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### An easy and efficient use of TiO<sub>2</sub> supported HZSM-5 and TiO<sub>2</sub> + HZSM-5 zeolite combinate in the photodegradation of aqueous phenol and *p*-chlorophenol<sup> $\ddagger$ </sup>

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#### Abstract

Titanium(IV) oxide of 2, 5, 10, and 15 wt.% was supported on HZSM-5 zeolite using solid state dispersion (SSD) method. These catalysts were characterized by BET surface area, XRD, UV–VIS–DR-spectra and SEM–EDAX. Characterization of TiO<sub>2</sub>/HZSM-5 (SSD) catalysts clearly shows that TiO<sub>2</sub> dispersed in solid state is free of interaction with the zeolite. The photocatalytic activity of these systems in the degradation of aqueous phenol and *p*-chlorophenol indicates that TiO<sub>2</sub>/HZSM-5 (SSD) is an active photocatalyst; the optimum photodegradation activity is seen at 10–15 wt.% TiO<sub>2</sub>/HZSM-5. The same activity is also achieved by simply suspending TiO<sub>2</sub> + HZSM-5 combinate (mechanical mixture) in aqueous phenol and *p*-chlorophenol. Based on these results, a model highlighting the photodegradation activity of both immobilized [TiO<sub>2</sub>/HZSM-5 (SSD)] and mobilized [TiO<sub>2</sub> + zeolite (combinate)] TiO<sub>2</sub>, which may lead to the development of an easy and effective technology in wastewater treatments, is proposed.

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#### 1. Introduction

The literature has well established the photocatalytic oxidation as an efficient method for purification of air and water pollutants [1-3]. Though, TiO<sub>2</sub> in anatase phase is the best photocatalyst reported so far, poor adsorption properties lead to great limitation in

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exploiting the photocatalyst to the best of its photoefficiency. Supporting TiO<sub>2</sub> is commonly reported to be less photoactive due to the interaction of TiO<sub>2</sub> with support during the thermal treatments [2]. Several attempts have been made to improve the photoefficiency of titania by adding adsorbents like silica, alumina, zeolites, clays, and active carbon [4–8]. This addition is expected to induce synergism because of the adsorption properties with respect to organic molecules. Synergistic effects were also evidenced when mixtures of TiO<sub>2</sub> and adsorbents like active carbon were employed for photooxidation of pollutants in gaseous and in aqueous phase [4,8]. Zeolite-based photocatalysis is new and the work reported so far involved the

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use of high TiO<sub>2</sub> loadings [9]. Photocatalytic activity of TiO<sub>2</sub>/HZSM-5 prepared by impregnating titania sol for the photodegradation of 4-chlorophenol is reported [10]. A method of supporting  $TiO_2$  on zeolite, without losing the photosensitization of TiO<sub>2</sub> and the adsorption properties of zeolite, is the important aspect while preparing zeolite-based photocatalysts. Studies in this laboratory [11] on preparation, characterization and photocatalytic evaluation of TiO2-supported zeolites prepared by Ti-isopropoxide (Ti-ISOP) and Ti-sol impregnation showed that photoefficiency of TiO<sub>2</sub> is suppressed when Ti is in interaction with the zeolite. With this background, we made an attempt to develop such a preparative method where  $TiO_2$  is supported on a zeolite without losing photoefficiency and affecting the adsorption properties of zeolite. The present investigation reports, the first results of supporting  $TiO_2$  on a zeolite along with an easy and efficient use of TiO2-zeolite mechanical mixture (combinate) for the degradation of aqueous phenol and *p*-chlorophenol.

#### 2. Experimental

#### 2.1. Chemicals

Phenol and *p*-chlorophenol were from Wako Pure Chemical Industries, Japan, with above 99% of purity. Titanium dioxide P25 is from Degussa Corporation, Germany. Sodium chloride, sodium sulphate and phthalic acid were of analar grade. Methanol employed was of HPLC grade. Zeolite HZSM-5 (30) was obtained from PQ Corporation, USA.

# 2.2. Preparation of TiO<sub>2</sub>-supported HZSM-5 catalysts

Zeolite-based photocatalysts were prepared by solid state dispersion (SSD) of TiO<sub>2</sub>. SSD initially involves mixing of TiO<sub>2</sub> and zeolite thoroughly using ethanol in agate pestle and mortar; the solvent was then removed by evaporation while mixing. Samples prepared by this method were dried at 110 °C and calcined in air at 450 °C for 6 h to obtain TiO<sub>2</sub>-supported zeolite catalysts. TiO<sub>2</sub> weight was maintained to obtain 2, 5, 10, and 15 wt.% in the finished forms of the catalyst. The same TiO<sub>2</sub>% is maintained while using

 $TiO_2 + HZSM-5$  mechanical mixtures (MECMIX) as a photocatalyst.

#### 2.3. Characterization of photocatalysts

BET surface areas of HZSM-5 and TiO<sub>2</sub>/HZSM-5 were measured in an all-glass high vacuum system by N<sub>2</sub> adsorption at 77 K. Powder diffraction patterns were recorded with a Siemens D-5000 powder X-ray diffractometer using Cu K $\alpha$  radiation. UV–VIS–DR-spectra were recorded on Cintra 10<sub>e</sub> spectrometer using pellets of 50 mg sample ground with 2.5 g of KBr. Samples were mounted on aluminium using double-sided adhesive tape, coated with gold in HUS–SGB vacuum coating unit and observed in Hitachi S-520 scanning electron microscope. Elemental analysis was carried out using Link, ISIS-300, Oxford EDAX detector.

#### 2.4. Photocatalytic experiments

Prior to photocatalytic experiments, photolysis experiments were carried out for phenol and *p*-chlorophenol under the same experimental conditions as used for photodegradation reactions. About 2.5% photolysis is observed for phenol at 30 min illumination. For *p*-chlorophenol, the conversion in photolysis experiment is very high and HPLC analysis showed about 11 products which undergo no further degradation. Earlier reports also confirm this observation [12,13]. The dark experiments of phenol and *p*-chlorophenol on bare TiO<sub>2</sub> show that the adsorptions of both these substrates on TiO<sub>2</sub> are relatively low (<10% of the initial concentration) compared to those on HZSM-5 zeolite (Figs. 4 and 5).

Degradation experiments were carried out on TiO<sub>2</sub>, HZSM-5, TiO<sub>2</sub>/HZSM-5 (SSD) and TiO<sub>2</sub> + HZSM-5 mechanical mixtures in aqueous suspensions. A 75 mg of the catalyst was suspended in 25 ml of phenol ( $10^{-4}$  M) and *p*-chlorophenol ( $10^{-3}$  M) in a Pyrex glass bottle, and the adsorption in the dark was followed for 1 h while stirring magnetically. After the dark experiment, a 500 W super high pressure mercury lamp illuminated the bottle through a water filter. The light intensity was 18 mW cm<sup>-2</sup> in the 330–390 nm region. Samples of the suspension were removed at regular intervals for analysis. Phenolic compounds were analyzed by a HPLC consisting of a Hitachi L-6000 pump and a M/s Shimadzu SPD-10A UV detector (at  $\geq$ 280 nm) with a reverse phase ODS column. Chloride and sulphate ions were analyzed by ion-chromatography consisting of the same pump as earlier and a conductivity detector, Shodex CD-4.

#### 3. Results and discussion

#### 3.1. Characterization of photocatalysts

TiO<sub>2</sub> samples supported over HY, HZSM-5 and H $\beta$  zeolites using various precursors like TiO<sub>2</sub>, Ti-isopropoxide (Ti-ISOP) and Ti-sol are extensively studied in this laboratory [11] for the photocatalytic degradation of aqueous phenol and *p*-chlorophenol. Of all the systems studied, TiO<sub>2</sub> dispersed in solid state over HZSM-5 is found to be the best photocatalyst. As the present paper is aimed at highlighting the TiO<sub>2</sub>/HZSM-5 (SSD) and TiO<sub>2</sub> + HZSM-5 mechanical mixture, the characterization of TiO<sub>2</sub>/HZSM-5 (SSD) is discussed in comparison with TiO<sub>2</sub>/HZSM-5 photocatalysts prepared by Ti-ISOP and Ti-sol impregnation to understand the structure–activity correlation on TiO<sub>2</sub>/HZSM-5 (SSD) photocatalysts.

#### 3.2. XRD

The XRD patterns of TiO2-supported HZSM-5 (SSD) are shown in Fig. 1. Both calcined and uncalcined catalysts show identical patterns, indicating no change on calcination. SSD of preformed TiO<sub>2</sub> with a particle size of 27 nm on HZSM-5 show all the characteristic lines of anatase at 10 wt.% TiO<sub>2</sub> loading. The anatase phase is observed only at higher TiO<sub>2</sub> loadings on Ti-ISOP impregnated HZSM-5 and no line broadening of anatase is observed on Ti-sol impregnated zeolite even at 15 wt.% TiO2 loading. A further sample, 30 wt.% TiO2/HZSM-5 using Ti-sol is prepared to examine the line broadening on this system. Earlier work [14-16] on Ti-precursors exchange with the zeolites and supporting TiO<sub>2</sub> colloids clearly demonstrates that formation of TiO<sub>2</sub> phase on supports is governed by the nature of the precursor and the method of preparation. Our XRD observations clearly show that Ti is in interaction with the zeolite when Ti-sol and Ti-ISOP are used as precursors, especially at lower loadings of TiO<sub>2</sub>. The presence of a well-defined anatase phase on 10 wt.% TiO<sub>2</sub>/HZSM-5 prepared by SSD indicates the minimum possibility of such an interaction on these catalysts.

#### 3.3. UV–VIS diffuse reflectance spectra

The monomodal DR-spectra of calcined and uncalcined TiO<sub>2</sub>/HZSM-5 (SSD) photocatalysts are shown in Fig. 2. These spectra are examined to understand the size quantization effect and the TiO<sub>2</sub> interaction with the zeolite. The position of the absorption edge for anatase around 380 nm corresponds to a band gap energy of 3.2 eV; it is blue-shifted by about 40-50 nm at low loadings of TiO2 and the shift is decreased with increasing TiO<sub>2</sub> loading. The DR-spectra of Ti-ISOP/HZSM-5 resemble TiO<sub>2</sub>/HZSM-5 (SSD) at higher TiO<sub>2</sub> loadings. This may be seen as an indirect indication of TiO<sub>2</sub> particle size resulting from the precursor and method of preparation. For example, Ti-ISOP may interact with zeolite at low loadings, and at higher loadings, the hydrolyzed precursor may decompose and form small crystallites directly during calcination in air. The shift is maximum on Ti-sol impregnated HZSM-5. One plausible explanation comes from the use of small particles of Ti-sol (nano size) that may interact with the zeolite during calcinations through dehydroxylation. Earlier studies on Ti-precursor exchanged zeolite show that, in the absence of microdomains and crystalline TiO<sub>2</sub> (XRD), the blue-shift in the DR-spectra is clear evidence for the formation of Ti–O–Si linkage [14]. A thorough examination of DR-spectra of Ti-ISOP and Ti-sol impregnated zeolites in our study show that in general on Ti-ISOP/zeolites, the blue-shift decreases with increasing TiO<sub>2</sub> and on Ti-sol/zeolites, the blue-shift decrease is nominal with increasing TiO<sub>2</sub> loading. Both these observations support the possibility of the Ti–O–Si linkage at low loadings of TiO<sub>2</sub> and, with increasing TiO<sub>2</sub>, formation of microdomains. Thus, a decrease in blue-shift value on TiO2/HZSM-5 (SSD) catalysts with increasing TiO<sub>2</sub> loading may confirm the absence of Ti-O-Si linkage in these catalysts. Slight differences observed in the band edge position on calcinations (Fig. 2B) may show that heat treatment improves the dispersion of TiO<sub>2</sub> in solid state.

#### 3.4. SEM-EDAX

SEM photographs of TiO<sub>2</sub>/HZSM-5 prepared by SSD are shown in Fig. 3. It is observed that HZSM-5



Fig. 1. XRD patterns of  $TiO_2$ /HZSM-5 (SSD) catalysts: (A) uncalcined and (B) calcined. Patterns: (1) HZSM-5, (2–5) 2, 5, 10, and 15 wt.%  $TiO_2$ /HZSM-5 and (6)  $TiO_2$ .

morphology is changed where preformed TiO<sub>2</sub> is dispersed by mixing HZSM-5 and TiO<sub>2</sub> mechanically. On Ti-ISOP and Ti-sol impregnated HZSM-5 at 2 wt.% loading, the morphology of HZSM-5 is unaffected and appears cloudy at higher TiO<sub>2</sub> loadings. This may be seen as due to the presence of microdomains or amorphous TiO<sub>2</sub>. SEM coupled with an EDAX microprobe furnished a semiquantitative Ti analysis showing a concentration gradient on the surface of the zeolite. Ti spectrophotometric analysis using  $H_2O_2$  and sulphuric acid [17] shows that the amount of TiO<sub>2</sub> taken is closer to the amount obtained on SSD samples and that relatively low values are obtained on Ti-ISOP and Ti-sol impregnated zeolites.

#### 3.5. BET surface area

The surface area of the parent zeolite HZSM-5  $(420 \text{ m}^2 \text{ g}^{-1})$  decreased in general on supporting TiO<sub>2</sub>; this decrease is more for catalysts prepared by SSD  $(350-280 \text{ m}^2 \text{ g}^{-1})$  compared with the catalysts prepared by Ti-ISOP and Ti-sol impregnation  $(400-354 \text{ m}^2 \text{ g}^{-1})$ . The surface area of the TiO<sub>2</sub>-supported zeolite may be taken as an index of



Fig. 2. UV–VIS–DR-spectra of TiO<sub>2</sub>/HZSM-5 (SSD) catalysts: (A) uncalcined and (B) calcined. Spectra: (a and f) are HZSM-5 and TiO<sub>2</sub>, (b–e) represent 2, 5, 10, and 15 wt.% TiO<sub>2</sub>/HZSM-5.

the available porosity. Use of preformed TiO<sub>2</sub> particle (27 nm) in the case of TiO<sub>2</sub>/HZSM-5 (SSD) is affecting the surface area more. Considering the particle sizes of TiO<sub>2</sub> and the sizes of HZSM-5 zeolite medium pores (<1 nm) we conclude that there is no possibility of TiO<sub>2</sub> particles entering the zeolite pores in SSD method of preparation.

#### 3.6. Photocatalytic activity

## 3.6.1. Phenol and p-chlorophenol adsorption and photodegradtion on TiO<sub>2</sub>/HZSM-5 (SSD)

The adsorption (dark experiment) and photodegradation (experiment under illumination) of phenol (30 min) and *p*-chlorophenol (180 min) on HZSM-5 and TiO<sub>2</sub>/HZSM-5 (SSD) are shown in Figs. 4 and 5. It is seen clearly from the figures that both phenol and *p*-chlorophenol adsorb on HZSM-5 in the dark to a considerable extent and phenol adsorption is more on HZSM-5 compared with *p*-chlorophenol. Under illumination, the adsorption level of phenol on HZSM-5 is maintained at the same level as observed in the dark. In the case of *p*-chlorophenol, in addition to adsorption in the dark, there is further decrease in the concentration of *p*-chlorophenol under illumination in the first 30 min, as shown in Fig. 5. This may be due to the photolysis of *p*-chlorophenol as discussed in Section 2. The analysis of this experiment does



(A)

(B)



Fig. 3. SEM photographs of TiO<sub>2</sub>/HZSM-5 (SSD) catalysts: (A-D) Images of 2, 5, 10 and 15 wt.% TiO<sub>2</sub>/HZSM-5, respectively.

not indicate the presence of  $Cl^-$  ion in the suspension. Adsorption of both the pollutants in the dark, decreased by increasing TiO<sub>2</sub> loading, indicating that the number of adsorption sites is decreased by TiO<sub>2</sub> loading on zeolite. One can clearly understand that, at low TiO<sub>2</sub> loading on HZSM-5, the adsorption is

predominant, while at high  $TiO_2$  loading the photodegradation is predominant. That is how the crossing of the photoactivity trends both in phenol and *p*-chlorophenol degradation on  $TiO_2/HZSM-5$  (SSD) is showing a point where degradation becomes more conspicuous than adsorption.



Fig. 4. Adsorption (dark) and photodegradation of phenol ( $10^{-4}$  M) on HZSM-5; TiO<sub>2</sub>/HZSM-5 (SSD) catalysts: ( $\Box$ ) HZSM-5, ( $\bigcirc$ ) 2 wt.% TiO<sub>2</sub>, ( $\triangle$ ) 5 wt.% TiO<sub>2</sub>, ( $\blacklozenge$ ) 10 wt.% TiO<sub>2</sub> and ( $\blacktriangle$ ) 15 wt.% TiO<sub>2</sub>.

The chloride ion formation during the *p*-chlorophenol degradation with TiO<sub>2</sub> loading is also shown as an insert graph in Fig. 5. When *p*-chlorophenol degradation and chloride ion formation are followed simultaneously, the degradation rates as well as the chloride ion formation for the first few minutes are high on TiO<sub>2</sub>/HZSM-5 catalysts. With time, the degradation rates are relatively slow with a changed slope in chloride ion formation on 2-5 wt.% TiO<sub>2</sub>/HZSM-5 catalysts. This observation may show the effect of adsorption of the pollutant on degradation at low TiO<sub>2</sub> loadings; as the number of adsorption sites is decreased with increasing TiO<sub>2</sub> loading, degradation

and formation of chloride ion appeared more linear with time. The results also show that  $TiO_2$  loading above 10% may not improve the photodegradation.

### 3.6.2. Comparison of phenol and p-chlorophenol degradation on TiO<sub>2</sub>, TiO<sub>2</sub>/HZSM-5 (SSD) and TiO<sub>2</sub> + HZSM-5 (MECMIX)

Based on the above results obtained in phenol and *p*-chlorophenol degradation over  $TiO_2/HZSM-5$ (SSD), we have continued our studies on  $TiO_2 +$ HZSM-5 mechanical mixture to strengthen our observation that  $TiO_2$  supported without any interaction



Fig. 5. Adsorption (dark) and photodegradation of *p*-chlorophenol ( $10^{-3}$  M) and formation of [Cl<sup>-</sup>] (insert) on HZSM-5, TiO<sub>2</sub>/HZSM-5(SSD) catalysts: ( $\Box$ ) HZSM-5, ( $\bigcirc$ ) 2 wt.% TiO<sub>2</sub>, ( $\triangle$ ) 5 wt.% TiO<sub>2</sub>, ( $\blacklozenge$ ) 10 wt.% TiO<sub>2</sub> and ( $\blacktriangle$ ) 15 wt.% TiO<sub>2</sub>.

is more effective in photodegradation reactions than  $TiO_2$  with interaction. Several experiments were carried out on  $TiO_2$  + zeolite mechanical mixtures and the results of a typical experiment are discussed later.

The photodegradation of phenol and *p*-chlorophenol was studied on: (1) 7.5 mg TiO<sub>2</sub> (TiO<sub>2</sub> amount equivalent to 10 wt.% in the catalyst), (2) 75 mg 10 wt.% TiO<sub>2</sub>/HZSM-5 (SSD), (3) 7.5 mg TiO<sub>2</sub> + 67.5 mg HZSM-5 (MECMIX); the results are shown in Fig. 6. The observed photodegradation activity for phenol and *p*-chlorophenol follows the order TiO<sub>2</sub> + HZSM-5 (MECMIX) > TiO<sub>2</sub>/HZSM-5 (SSD) > TiO<sub>2</sub>. Fur-

thermore from Fig. 6C, it is observed that the Cl<sup>-</sup> formation on TiO<sub>2</sub> + HZSM-5 (MECMIX) catalyst is about 80 at 99% *p*-chlorophenol disappearance, whereas only 55% Cl<sup>-</sup> formation is seen at 88% degradation on 10 wt.% TiO<sub>2</sub>/HZSM-5 (SSD). The results on photodegradation of phenol and *p*-chlorophenol on TiO<sub>2</sub> + HZSM-5 mechanical mixtures may indicate the following:

• The phenol disappearance either on TiO<sub>2</sub>-supported zeolite or on TiO<sub>2</sub> + HZSM-5 composite catalyst reveals only the apparent trend of degradation, whereas the extent of degradation activity may be



Fig. 6. Photodegradation of (A) phenol ( $10^{-4}$  M), (B) *p*-chlorophenol ( $10^{-3}$  M) and (C) [Cl<sup>-</sup>] formation on ( $\bigcirc$ ) 7.5 mg TiO<sub>2</sub>, ( $\bigstar$ ) 10 wt.% TiO<sub>2</sub>/HZSM-5 (SSD) and ( $\square$ ) 7.5 mg TiO<sub>2</sub> + 67.5 mg HZSM-5 (MECMIX).

followed by studying the chloride ion formation from *p*-chlorophenol degradation.

- TiO<sub>2</sub>/HZSM-5 (SSD) is more active than TiO<sub>2</sub> in phenol and *p*-chlorophenol degradation, but chloride ion formation is retarded on this system.
- TiO<sub>2</sub> + HZSM-5 (MECMIX) is showing high activity for disappearance of *p*-chlorophenol and appearance of Cl<sup>-</sup> formation.

These observations may strengthen the ideas that any interaction between titania and HZSM-5 may decrease the photodegradation activity and that their combination is working well in enhancing the photodegradation of pollutants. It may be seen from the results that HZSM-5 is playing a role in pooling the pollutant molecules and thus facilitating the photodegradation activity on TiO<sub>2</sub> where it is totally free from interaction. This may also indicate that immobilizing TiO<sub>2</sub> on zeolite in general minimizes the photoefficiency of TiO<sub>2</sub>. Our results [11] on Ti-ISOP and Ti-sol impregnation on HY, HZSM-5 and H $\beta$  support these observations. 3.6.3. Easy and efficient use of  $TiO_2 + HZSM-5$  combinate

From these results on preparation, characterization and evaluation of  $TiO_2/HZSM-5$  (SSD) systems for the photodegradation of aqueous phenol and *p*-chlorophenol, we may explain the use of a zeolite in enhancing the photodegradation activity.

The interaction between TiO<sub>2</sub> and zeolite may affect the photoefficiency of TiO<sub>2</sub> and the adsorption properties of zeolites. Supporting TiO<sub>2</sub> without any interaction may retain the photoefficiency of TiO<sub>2</sub> and adsorption properties of zeolite thus, enhancing photodegradation activity as shown in Fig. 7A. The photodegradation is further enhanced when TiO<sub>2</sub> and HZSM-5 are suspended in aqueous phenol and *p*-chlorophenol. The photodegradation activity is high on a combinate, since subtrate adsorbed on zeolite in active form could reach the mobile TiO<sub>2</sub> easily, making the photodegradation more effective as shown in Fig. 7B. The observed synergism may result from the combined effort of TiO<sub>2</sub> and HZSM-5, which retain their respective characteristics in a mechanical



Fig. 7. Model depicting the photoinduced phenol degradation on (A)  $TiO_2/HZSM$ -5 (SSD) catalyst and (B)  $TiO_2 + HZSM$ -5 (MECMIX) combinate.

mixture. Thus use of  $TiO_2 + HZSM-5$  combinate is easy, efficient and involves no preparation.

#### 4. Conclusion

The preparation, characterization and evaluation of  $TiO_2/HZSM$ -5 (SSD) in the present study illustrates the following:

• Supporting TiO<sub>2</sub> on a zeolite without interaction is enhancing the photodegradation of aqueous phenol and *p*-chlorophenol.

- Use of TiO<sub>2</sub>+zeolite combinate (a mechanical mixture) is more effective in the photodegradation of aqueous phenol and *p*-chlorophenol.
- The study clearly shows that the use of  $TiO_2$  + zeolite combinate is easy and is anticipated to be an efficient photocatalytic system to work with, as it involves no preparation and allows an easy and good catalyst separation from aqueous solutions (simple decantation).
- The study thus opens a new direction for further research to modify the zeolites as ideal adsorbents for several pollutants in photocatalytic degradations.

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