

Photocatalytic decomposition of gaseous acetic acid in fluidized reactor

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Abstract

Much work has been done on the photocatalytic treatment of environmental pollutants using semiconductors like TiO_2 and metal/ TiO_2 . However, the application has a limitation to use in industrial division because the observed performances were very low. In order to improve the photocatalytic decomposition of acetic acid, the fluidized reactor is designed. It is known that fluidized-bed is suitable reactor to increase contacting effect between photosource and catalyst. When acetic acid is decomposed in fluidized reactor, removal values are above 70% and if Al/ TiO_2 is used the removal values reach 90%. It is confirmed from calculated mass transfer coefficient and Al metal effects..

1. Introduction

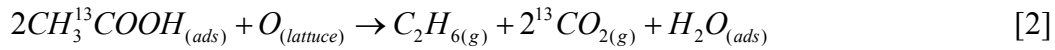
Photocatalysts were used for the purpose of cleaning the environment by photocatalytic decomposition. Recently, photocatalysis and has a strong impact on the design and construction of new light sources and photochemical reactors and on the preparation of novel photocatalysts and their supports.[1]

The application of photocatalytic reactor in removal of gaseous volatile organic compounds, fluidized bed reactor was considered as the proper reactor type for photocatalytic reactor.[2] Because fluidized bed reactor is controlled operations with easy handling and the rapid mixing of solids leads to close to isothermal condition throughout the reactor. And heat and mass transfer rates are high when compared with other modes of contacting.[3] When fluidized bed reactor used for photocatalytic reactor, we can have good catalyst-light and catalyst-gas contact. And catalyst can be continuously added and withdrawn without any erosion or plugging problems.[4] Therefore we used fluidized photocatalytic reactor and tested the decomposition efficiency in this work.

Acetic acid was employed as target pollutant. Because acetic acid is one of volatile organic compounds that is formed during photocatalytic oxidation of other organics.[5]

Photocatalytic decomposition of acetic acid was used in several studies[6-11]. Kraetler and Bard[6] used acetic acid and found that acetic acid decomposed to CH_4 along with small amounts of C_2H_6 and H_2 .

Muggli and Falconer[5] observed similar reaction that gas-phase acetic acid decomposes to CH_4 , CO_2 , and small amounts of C_2H_6 during photocatalytic decomposition. Using labeled acetic acid($CH_3^{13}COOH$), they proposed two parallel pathways for acetic acid photocatalytic decomposition on TiO_2 .



Their results indicated that the first step is dissociation of the O-H bond and photocatalytic decomposition then proceeds through the resulting acetate species.

In this study, we considered photocatalytic effect through no catalyst and no UV lamp condition. And we determined effect of catalysts amount compare with 5 g TiO_2 /L and 0.5 g TiO_2 /L. From above researches, we expect that if acidic catalyst are adopted, photocatalytic decomposition will enhanced. Thus Al was used in TiO_2 , photocatalytic decomposition of acetic acid is improved. Therefore we tested photodecomposition of acetic acid over Al/ TiO_2 catalyst.

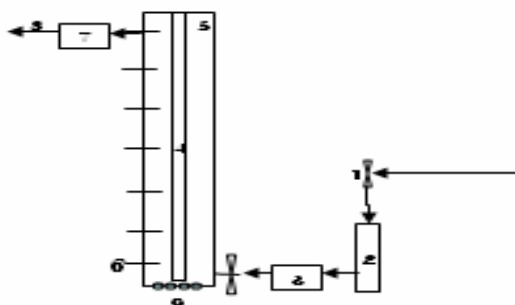
2. Experimental Method

2.1. Catalyst preparation

The preparations of TiO_2 and Al/ TiO_2 (1.0, 5.0, 10.0 wt%) catalysts used a conventional sol-gel method. Reagents used for preparation of sol-mixture were as follows : titanium tetra-isopropoxide(TTIP, 99.95%, Junsei Chemical, Japan) and aluminum iso-propoxide(AIP, 99.99%, Junsei Chemical, Japan), which were used as the titanium and aluminum precursors. Ethanol(Wako Pure Chem. Ltd) was used as solvent. TTIP and aluminum precursors were mixed with the alcoholic organic solvent in a 300ml beaker and the pH value was fixed at 2 by HNO_3 addition. TTIP was hydrolyzed by the OH group during evaporation at 80°C for 6h. The white precipitated materials were washed with distilled water and then dried at 100°C for 24h. Finally, crystallization of the TiO_2 and Al/ TiO_2 with anatase structure occurred after

calcinations at 500°C for 3h. Obtained photo-catalysts with powder used for fluidized reactor for acetic acid photodecomposition.

2.2. Experimental apparatus



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|-------------------------|-----------------------|--------------------------|
| 1. Air valve | 2. Acetic acid source | 3. Input sample tube |
| 4. UV lamp | 5. fluidized reactor | 6. Liquid sampling valve |
| 7. Outlet sampling tube | 8. vent line | 9. gas dispersant plate |

Fig. 1. Schematic of fluidized reactor

In this system, input acetic acid gas is injected into the bottom of a fluidized reactor through bubbler. The reactor column has a outer diameter of 7.5cm and inner diameter of 6.5cm with a height of 118cm and was made of pyrex materials. A 15W UV-C lamp was installed at the center of the reactor through the inside of the quartz tube of 2.2cm inner diameter and 90cm long. A gas dispersant plate whose inner diameter is 1mm was installed at the bottom of the reactor. Acetic acid gaseous bubble flowed up with air while water was steady. The photocatalysts employed in this study was Degussa P-25 TiO_2 and Al/TiO_2 . The slurry of catalysts and water were mixed by rising bubbles supplied from the air distributor.

The experimental procedure was as follows: The 200ml of acetic acid were charged to bubbler and air was supplied through the bubbler. The gas phase consisted of air and gaseous acetic acid. The gas phase passed through distributor and increased dispersion of catalysts particles in the bed. Liquid phase was water and 2L of water were charged in the bed. Solid phase was TiO_2 or Al/TiO_2 powders. The air flow rate was 1L/min. After 10min dark run, UV lamp power was turned on to initiate the photocatalytic reaction. Acetic acid concentration was measured every 1 hour by GC 17A(FID, hp 1 of capillary column used). The removal in percentage value was based on the disappearance of acetic acid during decomposition process. All experiments were performed at room temperature and atmosphere pressure.

3. Results and discussion

3.1 Effect of photo-catalysis

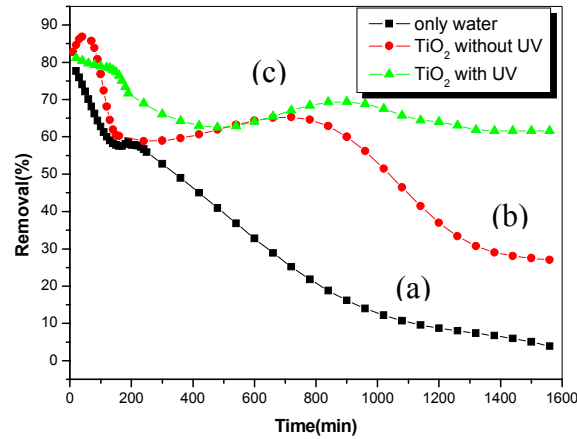


Fig2. The effect of photocatalysis (a) only water, (b) TiO_2 without UV and (c) photocatalytic fluidized system (water 2L, air flow 1L/min, 10 g TiO_2 used, continuously system)

To study the effect of photocatalysis on photocatalytic fluidized bed system, different conditions were tested. Fig 2. shows removal(%) verse time(min). Curve (a) shows removal verse time when only water was used without the catalyst and UV lamp. Initially acetic acid was absorbed by water but later the water was supersaturated by gaseous acetic acid. Thus the removal value was decreased. Curve (b) shows the effect of catalyst(TiO_2) without UV lamp. For this case there was no photocatalytic reaction since no UV source was used. Curve (c) shows the effect of catalyst when UV lamp was used. In this case, the system had active photocatalyst and UV lamp when compared with case (b). Removal percentage became steady at the second stage(around 400 mins) and remained constant through out the experiment. These results indicated that photocatalytic decomposition occurred continuously only when the photocatalytic reaction can occur.

3.2 Effect of catalyst weight

Since the photocatalytic reaction is governed by photo efficiency and mass transfer limitation. Fig.3 showed the removal(%) of acetic acid with different amounts of catalysts for fluidized reactor. It is believed that as the amount of catalyst increased, the number of photons absorbed and the number of reactant molecules absorbed were

increased due to an increase in the number of catalyst particles.[3] But we found that too excess particles interfered the photocatalytic decomposition as shown in Fig 3. In 5 g catal./L system, a screening effect of excess particles occurred and all the catalysts

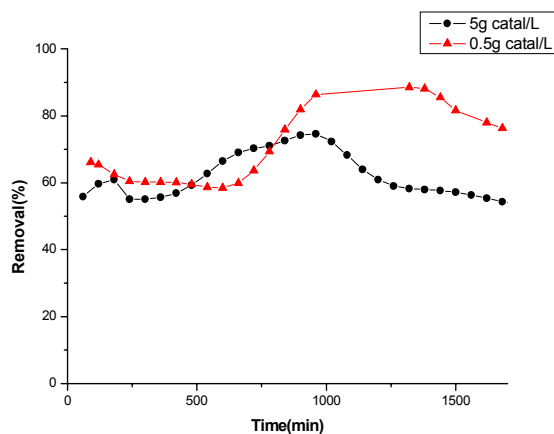


Fig. 3 The comparison of photodecomposition removal(%) of acetic acid with different catalyst loadings(water volume 2L, air flow rate 1L/min, continuously system)

surfaces could not be exposed to illumination. Therefore the increase of catalyst loading beyond a certain limit could not effectively increase the photocatalytic reaction rate.

3.3 Effect of Al/ TiO_2

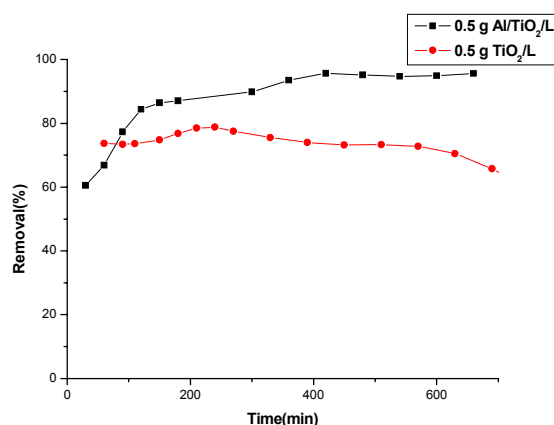


Fig 4. Acetic acid removal over Al/ TiO_2 and TiO_2 ; water 2L, air flow 1 L/min and 0.5 g catal/L and continuously system.

In a previous study, when Al metal was used in TiO_2 large amounts of acid site was

found as compare with pure- TiO_2 . And 10wt% Al/TiO_2 showed the best activity for hydrocarbon removal and the conversion value was kept without deactivation.[12] Thus in this study we used 10wt% Al/TiO_2 .

In Fig 4. we observed Al/TiO_2 had near 90% removal compared with TiO_2 which had 70%. And as time passed by, acetic acid removal value decreased over TiO_2 while acetic acid removal over Al/TiO_2 was kept constant for duration of 700min(11hr). These results were indicated that Al metal introduced acidic site and then acidic site was used as active site.[12] Increased active site increased removal efficiency over Al/TiO_2 .

3.4. Mass transfer coefficient.

The advantage of fluidized bed are good mass and heat transfer rates.[3] Compared each case when calculating mass transfer coefficient. Mass transfer coefficient calculated from Frossling relationship[13]:

$$Re = \frac{\rho d_p u}{\mu} = \frac{d_p u}{\nu} \quad [3]$$

$$Sc = \frac{\nu}{D_{AB}} \quad [4]$$

$$Sh = 2 + 0.6 Re^{0.5} Sc^{0.33} = \frac{k_c d_p}{D_{AB}} \quad [5]$$

Then we calculate Re , Sc and Sh . Through Frossling relationship, we obtain mass transfer coefficient(k_c).

Dimensionless num.	5 g TiO_2 /L	0.5 g TiO_2 /L	0.5 g Al/TiO_2 /L
Re. number	6.1475	6.1475	6.1475
Sc. number	917.65	800.25	768.74
Sh. Number	16.131	15.507	15.329
k_c	63.986	61.511	91.207

Table. 1 dimensionless number and mass transfer coefficient of each condition

All the cases had the same conditions. Air flow rate was 1L/min, bubble diameter 1.5mm and acetic acid kinetic viscosity was $0.0122 \text{ cm}^2 / \text{s}$. Thus they have the same Re . number. But they have different liquid kinetic viscosity and particle diameter. Therefore Sc . And Sh . number was different and k_c was different In our previous study obtained

particle diameter of TiO_2 was 30nm and particle diameter of Al/TiO_2 was 20nm. From these results we calculated mass transfer coefficient. Table 1. showed calculated dimensionless numbers and mass transfer coefficient. 5 g TiO_2 /L and 0.5 g TiO_2 /L had similar mass transfer coefficient but Al/TiO_2 had different value. It is because that Al/TiO_2 has more fine particle. Al/TiO_2 had higher mass transfer coefficient than TiO_2 and more higher removal value.

4. Conclusion

To improve photocatalytic decomposition we designed fluidized photocatalytic reactor and tested efficiency for decomposition of acetic acid.

Photocatalytic decomposition was kept continuously compared with non photocatalytic condition. When too excess particles were present during reaction, catalyst interfered the photocatalytic decomposition because of same area of the surface was not exposed UV illumination. Thus 0.5 g catalyst/L was more suitable case compared with 5 g catalyst/L.

When we compared photocatalytic decomposition over TiO_2 and Al/TiO_2 , Al/TiO_2 had higher removal rate than TiO_2 . It was because that Al metal increased acidic site and acidic site was used as active site. And calculated mass transfer coefficient supported these results.

5. Reference

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