst. Photochemical and thermal reactions are important in the photocatalytic degradation of phenol with white light lamps.

The results of the photocatalytic degradation of 4-chlorophenol under the same reaction conditions are presented in Fig. 4. These results indicate that TiO_2 has a higher photocatalytic activity than any of the other catalysts. In this case, only the catalyst identified

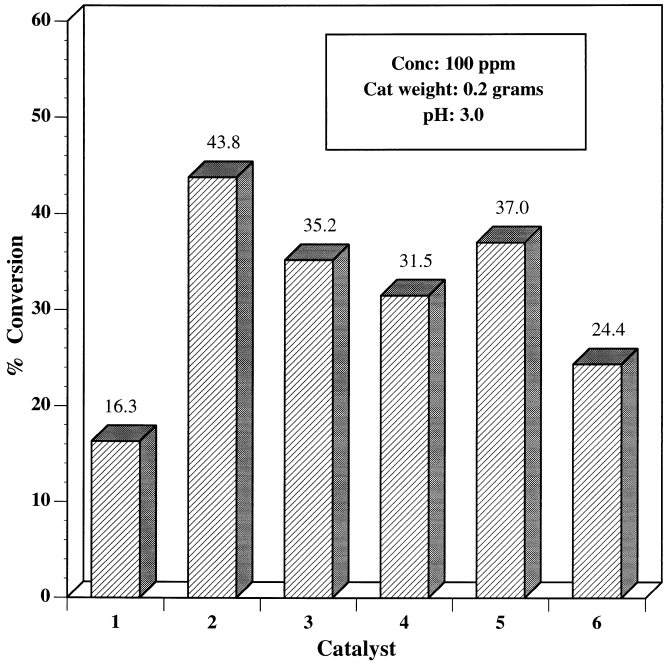

Fig. 3. Photocatalytic degradation of phenol with air injection at 40°C after 24 h of reaction: (1) Without catalysts; (2) TiO_2; (3) $BaTi_4O_9$; (4) Hollandite I; (5) Hollandite II; (6) Hollandite III.

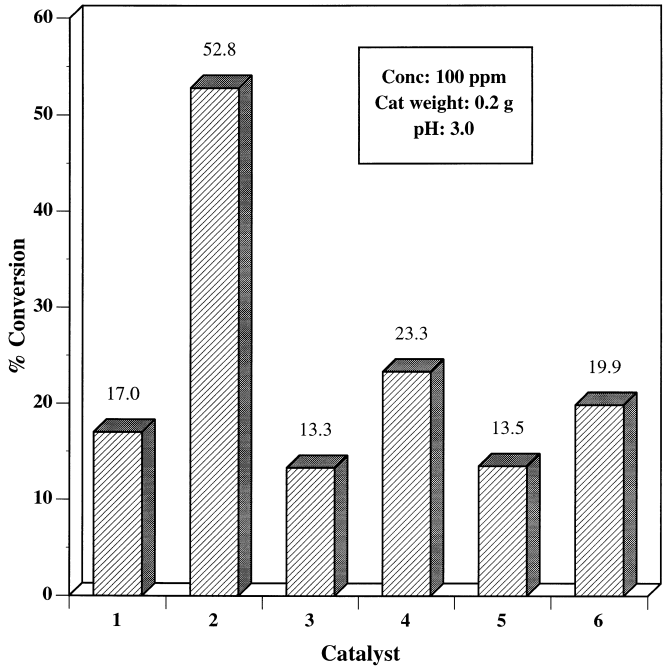

Fig. 4. Photocatalytic degradation of 4-chlorophenol with air injection at 40°C after 24 h of reaction: (1) Without catalysts; (2) TiO_2; (3) $BaTi_4O_9$; (4) Hollandite I; (5) Hollandite II; (6) Hollandite III.

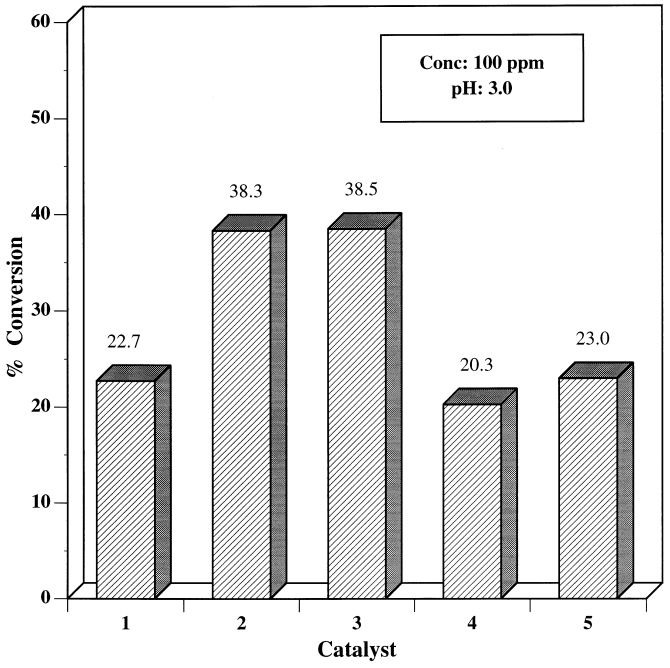

Fig. 5. Photocatalytic degradation of phenol with air injection at 30°C after 24 h of reaction: (1) Without catalysts; (2) 0.1 g of TiO_2; (3) 0.2 g of TiO_2; (4) 0.2 g of $BaTi_4O_9$; (5) 0.2 g of Hollandite II.

as Hollandite I produced slightly higher conversion than photochemical and thermal reactions produced without catalyst.

Since barium tetratitanate and Hollandite catalysts did not show high photocatalytic activities at 40°C, the reaction experiments at 30°C were carried out using 0.1 and 0.2 g of TiO_2, 0.2 g of barium tetratitanate and 0.2 g of Hollandite catalyst. The results of the photocatalytic degradation of phenol and 4-chlorophenol are presented in Figs. 5 and 6, respectively. These results confirm that titanium oxide is more active than the other catalysts. These results may also indicate that the photochemical reaction plays an important role for the degradation of phenol and 4-chlorophenol under these conditions.

Analysis of reaction samples of the photocatalytic degradation of phenol and 4-chlorophenol by HPLC showed the presence of hydroquinone and 1,4-benzoquinone. The identity of these reaction intermediates was confirmed by GC–MS analysis [31]. In these experiments, which were carried out in a slurry saturated with air and illuminated by a small fraction of long wave UV light, phenol and 4-chlorophenol undergo degradation primarily to form hydroquinone (HQ), which is then transformed to benzoquinone (BQ). Other studies [4,12,14–16] have also demonstrated that HQ is the major intermediate in air or nitrogen saturated slurry reactions.

The results of the photocatalytic degradation of phenol and 4-chlorophenol under UV light (λ_{max}=365 nm) are presented in Figs. 7 and 8, respectively. These results confirmed that phenol and 4-chlorophenol are easily degraded in the presence of TiO_2 illuminated by UV light. In this case, overall conversions of the reaction of phenol in the presence of barium titanate and Hollandite phase catalysts or without any catalyst are on the same order of magnitude. These results indicate that barium titanate and Hollandite catalysts can be slightly activated by UV light.

It is important to point out that barium titanate and Hollandite phase catalysts have very low surface areas in the order of 0.5 m^2/g and that the photocatalytic activities are reported in terms of catalysts weight instead of surface area. Since the catalytic activity usually increases with surface area, we have tried to prepare Hollandite phase catalysts by the sol–gel method in order to increase the surface area and

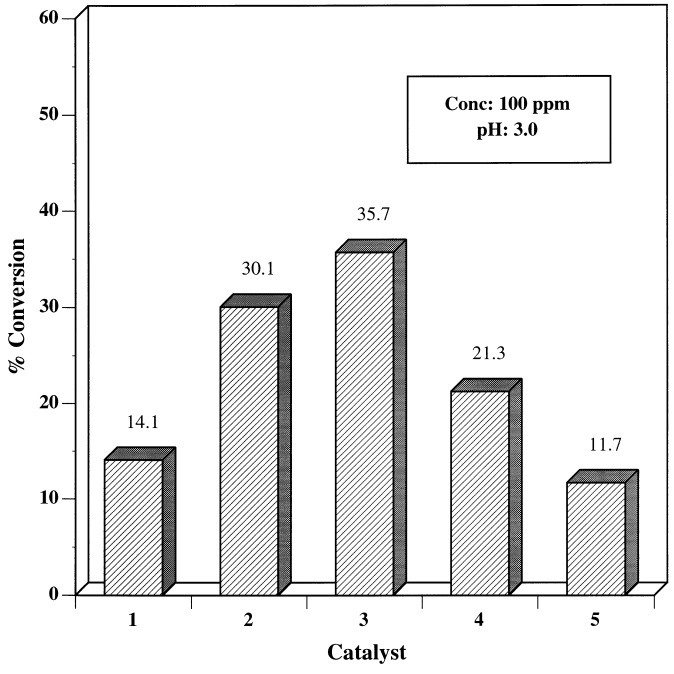

Fig. 6. Photocatalytic degradation of 4-chlorophenol with air injection at 30°C after 24 h of reaction: (1) Without catalysts; (2) 0.1 g of TiO_2; (3) 0.2 g of TiO_2; (4) 0.2 g of $BaTi_4O_9$; (5) 0.2 g of Hollandite II.

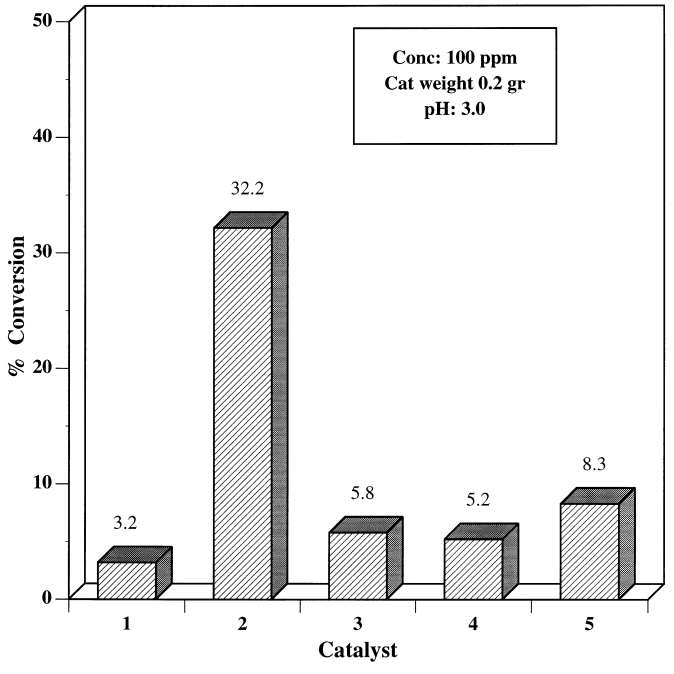

Fig. 7. Photocatalytic degradation of phenol with air injection at 30°C after 6 h of reaction under UV light illumination: (1) Without catalysts; (2) TiO_2; (3) BaT_4O_9; (4) Hollandite I; (5) Hollandite II.

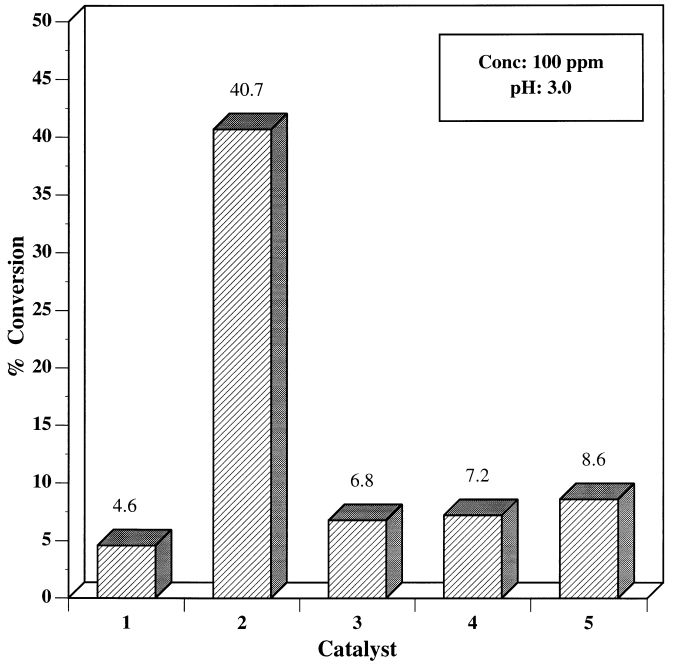

Fig. 8. Photocatalytic degradation of 4-chlorophenol with air injection at 30°C after 6 h of reaction under UV light illumination: (1) Without catalysts; (2) TiO_2; (3) $BaTi_4O_9$; (4) Hollandite I; (5) Hollandite II.

study the effect of surface area on the photocatalytic activity.

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