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Optical Properties of Pt-TiO_2 Catalyst and Photocatalytic Activities for Benzene Decomposition

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Abstract−In order to improve the photocatalytic decomposition activity of benzene, which has been regarded as a typical volatile organic compound in air, TiO_2 catalysts modified with metals (Pt, Cu, and Fe) were prepared and tested. Certain correlations between the photocatalytic activities and the optical properties of those catalysts were also found and discussed by using UV-visible spectroscopy and a photoluminescence spectroscopy. Among the metal impregnated TiO_2, the Pt impregnated TiO_2 showed the best activity and it was even better than that of P-25 which is widely used in commercial applications. For the various metal impregnated TiO_2 samples, certain proportional relationships were found between the observed photoluminescence values and photocatalytic activities. On the other hand, in UV-visible spectra for metal impregnated TiO_2 samples, the transmittance value was reduced depending upon the loading of metals. It was thought that photocatalytic activity increases from initial reaction state because the number of photo-excited electrons, which exist at Pt surface augment due to the band gap energy change of Pt and TiO_2 by sintering and light energy-absorbed electrons excited easily to conduction. In conclusion, it was confirmed that the enhanced photocatalytic activity for high metal loading on TiO_2 is related with the high concentration of excited electrons, which could be monitored through UV-visible spectra.

Key words: Photocatalytic Decomposition, Metal Impregnated TiO_2, UV-visible, Photoluminescence

INTRODUCTION

The increase of oil and organic compound use in everyday life results in the increase of the emitted volatile organic compounds (VOCs). These VOCs become a main source of environmental pollution such as the formation of optical smog, destruction of ozone layer, global warming, and odorous air pollution in the world. Also, the harmful properties of these VOCs have had a hazardous influence on the human body. The various techniques of photocatalytic decomposition of VOCs have been widely studied as a new promising method to solve the VOC problems [Linsebugler et al., 1995; Hoffman1 et al., 1995; Litter, 1999; Lee et al., 2001].

The role of photocatalysts is the same as with that of common catalysts in that they promote the reaction by decreasing activation energy. Through several article reviews [José et al., 1997; Rajeshwar, 1995; Fotou et al., 1994], it seems essential to suppress the recombination process and to increase the lifetime of separated electron-hole pairs for the achievement of high photocatalytic activity, so that fast electron transfer occurs from the surface on TiO_2 to adsorbed intermediates. Another method [Ohtani et al., 1997; Xianzhi et al., 1996; Obuchi et al., 1999] to promote photocatalytic activity is lowering the band gap energy to use visible light or suppressing the recombination of separated electron-hole pairs that diffuse to catalyst surface. From the report of Hagfeldt and Grätzel [1995], doping of transition metals or precious metals on the surface of TiO_2 could function as a trap in the process of recombination of photo-excited electron-hole pairs. In addition, as the report of Rahman et al. [1996], UV-visible transmittance pattern of TiO_2 could be an index of band gap energy. Also, photoluminescence spectroscopy as well as UV-visible transmittance spectroscopy might be a useful tool to confirm the excited electron-hole pair effect.

In this study, by applying these UV-visible spectroscopy and photoluminescence spectroscopy characterization methods, certain correlations between the photocatalytic activities and the optical properties of those catalysts were tried and discussed.

EXPERIMENTAL

1. The Preparation and Characterization of Catalysts

Metal-impregnated TiO_2 catalysts were prepared by sol-gel method and titanium ethoxide [$Ti(OC_2H_5)_4$] was used as a precursor of titania. Also, chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), copper nitrate [$Cu(NO_3)_2$] and iron nitrate [$Fe(NO_3)_3$] were used as a precursor of Pt, Cu and Fe, respectively [Lin et al., 1998].

Fig. 1 is a schematic flow chart of preparation process of metal-loaded TiO_2 catalysts. To prepare the TiO_2 particles, each precursor was added into the premixed solution of purified water, HCl, and ethanol at room temperature. This solution was mixed for 24 h to obtain amorphous TiO_2, and followed by spin-coating process on quartz or pyrex plate. For the removal of ethanol, the coated plate was dried for 1h at 90 °C and calcinated for 3 h at 400-700 °C. The resulted TiO_2 layer depth was 1-2 μm. Metal-TiO_2 photocatalysts were prepared by similar procedures of pure TiO_2 preparation. The difference was the addition of metal precursor into the premixed solution in the first step to pre-hydrolyze the metal precursor. The metal loading amounts were about 3 wt%, 5 wt%, and 10 wt% for each metal-TiO_2 catalyst samples.

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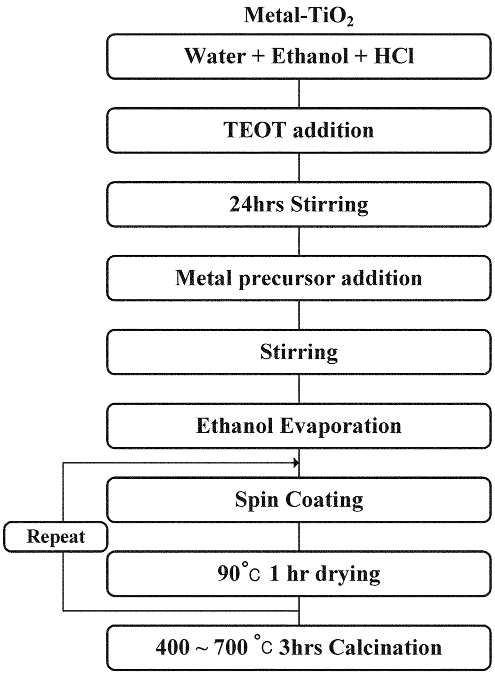

Fig. 1. Flow chart for Metal-TiO_2 preparation by sol-gel method.

The major phase of the obtained particles was analyzed by Rigaku D/Max-III (1.5 KW) X-ray diffraction analysis (XRD) by using nickel-filtered CuK_α radiation (λ=0.154 nm) target. The surface of prepared catalysts was observed by a scanning electron microscope (Lecia Model 440).

The light absorption of photocatalysts was measured with a Hitachi Double-beam U-2000 UV-vis spectrometer. The light absorption amount of photocatalysts was calculated by the Eq. (1):

$$A = \log\left(\frac{I_0}{I_t}\right) = \alpha l \tag{1}$$

Where, A is the absorbance, I_0 and I_t are incident and transmittance light intensity, respectively, and α is an absorption coefficient of photocatalysts and l represents light penetration distance.

Also, photoluminescence spectroscopy measurements were performed to examine the number of photo-excited electron-hole pairs for all samples. Photoluminescence of pure and metal impregnated TiO_2 was measured at liquid nitrogen temperature (77 K) by using an He-Cd laser line of 325 nm as an excitation wavelength.

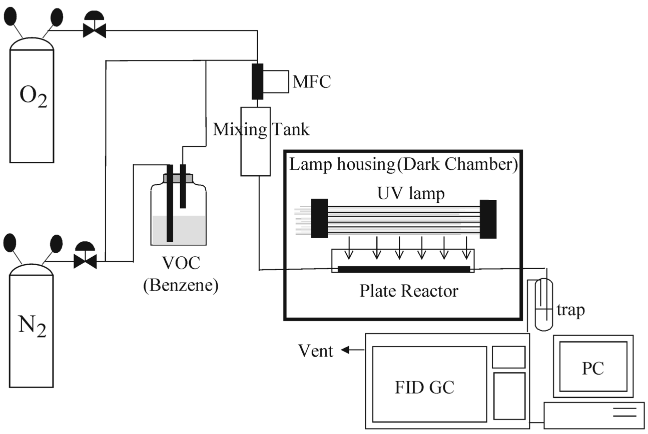

Fig. 2. Schematics of experimental apparatus.

2. Photocatalytic Activity Measurement Apparatus

The schematic diagram of measurement apparatus for photocatalytic activity is shown in Fig. 2. The reactor was a plate type (w×d×h: 120×200×30 mm) made of aluminum plate, with a quartz window in the middle of reactor plate to be illuminated UV light. The activity test of prepared catalysts was performed by continuous mode at 100 ppm of benzene as an initial concentration. A 18 W UV lamp (λ=253.7 nm, OSRAM) was used as a light source. The photocatalytic oxidation of benzene was carried out under illumination in ambient temperature for 2 hours. The concentration of benzene was analyzed in an HP 5890 gas chromatograph equipped with polydimethylsiloxane column (HP-1) and a flame ionization dector.

RESULTS AND DISCUSSION

1. Physical Properties of Catalysts

Fig. 3 shows the TiO_2 crystalline changes in XRD pattern with the changes in calcination temperatures. The ratio of anatase to rutile in TiO_2 was found to be 7 : 3 at 400 °C, 5 : 5 at 500 °C, and finally there was only rutile phase when calcined at 700 °C. The rutile phase ratio was calculated by following Eq. (2):

$$\%\text{Ruitle} = \frac{1}{[(A/R)0.884 + 1]} \times 100 \tag{2}$$

where, A and R are the peak areas in the diffractogram for the major anatase (2θ=25.3°) and rutile (2θ=27.5°) phase in TiO_2, respectively [Jung and Park, 2001]. Photocatalytic activity test for benzene decomposition was performed on TiO_2 catalysts samples calcined at 400 °C.

To investigate the changes in anatase to rutile ratio for the samples before and after coating, XRD patterns were compared in Fig. 4. The major anatase peak intensity decreased about 55% after coating, but 2θ value was almost same as that of pure TiO_2 catalyst. From this result, there were no changes in crystalline when TiO_2 was coated on quartz plate while its crystallinity decreased.

Similarly, as shown in Fig. 5, even in the case of metal-impreg-

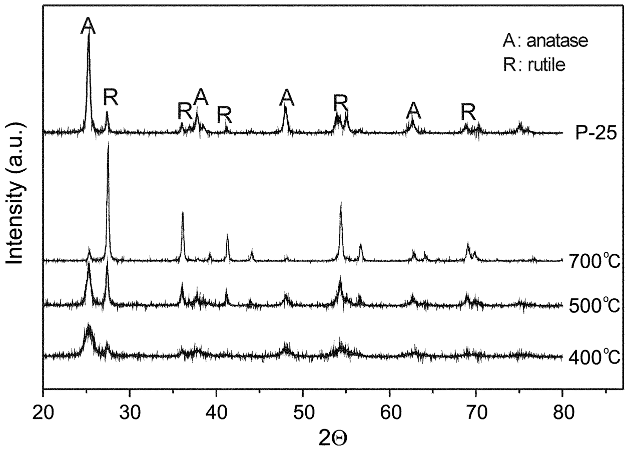

Fig. 3. XRD patterns of TiO_2 with various calcination temperatures.

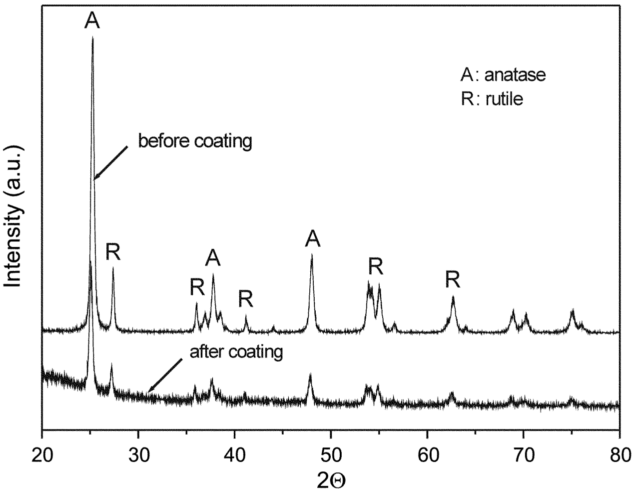

Fig. 4. XRD patterns of TiO_2 before and after coating.

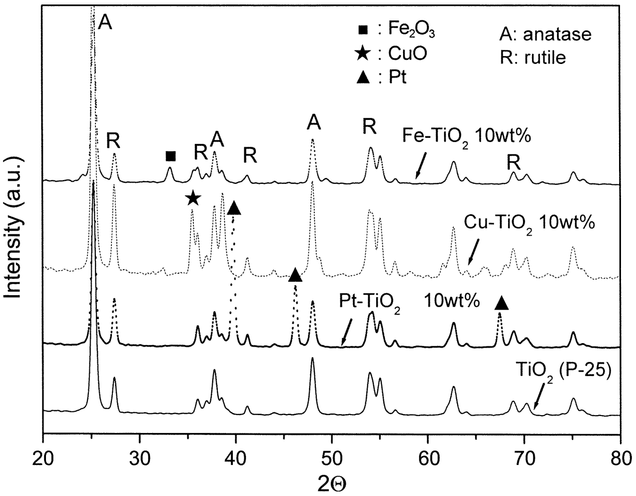

Fig. 5. XRD patterns of each 10 wt% metal-TiO_2.

nated catalysts, it was found that the main peaks of anatase and rutile phase were not changed by addition of metals; and it is found that 2θ values of 39.4° and 46.1° represent for Pt, 32.5° and 65.6° for CuO and 33.7° for Fe_2O_3, respectively. From the XRD analysis, we confirmed that Pt exists as a pure metal type on TiO_2 surface.

Fig. 6 shows the images of coated Pt-TiO_2 catalyst on quartz plate. Catalysts were coated by spin coating method with 1,500 rpm for 30 seconds 3 times. From the SEM photograph, it could be verified that coating depth was about 1.2 μm and catalysts were evenly coated. However, the shape of prepared TiO_2 is irregular so it is difficult to determine particle size.

2. Photocatalytic Activity of Metal (Pt, Cu and Fe) Impregnated TiO_2 Catalysts

In order to investigate the effect of metal impregnation on TiO_2 catalyst for photocatalytic activity, transition metals such as Cu and Fe together with a precious metal such as Pt have been impregnated at the loading amount of 10 wt% on TiO_2 catalyst, and photocatalytic decomposition was performed for the removal of 100 ppm benzene with carrier gas (mainly air). Also, finally, those photocatalytic activities of these catalysts were compared with that of commercialized TiO_2, P-25 as shown in Fig. 7.

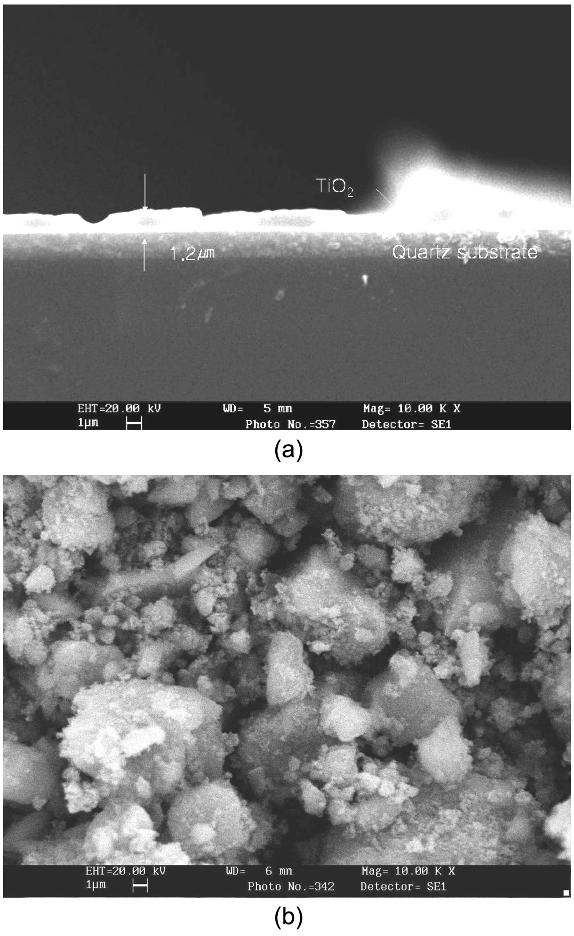

Fig. 6. SEM morphology of Pt-TiO_2 coated on quartz plate. (a) cross sectional view, (b) top view

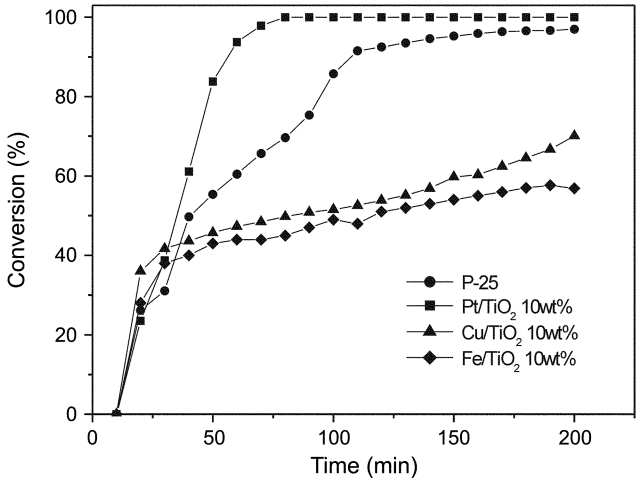

Fig. 7. Photocatalytic activities with various metal impregnations.

As it could be noticed in the figure, the photocatalytic activity for Pt-TiO_2 showed excellent conversion (over 95%) compared with that of others. It even showed superior conversion to that of P-25, especially at the early stage of photocatalytic reaction up to approximately 150 minutes. The high photocatalytic activities on TiO_2 might be elucidated as that, among the tested metal impregnated TiO_2 catalysts, only Pt-TiO_2 was able to make efficient spatial charge separation between Pt metal and TiO_2 surface, and consequently result in the recombination retardation of photo-excited electrons and holes. However, the transition metal-impregnated TiO_2 catalysts such as Cu-TiO_2 and Fe-TiO_2 showed relatively low catalytic activities. In those cases, it could be found that in the early stage of reaction, those showed similar photocatalytic activities as those of P-25 and Pt-TiO_2. However, with a lapse of reaction time, the photocatalytic activities on Cu-TiO_2 and Fe-TiO_2 lagged behind those on Pt-TiO_2 and P-25. Of course, it could be explained as the difference in the capacities of electron trap depending upon the kinds of metal impregnated on TiO_2 as mentioned above.

However, in addition, it might be explained as the changes in the role of metal as reaction time went on. According to the report by Navío et al. [1999], some metals such as Fe on TiO_2 change their role from electron trap to recombination center with the reaction time lapse, and consequently they interfere with the enhancement of photocatalytic activity. Therefore, from this point of view, it could be explained that the reaction activities of Fe- and Cu-TiO_2 catalysts become lowered as time goes on by a similar reason described above. The more detailed reaction mechanisms are still open to discussion.

Fig. 8 shows the photocatalytic activity changes for differently impregnated Pt-TiO_2 catalysts. As shown, the photocatalytic activity increased very rapidly especially in the early stage with an increase in the amount of Pt impregnation. However, the final activity was approximately all the same at around 90% conversion without regard to the difference in the amount of Pt impregnation. Therefore, it could be concluded that the impregnation of Pt on TiO_2 is strongly associated with how fast maximum conversion is reached in photocatalytic activity rather than the final activity: the higher the loading, the earlier the approaching the final activity.

3. Light Absorption Measurement Results by Using a UV-visible Spectroscopy

Fig. 9 shows the UV transmittance spectra of 3, 5 and 10 wt% Pt impregnated TiO_2 catalysts, respectively. We could find that there are three regions of UV-transmittance spectra in the figure. That is, UV-transmittance value decreases in the range of 450-340 nm, increases in 340-230 nm and finally decreases again rapidly below 230 nm. In general, the transmittance value under 230 nm is due to the absorption of light by a quartz plate itself rather than the catalyst coated on it. Therefore, it could be confirmed that there are three-transmittance bands related with coated photo catalysts. The first transmittance band is considered for Pt, wholly because it is not shown in pure TiO_2, P-25. Also, the second and third transmittance bands are thought for TiO_2. This interpretation is strongly supported by the report of Rahman et al. [1999] that the transmittance value between 230-400 nm signifies only the light interference phenomena between TiO_2 structure and impregnated metal substrate.

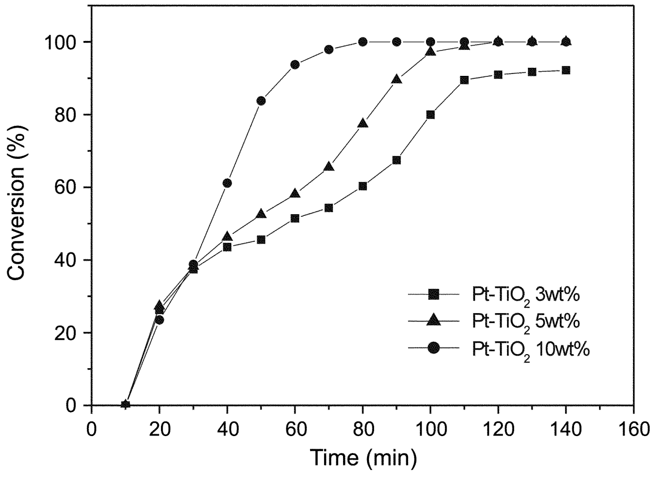

Fig. 8. Photocatalytic activities with different Pt loading amounts.

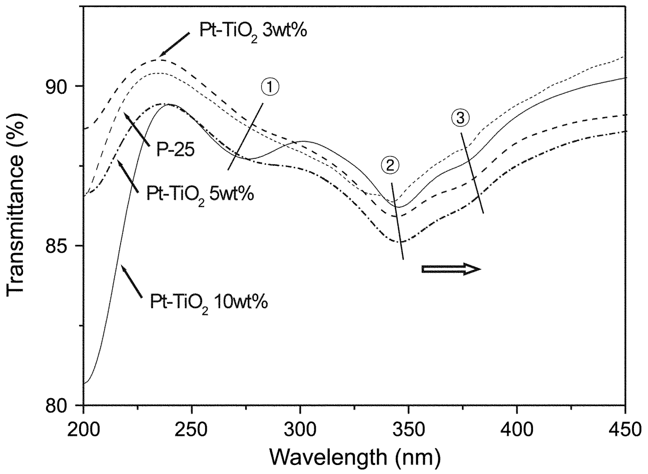

Fig. 9. UV-visible transmittance spectra with different Pt loading amounts.

As shown in Fig. 9, absorption band (①), which does not exist in pure TiO_2, is formed in case of Pt addition. The more the Pt impregnation amount, the more the first transmission band moves left, and the more the second (②) and third ones (③) move right, red shift. As a result, the band gap of Pt-impregnated TiO_2 is smaller

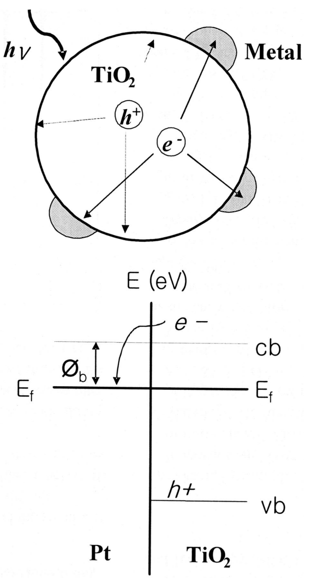

Fig. 10. Model diagram for a Pt-TiO_2 that shows the flow of cb electrons from the TiO_2 to Pt ($Ø_b$; Schottky barrier).

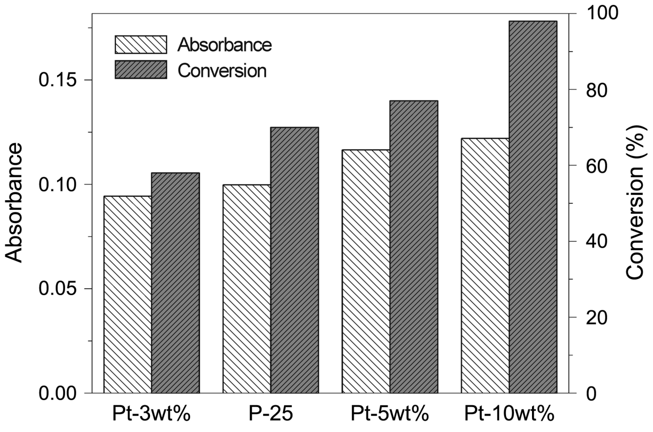

Fig. 11. Light absorption and activities with different Pt impregnation amount.

and electrons are easily photo-excited. Therefore, as previously described, impregnated Pt plays the role of electron trap to retard the recombination of photo-excited electron-hole pairs and that is considered as a reason for enhancement of the photocatalytic benzene decomposition activity. To explain the effect of Pt on TiO_2, the model depicted in Fig. 10 should be considered. When Pt clusters are deposited on the surface of a TiO_2 particle, a Schottky barrier ($\O_b$) between the metal and the TiO_2 is formed, while both metal and TiO_2 Fermi levels equilibrate. On irradiation, the conduction band (cb) electrons flow from the TiO_2 to the metal, in other words, to Pt site. Thus, the Schottky barrier acts as an efficient electron which decreases the recombination rate [Hoffman et al., 1995; Litter, 1999].

To find the relation between the photo-excited state of prepared catalysts and benzene decomposition activity, Fig. 11 shows maximum conversion and UV absorbance value calculated from transmittance spectra at wave number of activity test (λ=253 nm). As shown in the figure, the more Pt is impregnated, the more the increase in UV absorbance value and photocatalytic activity conversion. However, the more Pt is impregnated, the more the increase in surface coverage of TiO_2 by Pt cluster, and the UV transmittance value may decrease for this reason. In other words, the transmittance value of TiO_2 by itself might decrease but the UV-absorption amount of Pt-TiO_2 might increase. It is thought that much more photo-excited electron-hole pairs participate in photocatalytic reaction and with this result, the photocatalytic activities are improved.

Then, the recombination state of photo-excited electrons-hole pairs is measured by using photoluminescence spectroscopy to look into how much they actually take part in photocatalytic reaction.

4. The Relationship Between Photocatalytic Activity and Optical Properties

In Fig. 12, the photoluminescence emission values with different Pt impregnation amount on TiO_2 are shown. With an increase of metal impregnation amount, the maximum photoluminescence emission value decreases without shift of peak. The large difference between the bandgap energy (~3.14 eV) and emission peak energy (2.34 eV), which is about 0.8 eV, is described as the Stokes shift due to the Frank-Condon effect [Rahman et al., 1999]. No shift of peaks means that the band gap energy of prepared catalysts is not affected by the Pt impregnation amount. As discussed in Fig. 5, the result that there was no main peak position changes in XRD patterns, which represent for anatase and rutile phases of TiO_2, could be an another proof of no structural and band gap energy change for differently impregnated Pt-TiO_2 catalysts.

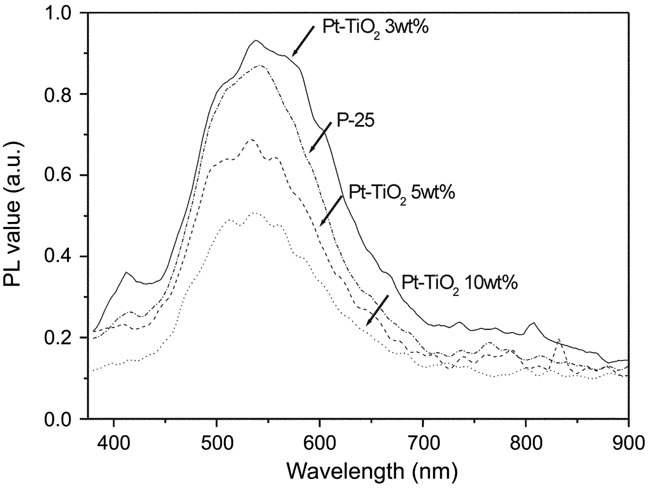

Fig. 12. Photoluminescence emission spectra with different Pt loading amounts.

When semiconducting material receives energy from outside, it emits absorbed energy as a light by the transition of inherent electron states, and then excited electron-hole pairs recombine depending upon the contents of materials. In this recombination process, there are radiative and non-radiative recombinations, and the former can be detected by photoluminescence spectroscopy. Principally, when the photoluminescence emission value is large, the number of recombination electrons should be also large since a large number of electrons are photo-excited. Therefore, the larger the emission value is, the more the photocatalytic reaction might be. So in this study we could postulate that the photoluminescence emission value increases depending upon Pt impregnation amount and could be considered as an index for photocatalytic activity. However, as shown in Fig. 13, the reverse proportional result could be monitored: the more the impregnation of Pt on TiO_2, the smaller the intensity of photoluminescence emission value. Also, the higher the

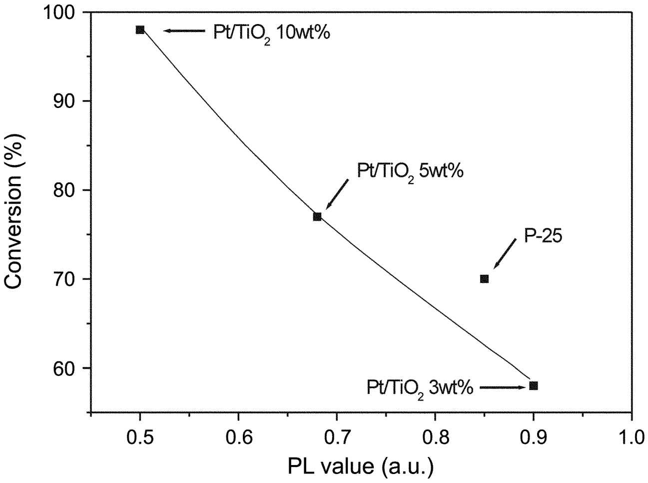

Fig. 13. Relationship between activity and PL value with different Pt loading amounts.

photoluminescence emission values were, the lower the photocatalytic activities that could be monitored in this study.

A reverse result contrary to our expectation could be thought of as caused by the reasons as follows:

The more Pt is impregnated, the amount of recombination of electron-hole pairs is decreases, and that could be due to photo-excited electrons joining in photocatalytic reaction rather than recombining with holes emitting the absorbed energy.

However, along with this, the more the Pt impregnation amount, the more Pt coverage on TiO_2 surface, and this could reduce the photo-excited electron-hole pair amount as Fujihara et al. [2000] reported that the intensity of a peak mainly depends on surface state of catalyst. Nevertheless, photocatalytic activity is promoted and from the result, it could be thought that a lifetime increase of photo-excited electron-hole pairs by Pt impregnation much more affects activity improvement than a decrease of photo-excited electron-hole pair amount by Pt coverage on TiO_2 surface [Furube et al., 2001].

Briefly, it seems that the recombination retardation of excited electron-hole pairs is a more effective factor for photocatalytic activity than the increase of excited electron-hole pair amount.

Also from a review of references, for the decrease of peak intensity and promotion of photocatalytic activity (Fig. 8 and Fig. 11), Raham et al. [1999] and Jung and Park [2001] reported that new defects would form on TiO_2 surface existing as Ti^{3+} form, and the Ti^{3+} could play a role as an electron acceptor so that might cause enhanced photocatalytic activity and increase in non-radiative recombination (relatively it decreased in radiative recombination) with the increase of Pt impregnation amount. Although all the vanished photo-excited electron-hole pairs by non-radiative recombination do not participate in catalytic reaction, if it is assumed that all the same for all tested catalysts but what take part in reaction, it could be thought that the increase of non-radiative recombination is proportional to the photocatalytic reaction.

Whereas, Toyoda et al. [2000] reported that Ti^{3+} defect on TiO_2 surface decrease photocatalytic activities because it might function as recombination center. However, in this study, it is well in accord with the result that activity is promoted with the decrease in photoluminescence emission value.

Table 1 shows the UV-visible light absorption amount at 253 nm wave number, photoluminescence emission intensity, and activities after 80 min lapse in time on metal-TiO_2 catalysts. As shown, the light absorption amount increases with increasing Pt loading amount. However, when looking into the relationship between photoluminescence spectra and catalytic conversion, it could be found to be in inverse proportion to each other as shown in Fig. 13.

Table 1. UV-vis absorbance, photoluminescence and photocatalytic activity

Catalysts	A	PL	Activity
P-25	4.7	0.85	70
Pt-3 wt%	4.5	0.9	58
Pt-5 wt%	5.1	0.68	77
Pt-10 wt%	5.2	0.5	98

A: UV-vis. Absorbance (%). PL: Photoluminescence emission intensity (arbitrary unit). Activity: Photocatalytic activities at 80 min (%).

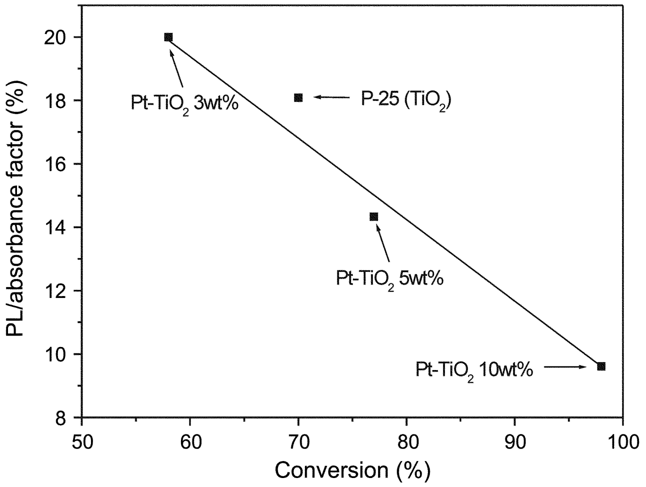

Fig. 14. Relationship between photocatalytic activity and PL/absorbance factor at 80 min lapse of activity test.

It is anticipated that the electrons that are actually participating in photocatalytic reaction are not all light-absorbed photo-excited electrons but the disappearing electrons in interfacial charge transfer. To make an index that is related with that, we have divided photoluminescence emission values by absorption value. Therefore, because the index value is small means photo-excited electron-hole pairs actually participate much in reaction, it could be also thought that photocatalytic reaction is enhanced.

Fig. 14 shows that when comparing the photocatalytic conversion after 80 min lapse of activity test with the index value of photoluminescence emission/absorbance, it could be found that those are in reverse proportion to each other.

CONCLUSIONS

To enhance the performance of photocatalytic activities for benzene decomposition, TiO_2 catalysts modified with metal (Pt, Cu and Fe) impregnation was tested and the photocatalytic activity of Pt-TiO_2 showed excellent conversion (over 95%) when compared with others.

However, the photocatalytic activity on Pt impregnated TiO_2 is strongly associated with how fast maximum conversion is reached rather than the final one: the higher the loading, the earlier the approaching the final activity. It could be suggested that the impregnated Pt metal functions as a trap collecting the excited electrons temporarily, and consequently it retarded the speed of recombination between electrons and holes on TiO_2, and therefore it gives more enhanced photocatalytic activity by interfering with the interfacial charge transfer between electron and hole.

The more Pt is impregnated, the more the decrease in UV transmittance value of TiO_2 but at the same time, the surface coverage of it by Pt cluster may increase for this reason. In this result, transmittance value of TiO_2 by itself might decrease, but UV-absorption amount of Pt-TiO_2 might increase.

Also, the higher the photoluminescence emission values were, the lower the photocatalytic activities could be monitored. The result could be thought that the more Pt is impregnated, the amount of recombination of electron-hole pairs is decreased, which could be due to photo-excited electrons joining in photo catalytic reaction rather than recombining with holes emitting the absorbed energy.

When comparing the photocatalytic conversion after 80 min lapse of activity test with the index value of photoluminescence emission/absorbance, it could be found that those are in reverse proportion to each other.

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