Synthesis of benzaldehyde from toluene by a photocatalytic oxidation using TiO2-pillared clays

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ABSTRACT

Photo-oxidation of toluene was investigated by using TiO2-pillared montmorillonite (Ti-montmorillonite). The main intermediates of toluene oxidation were benzaldehyde and *p*-cresol while traces of benzyl alcohol, benzoic acid, pyrogallol and hydroquinone were also found. The solvent effect on the photo-oxidation of toluene on Ti-montmorillonite was significant; the activity was increased by an addition of 10% water in acetonitrile solvent and it was further increased when the reaction was performed in an aqueous environment. In the latter condition, Ti-montmorillonite showed higher activity to benzaldehyde (the desired product) than TiO2 (Degussa P25), possibly because of the difference value of its surface area and the hydrophobic nature of pillared clay. The maximum yields in benzaldehyde using Ti-montmorillonite and TiO2 P25 as photocatalysts were 48 and 27%, respectively, after 1 h reaction time in the best experimental conditions.

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1. Introduction

The oxidation of aromatics to their corresponding compounds offers an attractive synthesis of higher-value products from relatively inexpensive feedstocks. However, many of the current pathways to produce these products are environmentally hazardous. From the environmental and economical point of view, recent research has focused on the oxidation under mild condition [1–5]. Heterogeneous photocatalysis employing semiconductive photocatalysts, such as TiO2, can offer an alternative catalytic oxidation technology, because the reaction is promoted under ambient temperature and pressure [6–14]. However, due to the high positive energy of the photogenerated holes on TiO2, the use of TiO2 has a potential problem that most organic compounds will undergo complete oxidation. In order to use it as a selective oxidation catalyst for fine chemical production, it is necessary to control its high oxidation power.

In thermally catalyzed oxidation, modification of the catalyst, such as an addition of promoters and formation of mixed oxides, is usually done in order to improve the selectivity. For the photocatalysis by TiO2, such attempts have not succeeded, because impurities and defects produced by such modifications drastically decrease the activity by increasing the recombination rate of the photoproduced charges [6,8]. On the other hand, it has been reported that there are some effects of solvent on the photo-oxidation of

liquid hydrocarbons by TiO2 [11,15]. For example Almquist and Biswas [15] recently showed that the reaction rate and selectivity to the formation of cyclohexanol and cyclohexanone in the photo-oxidation of cyclohexane on TiO2 depend on the solvent nature. It is therefore expected that the effectiveness of TiO2 photocatalysts for the partial oxidation reaction can be improved by controlling reaction environments.

It is well known that TiO2-pillared clays can provide large surface area and pores volume [16–21], which are beneficial for organic compounds to reach and leave the active sites on the surface. The size of the TiO2 pillars incorporated between the silicate layers is of nanometer dimension. It has been reported that TiO2-pillared clay is fairly effective for the photocatalytic degradation of organic substrates [18–20], and it exhibits shape selectivity because of its pore structure [18]. It is also expected that the sorption behavior of photocatalysts can be changed by including TiO2 particles in the silicate layer of the clays, and hence different property can be obtained for the photocatalytic reaction, depending on the surface properties of the host clays.

Toluene oxidation studies have been previously reported [22–34] Fujihira et al. [22] showed the formation of cresols by means of an oxidative attack to the aromatic ring and benzaldehyde and benzyl alcohol by side-chain oxidation, depending on the pH of the solution. The results reported in [22] were confirmed by Navio et al. [23] as they found benzyl alcohol, benzoic acid and benzaldehyde as products. They reported that benzaldehyde was the main product in all the experimental conditions investigated. Augugliaro et al. [35] have studied the photocatalytic oxidation of gaseous toluene on anatase catalyst and they indicated that

a highest molar conversion of toluene to benzaldehyde was ca. 20%. Using the heterogeneous CoSBA-15 catalyst for alkylaromatics liquid phase oxidation, Brutchey et al. [36] obtained maximum toluene conversion of 8% with 64% selectivity for benzaldehyde. The toluene oxidation studied by Rao et al. [37] yields about 22% conversion and 76% selectivity towards benzaldehyde. Liquid phase toluene oxidation with homogeneous metal salt catalysts has been realized industrially in the Rhodia, Dow, and Snia-Biscosa process using oxygen or peroxides as oxidants [25,38]. These processes operate at 165 °C in air under pressure of 10 atm in the presence of a homogeneous cobalt catalyst in acetic acid. Liquid withdrawn from the oxidation stage was fractionated and purified by distillation. In the first column (15–20 real plates), the light components, no transformed toluene, benzaldehyde, benzyl alcohol, formic and acetic acids, water, etc. were removed. The separation of organic and aqueous phases was done by cooling and decantation; then the organic phase was recycled again to the reactors whereas the aqueous has been sent to the waste water treatment. The recovered benzoic acid at the bottom is purified up to 99% (w/w) in a second column (≈20 plates) operating under vacuum (185 °C, 13 kPa at the top). One part of the withdrawn liquid constituted of benzyl benzoate, cobalt salt and heavy products is turned into the reaction section and the another one having low content in organic derivatives was water extracted for recovery of the catalyst, which will be recycled. In order to reach a sufficiently high level of benzaldehyde selectivity (91–93% molar), the conversion of toluene should be limited at maximum rate of 40% [39].

The aim of the present study was to use TiO_2-pillared clay for the photo-oxidation of toluene under mild conditions. Characterization of TiO_2-pillared clay is presented, which will show that the TiO_2 particles with almost the same structure are incorporated in clay. Reaction studies are focused on the effects of the solvent and pillaring process of clay for the selective oxidation of toluene. The solvent used was water/acetonitrile at different ratio. The addition of acetonitrile was for helping the dissolution of toluene in water. It is demonstrated that the use of water as a solvent and the inclusion of TiO_2 particles in the interlayer space of clay are effective to improve the activity of TiO_2 for the selective photo-oxidation catalysis.

2. Experimental

2.1. Preparation of oxidation catalysts

The pillared montmorillonite clays were prepared using bentonite from deposits of Maghnia in western Algeria. Its chemical composition in (wt.%) is SiO_2 69.4; Al_2O_3 14.7; Fe_2O_3 1.2; MgO 1.1; K_2O 0.8; Na_2O 0.5; CaO 0.3; TiO_2 0.2; As 0.05; LOI 11.65 (LOI: loss on ignition at 900 °C in wt.%) [40]. According to a previously reported procedure [40], the purified raw bentonite was dispersed in 1 M NaCl, separated from the solution and washed with water up to obtain a constant conductivity. The resulting suspension was placed in a graduate cylinder for allowing particles >2 μm in size to settle down. The suspension at the depth of 10 cm containing only particles of size <2 μm was collected with a "Robinson–Kohn" pipette. This operation was repeated several times until the suspension became almost transparent at the depth of 10 cm. Particles of a size <2 μm were recovered by centrifugation, washed with water and dialyzed to eliminate chloride ions in excess and finally dried at 40 °C for 72 h.

Na-montmorillonite was used for the pillaring process following a procedure previously reported [41]. Titanium tetraisopropoxide in solution was added to hydrochloric acid (5 M) in order to obtain a HCl/Ti molar ratio of 2.5. This solution was stirred at room temperature for 3 h. The intercalation was performed by adding
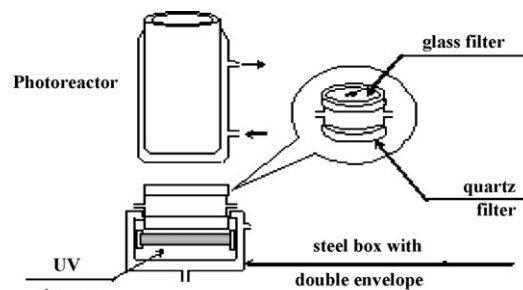

Fig. 1. Scheme of photoreactor.

(drop by drop) the pillaring solution to a water suspension of Na-montmorillonite (0.5 wt.%) up to reach a Ti/Na-montmorillonite ratio of 10 mmol/g. This mixture, with an acid concentration of 0.1 M, was stirred and allowed to react at room temperature for 12 h. The product was then centrifuged, washed with deionised water until chloride free. The solid was dried in a microwave oven with an average power of 300 W for 5 min and calcinated for 15 min at 500 W. This pillared sample was referred to as Ti-montmorillonite.

The TiO_2 employed for the reaction to study the effects of pillaring process was well characterized Degussa P25. It is known that this catalyst is 80/20 anatase-rutile phase and has a BET surface area and average particle size of 50 ± 10 m^2/g and 30 nm, respectively.

2.2. Physicochemical methods

X-ray diffraction (XRD) patterns were obtained using a diffractometer type Philips model PW 1840 with Ni-filtered Cu Kα radiation. In order to maximize the (0 0 1) reflection intensities, oriented specimens were prepared by spreading the sample on a glass slide and drying them at room temperature for 24 h.

Fourier Transform Infrared (FTIR) spectra were recorded with Shimadzu model 8900 spectrophotometer on KBr disc containing 0.5 wt.% of sample in KBr. Na- and Ti-montmorillonite sample were calcined before the analysis, but clay samples with adsorbed toluene was quite dried at 313 K during the night before analysis.

Surface areas and pore volumes were determined using nitrogen as the sorbate at −196 °C in a static volumetric apparatus (Micromeritics ASAP 2010 Sorptometer). The pillared clays were previously outgassed at 180 °C for 16 h under a vacuum of 6.6×10^{-9} bar. The surface areas were calculated using the BET equation from the linear part of the graph, usually located between 0.05 and 0.30 P/P_0. While the total pores volumes were evaluated by nitrogen physisorption at a relative pressure (p/p_0) of N_2 equal to 0.99.

2.3. Photocatalytic experiments

The photoreactor was a cylindrical flask (100 ml) made of Pyrex (Fig. 1), transmitting wavelength ≥340 nm. The irradiance spectrum of the Hg lamp (similar to the spectrum inside the reactor) is shown in Fig. 2. After cooling down to room temperature, toluene (0.5 mg/ml), water (20 ml) and catalyst (50 mg) were added into a reactor. The photoreactor was equipped with a condenser in order to prevent the toluene evaporation. The reaction mixture was stirred by magnetic stirrer and irradiated with a 125 W Hg lamp. The radiation energy incident on the suspension, measured by using a radiometer VLX-3W Digital mounted above the lamp at the same position as the photoreactor, was 40 mW cm^{-2} (corresponds to wavelength of 365 nm). After the toluene oxidation, the solution containing catalysts was filtered, and the products were
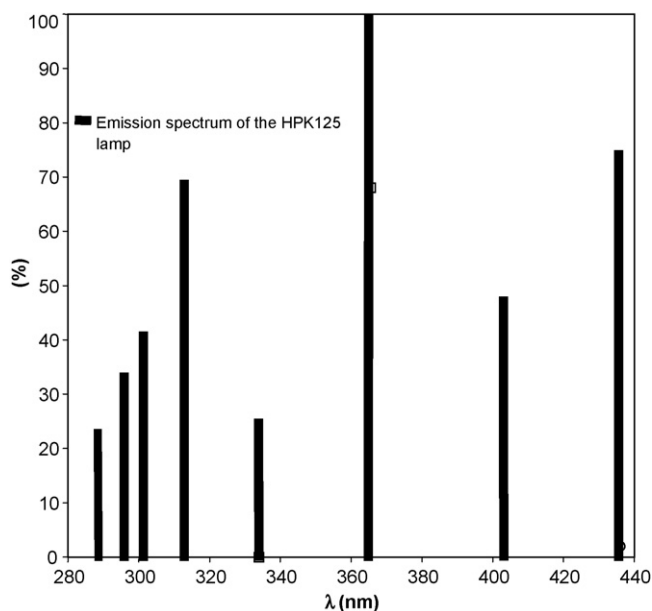
analyzed by HPLC (Shimadzu LC-10AT) and a Mightysil RD-18 GP column with UV detector.

Some experiments were carried out by using acetonitrile and mixture with water as solvent in order to demonstrate the major role played by water and the effect of the water addition to the acetonitrile solvent which is less polar than water, on the activity of Ti-montmorillonite in the toluene photo-oxidation.

In order to compare the photocatalytic activities of bentonite based catalyst, tests were carried out by shaking 15 mg of TiO_2 Degussa P25 (This quantity has been chosen taking into account that the TiO_2 content in the Ti-pillared montmorillonite is about 30% (w/w) so, we obtain a precise quantitative comparison with TiO_2) in 20 ml of water containing toluene (0.5 mg/ml) for 3 h.

3. Results and discussion

3.1. Characterization of catalysts

Extensive investigations on the physicochemical characterization of Ti-pillared clays have been previously reported [42–51]. XRD patterns and of Na-montmorillonite, Ti-montmorillonite and TiO_2 P25 are reported in Fig. 3. Relative basal spacing of the materials here investigated (Na-montmorillonite and Ti-montmorillonite) are reported in Table 1. The XRD patterns in the wide angle range indicates that Ti-montmorillonite show reflection at $2\theta = 25°$ due to the presence of anatase phase [45].

The reflections at small angle due to the basal d_{001} reflection of silicate layers allowed us to obtain information about the effect of intercalation on the basal spacing of the clay. In particular, it is seen that the diffraction peak at $2\theta = 7.0°$ of Na-montmorillonite is shifted to about $5.0°$ in Ti-montmorillonite. This shift clearly indicates an enlargement of the basal spacing of the clay as a consequence of the pillaring process (from 12.6 Å of the Na-montmorillonite to around 22 Å of the Ti-montmorillonite, see
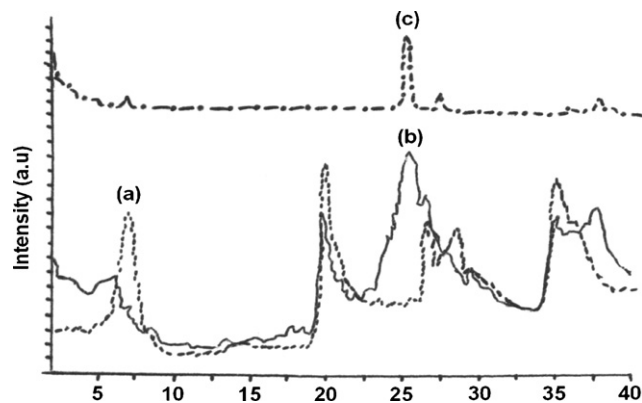

Fig. 3. X-ray diffraction pattern of (a) Na-montmorillonite, (b) Ti-montmorillonite and (c) TiO_2 P25.
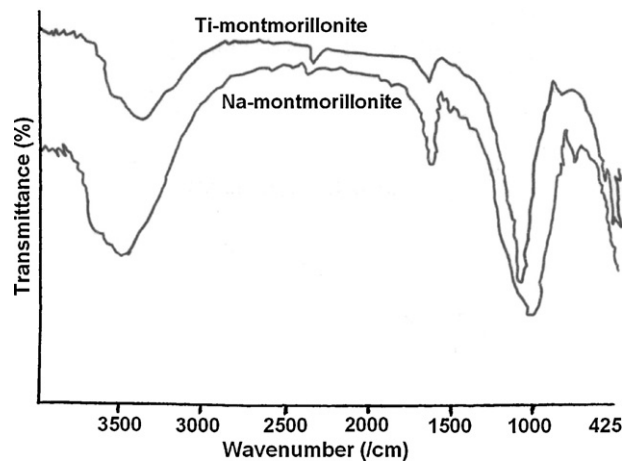

Fig. 4. IR spectra of Na-montmorillonite and pillared Ti-montmorillonite.

in Table 1). The observed enlargement of the basal spacing is due to the insertion of titanium species between montmorillonite layers. It is to note that a more intense and narrow diffraction peak in pillared clay could be due to the existence of different hydration states (adsorption of water during the purification of the clay), to the crystallization of the Ti polyoxocations, to the loss of the adsorbed hydration water (dehydration during the drying and the calcination of the pillared clay) or even to the different structures of titanium oxide (anatase and rutile) that may generate a more homogeneous pillar distribution (different Ti pillars similar in size) [52].

As a consequence of the pillaring process, the texture of the resulting clay is open and so, more accessible to adsorbate molecules. It can be seen in Table 1 that the specific surface area of the investigated pillared clay are about three times larger than that of the parent Na-montmorillonite due principally to the creation of a remarkable microporous network. The TiO_2 loading is mainly located in the interlayer spacing as pillars, although it is possible that it can be also settled in minor amounts over the montmorillonite sheets.

Fig. 4 shows the FTIR spectra of Na-montmorillonite and Ti-montmorillonite. Stretching vibrations of water molecules may

Table 1
Results of different characterization of catalysts.

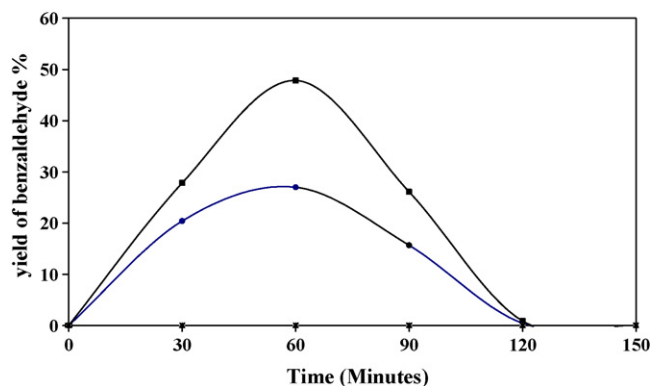|	Basal spacing (nm)	Specific surface (m²/g)	Pore volume (cm³/g)
Na-montmorillonite	1.26	78	0.10
Ti-montmorillonite	2.20	254	0.25

Fig. 5. Molar yield of benzaldehyde as a function of time in the photo-oxidation of toluene on Ti-montmorillonite and TiO₂ (P25). (■) Ti-pillared montmorillonite; (●) TiO₂ Degussa P25; (▲) irradiation without catalyst; (*) catalyst without irradiation. Reaction conditions: toluene 0.5 mg/ml, H₂O 20 ml, catalyst: 50 mg (Ti-montmorillonite) and 15 mg (TiO₂ P25).

contribute to −OH peaks $(3500\,cm^{-1})$. On pillaring, the band broadens due to the introduction of more −OH groups of the pillar, which is interpreted as an effect of pillaring [53]. The decrease in intensity arises from the dehydration and dehydroxylation steps during pillaring. Peak at around $1600\,cm^{-1}$ is due to bending vibrations of water. Pillaring process replaces a large amount of interlayer cations that generally exist as hydrated and it decreases the intensity of −OH peaks. Pillared clay has low amount of adsorbed/coordinated water due to the non-swellable nature. Thus, as a result of pillaring, intensity of the band around $1600\,cm^{-1}$ decreases [54]. The band around $1060\,cm^{-1}$ is due to asymmetric stretching vibrations of SiO_2 tetrahedra. A band around $800\,cm^{-1}$ is due to stretching vibration of Al^{IV} tetrahedra, and absorption at $526–471\,cm^{-1}$ is due to bending of Si–O vibration. Absorption bands due to adsorbed toluene (not shown) appear at the $3100–2800\,cm^{-1}$ (CH stretchings) and $1610–1500\,cm^{-1}$ (ring stretchings, CH deformations) ranges.

3.2. Oxidation of toluene

No measurable amount of oxidation products was obtained in the absence of the photo-irradiation or the catalyst. Such blank experiments were performed separately and in experimental conditions similar to those used for the photoreactivity experiments, indicating that the reaction was proceeding via a photocatalyzed mechanism. According to these results, it was observed that the maximum yield of benzaldehyde in the photo-oxidation of toluene in the absence of the photo-irradiation or without catalyst was very low (Fig. 5 curves almost identical with X-axis). Table 2 shows the effect of the solvent on the photo-oxidation of toluene over Ti-montmorillonite. Oxidation products were identified by HPLC using authentic standards and their quantification were obtained using a calibration curve for each product. The main oxidation product was benzaldehyde but also p-cresol, benzyl alcohol, benzoic acid, pyrogallol and hydroquinone were detected in the product. The result in Table 2 clearly shows that there is a significant effect of solvent on the activity and product distribution in the photo-oxidation of toluene. In the case of the acetonitrile as a solvent, the lowest activity for the partial oxidation of toluene was obtained. When 10% water was added to the acetonitrile solvent, the partial oxidation of toluene occurred as a main reaction, giving various products, and the yield for the product formation increased by a factor of ca. 2.6. This result is consistent with the previous report by Navio et al. [23], who observed that traces of water present in the reaction system play an important role in the distribution of products in the oxidation of neat toluene in liquid organic oxygenated dis-

Table 2
Photo-oxidation of toluene on Ti-montmorillonite by using various solvents[a].

	Solvent		
	CH₃CN	CH₃CN (10% H₂O)	H₂O
Products concentration (mg/ml) ×10³ (yield mol%)[b]			
Benzaldehyde	57.4 (10)	148.2 (25.7)	276.5 (48.01)
p-Cresol	35.0 (5.9)	89.7 (15.25)	128.2 (22.7)
Benzyl alcohol	2.2 (1.4)	5.8 (1.02)	7.8 (1.36)
Benzoic acid	1.6 (0.23)	3.9 (0.6)	5.6 (0.83)
Pyrogallol	0.8 (0.15)	1.8 (0.29)	2.7 (0.36)
Hydroquinone	0.6 (0.08)	1.5 (0.25)	2.5 (0.41)
Σ Oxygenates[c]	97.6 (17.8)	250.9 (43.1)	423.3 (73.6)

[a] Reaction conditions: toluene 0.5 mg/ml, solvent 20 ml, catalyst 50 mg Ti-montmorillonite, reaction time 1 h.
[b] Yield is calculated as concentrations of specified products (mg/ml)/toluene initial concentration (mg/ml).
[c] Sum of the oxygenates concentration.

persions containing pure or iron-doped titania photocatalysts. A similar effect of water was also reported by Gonzalez et al. [12], who showed that use of water as a solvent is effective to achieve high activity in the liquid phase selective oxidation of hydrocarbons on TiO₂ photocatalyst.

When the reaction was performed by using the water alone as a solvent, the partial oxidation of toluene occurred as a main reaction, and the highest activity was observed. The yield to the oxidation product was ca. four times higher than in the acetonitrile alone. The observed increase in the activity may be due to the enhanced amount of hydroxyl radicals formed by the oxidation of water by positive holes on the TiO₂ pillars. This result is consistent with the previous report by Shimizu et al. [44], who demonstrate the solvent effect, both on the activity and the selectivity of the TiO₂-pillared clays in the photo-oxidation of benzene. This present catalyst (Ti-montmorillonite) exhibits so interesting yield (48%) and selectivity (65%) of toluene conversion into benzaldehyde when compared with those obtained previously [35–37].

Fig. 5 shows the time course of benzaldehyde (the desired product because it is important as it is largely used to synthesize pharmaceutical products or to aromatize perfumes) in the photo-oxidation of toluene on Ti-montmorillonite and P25. Ti-montmorillonite showed the higher activity of toluene partial oxidation than P25. The yields of benzaldehyde on Ti-montmorillonite and P25 were around 48 and 27%, respectively after 1 h reaction time using water as solvent. (In acetonitrile, they were 9.5 and 5.2%, respectively, and 25 and 10.5%, respectively by addition of 10% water to the acetonitrile.) The result in Fig. 5 clearly shows that the pillaring process has a positive effect on the yield enhancement of the photo-oxidation of toluene on TiO₂. Previously, Malla et al. [17] reported an unusual water adsorption behavior of various pillared clays, which should be indicative of the hydrophobic nature of the surface of the pillared clays. Adsorption isotherms of toluene on Ti-montmorillonite and Na-montmorillonite (Fig. 6) were carried out in order to justify an extensive adsorption capacity of toluene on the photocatalyst synthesized. As shown in (Fig. 6), Ti-montmorillonite exhibits higher affinity for the toluene rather than Na-montmorillonite. This indicates the hydrophobic character of Ti-montmorillonite. A similar result was also reported by Shimizu et al. [44], who showed the hydrophobic nature of the surface of TiO₂-pillared clays as compared with P25 in competitive adsorption experiments using benzene and phenol as substrate. The hydrophilicity of the TiO₂ originates from the surface hydroxyl groups. In the literature, it was conjectured that the surface hydrophobicity of pillared clays was related to the decrease in polarity of the clay surface by exchange of cations in the interlayer with metal oxide pillar [55–58]. The observed activity enhance-
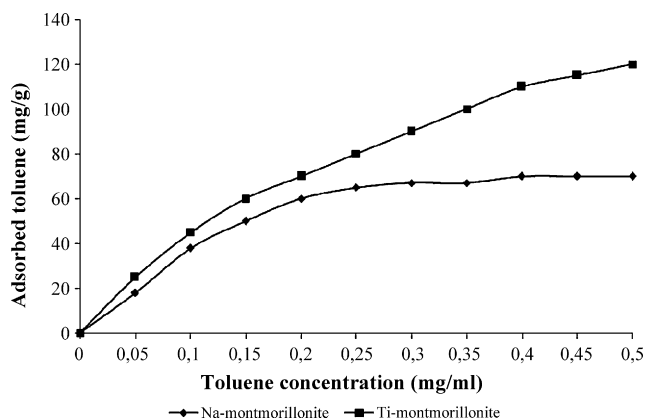
Fig. 6. Adsorption isotherms of toluene on Ti-montmorillonite and Na-montmorillonite.

ment of TiO_2 photocatalyst by using clay host may be explained as follows. Nonpolar substrate, hydrocarbon (toluene), would be more accessible to the hydrophobic surface of Ti-montmorillonite than to the hydrophilic surface of TiO_2. When the partially oxygenated product (benzaldehyde) is produced on the catalysts, the adsorption of the polar products on the hydrophobic Ti-montmorillonite is inhibited by nonpolar hydrocarbon, and the oxidation product is desorbed in the aqueous phase, resulting in its higher activity. On the other hand, the products can be present on hydrophilic surface of TiO_2, which will result in the over-oxidation to CO_2.

4. Conclusion

In the Ti-montmorillonite prepared in the aqueous solution of hydrochloric acid, TiO_2 small particles with anatase-like structure are present in the silicate layers of clay. For the photo-oxidation of toluene, there is a significant effect of solvent on the activity of Ti-montmorillonite. When the photocatalytic reaction was performed in the aqueous environment by using the water as a solvent, the highest activity was obtained. Ti-montmorillonite showed higher activity for benzaldehyde (the desired product) than TiO_2 (P25), thus the inclusion of TiO_2 in clay host is effective for the activity enhancement in the partial oxidation of toluene, possibly because of the hydrophobic nature and the higher of the specific surface area of pillared clay.

References

[1] S. Ito, A. Kunai, H. Okada, K. Sasaki, Direct conversion of benzene to hydroquinone. Cooperative action of copper (I) ion and dioxygen, Journal of Organic Chemistry 53 (1988) 296.
[2] T. Ohtani, S. Nishiyama, S. Tsuruya, M. Masai, Liquid-phase benzene oxidation to phenol with molecular-oxygen catalyzed by Cu-zeolites, Journal of Catalysis 155 (1995) 158.
[3] N. Komiya, T. Naota, Y. Oda, S.I. Murahashi, Aerobic oxidation of alkanes and alkenes in the presence of aldehydes catalyzed by copper salts and copper-crown ether, Journal of Molecular Catalysis A: Chemical 117 (1997) 21.
[4] I. Yamanaka, M. Katagiri, S. Takenaka, K. Otsuka, Direct synthesis of phenol from benzene with O_2 over VMo-oxide/SiO_2 catalyst, Studies in Surface Science and Catalysis 130 (2000) 809.
[5] K. Teramura, T. Tanaka, M. Kani, T. Hosokawa, T. Funabiki, Selective photo-oxidation of neat cyclohexane in the liquid phase over V_2O_5/Al_2O_3, Journal of Molecular Catalysis A: Chemical 208 (2004) 299.
[6] W. Mu, J. Herrmann, P. Pichat, Room temperature photocatalytic oxidation of liquid cyclohexane into cyclohexanone over neat and modified TiO_2, Catalysis Letters 3 (1989) 73.
[7] M.A. Fox, H. Ogawa, P. Pichat, Regioselectivity in the semiconductor-mediated photooxidation of 1,4-pentanediol, Journal of Organic Chemistry 54 (1989) 3847.
[8] P. Pichat, Partial or complete heterogeneous photocatalytic oxidation of organic compounds in liquid organic or aqueous phases, Catalysis Today 19 (1994) 313.
[9] H. Yamashita, S. Kawasaki, Y. Ichihashi, M. Harada, M. Takeuchi, M. Anpo, G. Stewart, M.A. Fox, C. Louis, M. Che, Characterization of titanium−silicon binary oxide catalysts prepared by the sol−gel method and their photocatalytic reactivity for the liquid-phase oxidation of 1-octanol, Journal of Physical Chemistry B 102 (1998) 5870.
[10] T. Ohno, K. Nakabeya, M. Matsumura, Epoxidation of olefins on photoirradiated titanium dioxide powder using molecular oxygen as an oxidant, Journal of Catalysis 176 (1998) 76.
[11] P. Boarini, V. Carassiti, A. Maldotti, R. Amadelli, Photocatalytic oxygenation of cyclohexane on titanium dioxide suspensions: effect of the solvent and of oxygen, Langmuir 14 (1998) 2080.
[12] M.A. Gonzalez, S.G. Howell, S.K. Sikdar, Research note photocatalytic selective oxidation of hydrocarbons in the aqueous phase, Journal of Catalysis 183 (1999) 159.
[13] K. Teramura, T. Tanaka, T. Yamamoto, T. Funabiki, Photo-oxidation of cyclohexane over alumina-supported vanadium oxide catalyst, Journal of Molecular Catalysis A: Chemical 165 (2001) 299.
[14] P. Du, J.A. Moulijn, G. Mul, Selective photo(catalytic)-oxidation of cyclohexane: effect of wavelength and TiO_2 structure on product yields, Journal of Catalysis 238 (2006) 342.
[15] C.B. Almquist, P. Biswas, The photo-oxidation of cyclohexane on titanium dioxide: an investigation of competitive adsorption and its effects on product formation and selectivity, Applied Catalysis A: General 214 (2001) 259.
[16] S. Yamanaka, T. Nishihara, M. Hattori, Preparation and properties of titania pillared clay, Materials Chemistry and Physics 17 (1987) 87.
[17] P. Malla, S. Yamanaka, S. Komaneri, Unusual water vapor adsorption behavior of montmorillonite pillared with ceramic oxides, Solid State Ionics 32/33 (1989) 354.
[18] H. Yoneyama, S. Haga, S. Yamanaka, Photocatalytic activities of microcrystalline titania incorporated in sheet silicates of clay, Journal of Physical Chemistry 93 (1989) 4833.
[19] C. Ooka, S. Akita, Y. Ohashi, T. Horiuchi, K. Suzuki, S. Komai, H. Yoshida, T. Hattori, Crystallization of hydrothermally treated TiO_2 pillars in pillared montmorillonite for improvement of the photocatalytic activity, Journal of Materials Chemistry 9 (1999) 2943.
[20] Z. Ding, H.Y. Zhu, G.Q. Lu, P.F. Greenfield, Photocatalytic properties of titania pillared clays by different drying methods, Journal of Colloid and Interface Science 209 (1999) 193.
[21] Y. Kitayama, T. Kodama, M. Abe, H. Shimitsuma, Y. Matsuda, Synthesis of titania pillared saponite in aqueous solution of acetic acid, Journal of Porous Materials 5 (1998) 121.
[22] M. Fujihira, Y. Satoh, T. Osa, Heterogeneous photocatalytic oxidation of aromatic compounds on TiO_2, Nature 293 (1981) 206.
[23] J.A. Navio, M.G. Gómez, M.A.P. Adrian, J.F. Mota, Partial or complete heterogeneous photocatalytic oxidation of neat toluene and 4-picoline in liquid organic oxygenated dispersions containing pure or iron-doped titania photocatalysts, Journal of Molecular Catalysis A: Chemical 104 (1996) 329.
[24] G. Marci, M. Addamo, V. Augugliaro, S. Coluccia, Photocatalytic oxidation of toluene on irradiated TiO_2: comparison of degradation performance in humidified air, in water and in water containing a zwitterionic surfactant, Journal of Photochemistry and Photobiology A: Chemistry 160 (2003) 105.
[25] K. Nomiya, K. Hashino, Y. Nemoto, M. Watanabe, Oxidation of toluene and nitrobenzene with 30% aqueous hydrogen peroxide catalyzed by vanadium (V)-substituted polyoxometalates, Journal of Molecular Catalysis A: Chemical 176 (2001) 79.
[26] A. Dimitri, Transient kinetics of toluene partial oxidation over V/Ti oxide catalysts, Catalysis Today 61 (2000) 271.
[27] B. Louis, F. Rainone, B. Viswanathan, A. Renken, T.K. Varadarajan, Partial oxidation of toluene by O_2 over mesoporous Cr–AlPO, Catalysis Communications 3 (2002) 45.
[28] H. Einaga, Heterogeneous photocatalytic oxidation of benzene, toluene, cyclohexene and cyclohexane in humidified air: comparison of decomposition behavior on photoirradiated TiO_2 catalyst, Applied Catalysis B: Environmental 38 (2002) 215.
[29] L. Cao, Z. Gao, S.L. Suib, N. Obee, O. Hay, J.D. Freihaut, Photocatalytic oxidation of toluene on nanoscale TiO_2 catalysts: studies of deactivation and regeneration, Journal of Catalysis 196 (2000) 253.
[30] E.C. Butler, A.P. Davis, Photocatalytic oxidation in aqueous titanium dioxide suspensions: the influence of dissolved transition metals, Journal of Photochemistry and Photobiology A: Chemistry 70 (1993) 273.
[31] M. Sleiman, P. Conchon, C. Ferronato, J.-M. Chovelon, Photocatalytic oxidation of toluene at indoor air levels (ppbv): towards a better assessment of conversion, reaction intermediates and mineralization, Applied Catalysis B: Environmental 86 (2009) 159–165.
[32] D. Kibanova, M. Trejo, H. Destaillats, J.C. Silva, Synthesis of hectorite–TiO_2 and kaolinite–TiO_2 nanocomposites with photocatalytic activity for the degradation of model air pollutants, Applied Clay Science 42 (2009) 563.
[33] R. Khan, T.-J. Kim, Preparation and application of visible-light-responsive Ni-doped and SnO_2-coupled TiO_2 nanocomposite photocatalysts, Journal of Hazardous Materials 163 (2009) 1179.
[34] D. Kibanova, J. Cervini-Silva, H. Destaillats, Efficiency of clay-TiO_2 nanocomposites on the photocatalytic elimination of a model hydrophobic air pollutant, Environmental Science and Technology 43 (2009) 1500.
[35] V. Augugliaro, S. Coluccia, V. Loddo, L. Marchese, G. Martra, L. Palmisano, M. Schiavello, Photocatalytic oxidation of gaseous toluene on anatase TiO_2 catalyst: mechanistic aspects and FT-IR investigation, Applied Catalysis B: Environmental 20 (1999) 15.

[36] R.L. Brutchey, I.J. Drake, A.T. Bell, T.D. Tilley, Liquid-phase oxidation of alkylaromatics by a H-atom transfer mechanism with a new heterogeneous CoSBA-15 catalyst, Chemical Communications (2005) 3736.

[37] K.T. Venkateswara Rao, P.S.N. Rao, P. Nagaraju, P.S. Sai Prasad, N. Lingaiah, Room temperature selective oxidation of toluene over vanadium substituted polyoxometalate catalysts, Journal of Molecular Catalysis A: Chemical 303 (2009) 84.

[38] Y. Ishii, S. Sakaguchi, T. Iwahama, Innovation of hydrocarbon oxidation with molecular oxygen and related reactions, Advanced Synthesis & Catalysis 343 (2001) 393.

[39] A. Chauvel, G. Lefebre, L. Gastex, Procédés de pétrochimie, caractéristiques techniques et économiques, Les grands intermédiaires oxygénés, chlorés et nitres, Tome 2, 2e édition, Paris, 1986, pp. 210–225.

[40] H. Khalaf, O. Bouras, V. Perrichon, Synthesis and characterisation of Al-pillared and cationic surfactant modified Algerian bentonite, Microporous Material 8 (1997) 141.

[41] J.L. Valverde, P. Sanchez, F. Dorado, C.B. Molina, A. Romero, Influence of the synthesis conditions on the preparation of titanium-pillared clays using hydrolyzed titanium ethoxide as the pillaring agent, Microporous and Mesoporous Materials 54 (2002) 155.

[42] J.L. Valverde, P. Sanchez, F. Dorado, I. Asencio, A. Romero, preparation and characterization of Ti-pillared clays using Ti alkoxides. Influence of the synthesis parameters, Clays and Clay Minerals 51 (2003) 41.

[43] A. Romero, F. Dorado, I. Asencio, P.B. Garcia, J.L. Valverde, Ti-pillared clays: synthesis and general characterization, Clays and Clay Minerals 54 (2006) 737.

[44] K.-I. Shimizu, T. Kaneko, T. Fujishima, T. Kodama, H. Yoshida, Y. Kitayama, Selective oxidation of liquid hydrocarbons over photoirradiated TiO_2 pillared clays, Applied Catalysis A: General 225 (2002) 185.

[45] N. Jagtap, V. Ramaswamy, Oxidation of aniline over titania pillared montmorillonite clays, Applied Clay Science 33 (2006) 89.

[46] N.N. Binitha, S. Sugunan, Preparation, characterization and catalytic activity of titania pillared montmorillonite clays, Microporous and Mesoporous Materials 93 (2006) 82.

[47] B. Damardji, H. Khalaf, L. Duclaux, B. David, Preparation of TiO_2-pillared montmorillonite as photocatalyst. Part I. Microwave calcination, characterisation, and adsorption of a textile azo dye, Applied Clay Science 44 (2009) 201.

[48] S. Yamanaka, K. Makita, Optical and electrochemical properties of titania pillared clays, Journal of Porous Materials 1 (1995) 29.

[49] P. Pichat, H. Khalaf, D. Tabet, M. Houari, M. Saidi, Ti-montmorillonite as photocatalyst to remove 4-chlorophenol in water and methanol in air, Environmental Chemistry Letters 2 (2005) 191.

[50] C. Ookaa, H. Yoshida, M. Horio, K. Suzuki, T. Hattori, Adsorptive and photocatalytic performance of TiO_2 pillared montmorillonite in degradation of endocrine disruptors having different hydrophobicity, Applied Catalysis B: Environmental 41 (2003) 313.

[51] O. Bouras, T. Chami, M. Houari, H. Khalaf, J.C. Bollinger, M. Baudu, Removal of sulfacid pink from an aqueous stream by adsorption onto surfactant modified Ti-pillared montmorillonite, Environmental Technology 23 (2002) 405.

[52] K. Bahranowski, E.M. Serwicka, ESR study of vanadium-doped alumina- and titania-pillared montmorillonites, Colloids and Surfaces A: Physicochemical and Engineering Aspects 72 (1993) 153.

[53] M. Kurian, S. Sugunan, Liquid phase benzylation of o-xylene over pillared clays, Indian Journal of Chemistry 42A (2003) 2480.

[54] L. Poppl, E. Toth, I. Paszli, V. Izvekov, M. Gabor, Synthesis and characterizations of hydroxy-aluminum cross-linked montmorillonite, Journal of Thermal Analysis and Calorimetry 53 (1998) 585.

[55] P.B. Malla, S. Komarneni, Synthesis of highly microporous and hydrophilic alumina-pillared montmorillonite: water-sorption properties, Clays and Clay Minerals 38 (1990) 363.

[56] H.Y. Zhu, W.H. Gao, E.F. Vansant, The porosity and water adsorption of alumina pillared montmorillonite, Journal of Colloid and Interface Science 171 (1995) 377.

[57] H.Y. Zhu, S. Yamanaka, Molecular recognition by Na-loaded alumina pillared clay, Journal of Chemical Society 93 (1997) 477.

[58] C. Ooka, H. Yoshida, K. Suzuki, T. Hattori, Highly hydrophobic TiO_2 pillared clay for photocatalytic degradation of organic compounds in water, Microporous and Mesoporous Materials 67 (2004) 143.