REMOVAL OF BENZOTHIOPHENE FROM ORGANIC SOLUTION BY A COMBINED PHOTODEGRADATION- ADSORPTION METHOD

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ABSTRACT

A combined photodegradation-adsorption method was established for removal of benzothiphene from organic solution. In the first stage, the photocatalyst was prepared by immobilization of nano-crystalline titanium dioxide on natural zeolite; clinoptilolite by sol-gel process. The synthesized photocatalyst was characterized by XRD, TEM, SEM and FTIR techniques. Photodegradation of benzothiphene in n-hexane solution was studied under ultraviolet irradiation. The effect of different parameters such as irradiation time, photocatalyst amount, TiO₂ content and initial concentration of benzothiphene was studied and optimized. The results showed that the kinetics of reaction is first order and at optimized conditions 92% of benzothiphene was decomposed. The reaction products were identified by GC and GC-MS techniques. Adsorption of the products by two zeolites clinoptilolite and β- zeolite was examined. The results showed that β-zeolite removed all sulfur containing degradation products so that the remaining product was deeply desulfurized.

KEYWORDS: Benzothiophene; Photodegradation; Titanium isopropoxide; Clinoptilolite; β-zeolite.
1. INTRODUCTION

The presence of sulfur compounds in fuels is a major source of atmospheric pollution (Juan et al. 2010). Recently, many attentions have been focused on decreasing the sulfur content of gas oil used in diesel engines (Matsuzawa et al. 2002). Hydrogenation desulfurization is the predominant clean–fuel technique and contributes to the removal of thiols, thioethers, bisulfides and other linear sulfides. This method cannot successfully remove aromatic thiophenes and their derivatives. Moreover, it needs high operating pressures and temperatures and highly pure hydrogen (Ping et al. 2009; Campos-Martin et al. 2010). The oxidative desulfurization (ODS) is considered to be one of the promising new methods for deep desulfurization of the fuels. It can be carried out under very mild conditions, room temperature and atmospheric pressure. Thiophene and its derivatives are major sulfur compounds in the fuels with boiling point higher than 100°C. They usually sum up to 50–80% of the total sulfur content in diesel and jet fuels.

Benzothiophene is a model for sulfur heterocycles whose presence in fuels is undesirable. Given the legal regulations limiting the sulfur content in fuels, there is a large interest in developing efficient desulfurization procedures in organic media (Liu et al. 2008; Dai et al. 2008; Alvaro et al. 2005). Heterogeneous photocatalysis involving semiconductors, mainly titanium dioxide has attracted considerable attentions in recent years for destruction of undesirable organic pollutants with the help of solar or artificial light (Qamar, 2010). TiO$_2$ has been most widely used photocatalyst because it is easily available, inexpensive, non-toxic, and shows relative high chemical and photocatalytic stability (Qourzal et al. 2009). TiO$_2$ can be used in the form of fine powder or crystals dispersed in the solution. However, the need to filter TiO$_2$ after the reaction makes such a process troublesome and more costly. In order to solve this problem, many researchers have examined methods for fixing
Zeolites are a family of crystalline aluminosilicate minerals whose rigid framework defines channels and cavities of strictly regular dimensions in the nanometer scale. Clinoptilolite is an abundant naturally occurring zeolite, formed by the diversification of volcanic ash in lake and marine waters millions of years ago (Faghihian and Vafadar, 2007; Alvaro et al. 2004). In this study, at the first stage, we report a photocatalytic oxidation system using TiO$_2$-clinoptilolite as photocatalyst and its application for photodegradation of benzothiophene in hexane solution. In the second part, the removal of sulfur-containing photodegradation products was examined by two zeolite; clinoptilolite and β-zeolite.

2. EXPERIMENTAL

2.1 Materials and Methods

All chemicals, benzothiophene (Merck), n-hexane (Merck) and titanium isopropoxide (Merck) are in analytical grade. FTIR spectra were taken using a Perkin Elmer 65 Model infrared spectrophotometer. XRD patterns were taken by Bruker, D8Advance X-ray diffractometer using CuK$_\alpha$ radiation. Benzothiophene concentration was measured by HPLC (Agilent 1200 model) with column of Zorbax, Eclipse XDB-C$_{18}$. Capillary gas chromatographs (Agilent technologies 7890 A) and GC-MS (Agilent technologies 5975 C) with 30 m HP-5MS capillary column were used to identify reaction products. The enjection port temperature was 250°C. The mass spectra were produced by electron impact (70 ev).

2.2 Synthesis of TiO$_2$

Synthesis of TiO$_2$ was carried out using sol-gel technique by hydrolysis and condensation of titanium isopropoxide (Mahshid et al. 2007). The precursor
solution was a mixture containing 5 mL titanium isopropoxide (TTIP) and 15 mL isopropanol (99%). 250 mL of distilled water with known pH was used as the hydrolysis catalyst. The desired pH of the solution was adjusted by HNO₃ or NH₄OH. The gel preparation process started when both solutions were mixed together under vigorous stirring. Hydrolysis of titanium isopropoxide offered a turbid solution which was heated up to 60-70°C for 18-20 h (peptization). After peptization, the volume of the solution was decreased to 50 mL until a suspension was produced. After precipitation, the solid product was filtered and washed with ethanol and dried at 100°C. Finally, the prepared powder was annealed at temperature from 200 to 800°C for 2 h.

2.3 Preparation of photocatalyst

Solid state dispersion (SSD) method was used for preparing the zeolite-based photocatalyst. 1g of TiO₂ was mixed with 4 g of zeolite by agate pestle and mortar using ethanol as solvent. The solvent was then removed by evaporation. Samples prepared by this method were dried at 110°C and calcined at 450°C for 5 h in air condition to obtain TiO₂-supported zeolite catalyst (Nikazar et al. 2008).

2.4 Degradation Experiments

0.2 g of photocatalyst was added to 10 mL of 100mg/L hexane solution of benzothiophene. The mixture was irradiated by a 30W UV source for known period of time at room temperature. The concentration of benzothiophene was measured by HPLC. The effect of different parameters on degradation of the samples was studied and optimized.

3. RESULTS AND DISCUSSION

3.1 Characterization of the photocatalyst

The crystallinity of the catalyst was examined by XRD technique. Figure 1 shows the XRD patterns of clinoptilolite, TiO₂, and TiO₂-clinoptilolite. The
diffraction lines at $2\theta=25$ corresponded to TiO$_2$ is observed in TiO$_2$-clinoptilolite but with lower intensity, (Nikazar et al. 2006) (Fig1-c). Compared to the XRD pattern of clinoptilolite, no major changes was observed in the line intensity and position of TiO$_2$-clinoptilolite indicating that the zeolite framework remained unchanged after TiO$_2$ loading. The average particle size of TiO$_2$ was determined from XRD patterns of the samples according to the Scherrer's equation:

$$D = \frac{K \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where $D$ is average particle size (nm), $\lambda$ is wavelength of the radiation, $\theta$ is the Bragg's angle and $\beta$ is the full width at half maximum (radian). The average particle size for TiO$_2$ was obtained 6.3 nm.

Figure 2a shows FT-IR spectrum of TiO$_2$. The absorption peak observed in 3000-3500 cm$^{-1}$ range is assigned to the stretching modes of OH bonds and related to free water. The peak near 558 cm$^{-1}$ is attributed to the stretching vibration of Ti-O bonds. The peak at $\sim$ 1626 cm$^{-1}$ is attributed to the adsorbed water. In the infrared spectrum of TiO$_2$-clinoptilolite (2b), the bands are mostly similar to those of clinoptilolite. The band covers a range from 945 to 950 cm$^{-1}$ corresponding to the stretching vibration of Ti-O-Si and Ti-O-Al. The stretching vibration of O-H (3632 cm$^{-1}$), corresponding to the surface –OH, become weaker after TiO$_2$ loading, indicating that a certain amount of –OH has been demolished by loading of TiO$_2$ (Nikazar et al. 2007; Hayashi and Nasayama, 2008).

Figure 3 shows TEM micrographs of the TiO$_2$ powders. The average particle diameter of TiO$_2$ obtained by this technique was about 6.29 nm and very near to the value calculated by Scherrer's equation (Su et al. 2004).

Figure 4 shows the SEM image of TiO$_2$-clinoptilolite which reveals that TiO$_2$ nano-particles are aggregated on the zeolite surface.
3.2 Photodegradation Experiments

3.2.1 Effect of irradiation time

To investigate the effect of irradiation time, 10 mL of benzothiophene solution (100 mg/L) and 0.2 g photocatalyst were mixed and placed in dark room under UV irradiation for different reaction times. Degradation was increased with the prolonged reaction time up to 5 h and then leveled off beyond this time (figure 5). As the irradiation time increased more free radicals are produced and causing degradation of benzothiophene until the concentration of benzothiophene on the photocatalyst surface is reduced.

3.2.2 Effect of photocatalyst amount

Figure 6 shows that a swift increase of degradation was occurred as photocatalyst amount was increased. Increasing photocatalyst amount accelerated charge transfer and consequently accelerating photocatalytic oxidation of, benzothiophene while an excessive amount of photocatalysts would partly shield the UV light source. Thus, the photocatalyst amount had an optimal value of 0.4 g.

3.2.3 Effect of initial concentration

The effect of initial concentration on degradation of BT is shown in Figure 7. It was observed that maximal degradation (90%) occurred at concentration of 200 mg/L. It is likely that at higher concentrations the light source intensity is not sufficient to decompose 90% of benzothiophene.

3.2.4 Effect of TiO₂ content

In a series of test, 0.4 g of photocatalyst with different TiO₂ content (5-20%) was added to 10 mL of n-hexane solution of benzothiophene (200 mg/L). The samples were placed in dark room under UV irradiation for 5h. The mixture was filtered and the amount of remaining benzothiophene was measured in the filtrate. It was observed that degradation increased as TiO₂ content of
photocatalyst increased up to 15% and then remained constant (figure 8). The optimized value was between 15-20% wt of TiO$_2$.

3.2.5 Kinetics of the reaction

Reaction kinetics is of great importance in explaining the reaction mechanism. The rate constant for the apparent consumption of BT was obtained from the pseudo first-order equation:

$$-\ln \frac{C_t}{C_0} = k_p t$$

Where $C_t$ and $C_0$ are respectively the concentrations of the compound at time zero and time $t$ (s), and $k_p$ is the first–order rate constant. When $-\ln \left( \frac{C_t}{C_0} \right)$ was plotted against $t$, a straight line was fitted to the data (figure 9), and correlation factor of ($R= 0.961$) was obtained, suggesting that the reaction follows first order kinetics.

3.3 Identification and adsorption of degradation products by β-zeolite and clinoptilolite

The degradation products were identified by GC-MS techniques. The compounds recognized from ion chromatogram (figure 10) are listed in Table 1.

Among these compounds; benzothiophene, 1,2 di (thiophene-2-eil) ethan and 2- pentyliophene are sulfur containing materials and are to be removed from the solution. The removal efficiency of two zeolites; clinoptilolite and β-zeolite was examined for the removal of these compounds. To study the removal efficiency, 50 mL of the solution was mixed with 0.3 g of β-zeolite or clinoptilolite. The mixture was shaken for 24 hours at room temperature and the solid was separated by centrifugation. The ion chromatogram of the solution was obtained under similar conditions applied for degradation products (Figure 11 and 12). The remaining compounds were identified from the ion chromatograms and are listed in tables 2 and 3. By comparing these remaining compounds with those listed in table (1), it may be concluded that:
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- Two sulfur compounds of 1, 2 di( thiophene- 2- eil) ethan and 2-pentylthiophene are completely removed by clinoptilolite, whereas diphenylene sulfide is not fully removed. Thus, under experimental conditions clinoptilolite as an adsorbent removed most of sulfur containing compounds, but desulfurization is still incomplete.

- In the same way by comparing the remaining compounds after adsorption by β-zeolite (table 3) with those in table 1, it is concluded that all sulfur compounds including benzothiophene are fully removed.

3.4 Reuseability of the photocatalyst

It is important to use the catalysts in which active species loaded on zeolite to be reusable without significant loss of activity and with minimal need for regeneration. In order to investigate the reusability of the catalyst, desulfurization experiments were performed under similar conditions for four cycles. After each step, the photocatalyst was washed with n-hexane solution and calcined at 450°C for 2 hours, (figure 13). It was concluded that after 4 cycle 76% of desulfurization efficiency was remained. The full efficiency of the photocatalyst was recovered by adding calculated amount of new catalyst to the mixture.

4. CONCLUSION

Benzothiophene is a major sulfur compound in the fuels with boiling point of higher 100°C. It is not efficiently removed by the conventional desulfurization method. The results of this study showed that by combination of photodegradation and adsorption method, at photodegradation stage 92% of benzothiophene was decomposed and at the adsorption stage with clinoptilolite most of the sulfur containing degradation products and the remaining benzothiophene were removed. With β-zeolite deep desulfurization was occurred. It was concluded that the combined degradation–adsorption process can be considered as a practical method for desulfurization of fuels.
REFERENCES


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