

# Bio safety of visible light responsive photocatalyst

Reference :

"visible light responsive photocatalyst", p. 167~177



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## **Bio-safety of TiO<sub>2</sub> photocatalyst itself**

Titanium dioxide (TiO<sub>2</sub>) is inert where there is no light. It is also difficult to absorb into the body and is non-toxic. It does not show irritation to the skin or eyes. It doesn't cause skin allergies, either. As for mutagenicity (genotoxicity), the negative was shown in many tests, including DNA damage and mutagenicity tests using bacteria, and chromosomal abnormalities using cultured cells.

In the case of long term exposure due to extremely high concentrations of dust, large amounts of particles were likely to remain calm in the lungs, causing pulmonary fibrosis, but it is considered impossible to obtain them in the context of use of visible light responsible photocatalysts. There is no carcinogenicity in oral administration. IARC (International Agency for Research on Cancer) does not classify as cancer potential (Group 3).

Under ultraviolet irradiation, cytotoxicity was remarkable in the mutagenicity test and positive in the light DNA damage and chromosomal aberration test using cultured cells. It was negative in the light mutable test and the photic stimulation test. No results were obtained from the photo allergy test.

As above, TiO<sub>2</sub> has essentially been identified by inert matter or ultraviolet irradiation under photorespectomy, the effects of DNA and chromosomes. The mutagenicity and irritability tests were negative regardless of the presence or absence of ultraviolet irradiation. Photo allergy information was not available.

## **Bio-safety of TiO<sub>2</sub> photocatalyst reaction intermediates**

In order to evaluate bio safety other than photocatalysts themselves, it is necessary to consider active oxygen generated on the surface of the catalyst and intermediates derived from the material subject to decomposition..

<Reactive Oxygen species>

When TiO<sub>2</sub> absorbs light, it reacts with oxygen and water in the air on the catalytic surface, resulting in four active oxygen of O<sub>2</sub><sup>-</sup>, ·OH, H<sub>2</sub>O<sub>2</sub> and <sup>1</sup>O<sub>2</sub>. Although highly reactive as shown below, the life span and spread distance are extremely small, such that it is not measured by a few mm away from the catalytic surface - due to instability. It is considered extremely unlikely to affect bio-safety under

actual conditions of use.

$O_2^-$  : Low reactivity, but becomes precursor of  $\cdot OH$  and  $H_2O_2$ .

$\cdot OH$  : It is the most reactive and causes a chain reaction with all kinds of materials. There are also reports of DNA damage.

$H_2O_2$  : It is less reactive, but passes through the cell membrane and becomes an  $\cdot OH$

$^1O_2$  : It is highly reactive but does not have a chain reaction because it is not radical.

<Intermediate of decomposing target material>

For toluene and acetaldehyde, the decomposition process was extensively investigated as a decomposition intermediate under ultraviolet irradiation. Independent information was investigated for various substances detected.

The decomposition process of toluene is as shown in 図 3.

Toluene has an effect on the central nervous system and is designated as a deleterious substance in the toxic and deleterious substance handling laws, but it is not designated for benzaldehyde that occurs as a main product.

However, benzene, which is caused by transient, is classified as (Group 1) as an IARC carcinogen.

The decomposition process of acetaldehyde is shown in 図 4. Acetaldehyde is not designated as a poison, but IARC contains as carcinogenic substances (Group 2B). In addition to the acetic acid ( $CH_3COOH$ ), which is routinely ingested by humans, formic acid ( $HCOOH$ ) and formaldehyde ( $HCHO$ ) are created as decomposition intermediate.  $HCHO$  is classified as a carcinogen (Group 1) in the IARC.

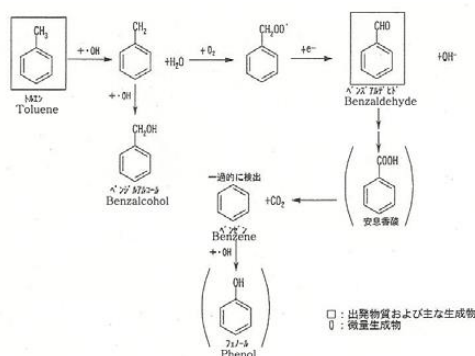


図3 トルエンの光触媒による分解過程 (紫外線照射)<sup>23)</sup>

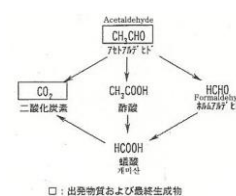


図4 アセトアルデヒドの光触媒による分解過程 (紫外線照射)<sup>29)</sup>

Above are extremely unlikely to affect bio-safety as they are extremely quickly lost due to instability in active oxygen. Toluene and acetaldehyde decomposition intermediates have cases in which substances that are more toxic than the starting material are detected after ultraviolet irradiation.

However, it is only a report in the process of generating and decomposing the decomposition intermediate, not a report that is interpreted quantitatively considering the actual use situation. Therefore, a risk assessment is also required about these decomposing intermediates to increase or decrease the risk as a whole.

<Photocatalytic Decomposition Risk Assessment of Toluene Using Visible Responsive Photocatalyst >

Table 2. Light decomposition risk treatment of Toluene using photocatalyst

	Guideline value	Maximum generation (50%decomposition rate)	Before decomposing	After decomposing 50%	Concentration/Guideline Concentration	
	$\mu\text{g}/\text{m}^3$	Percentage of generation for disassembly toluene %	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	Before decomposing	After decomposing
Toluene	260*	-	260	130	1	0.5
Formaldehyde	100*	0.53	0	0.69	0	0.007
Acetaldehyde	48*	1.23	0	1.60	0	0.033
Benzaldehyde	330**	0.05	0	0.07	0	0.0002
Total					1.00	0.54

\* : Japanese Ministry of Health, Labor and Welfare Guidelines

\*\* : Calculated based on U.S. EPA safety standards

The photocatalytic decomposition reaction of toluene confirmed the parabiotoxic of trace amounts of acetaldehyde, and the risk assessment in this case was carried out as follows.

For toluene, formaldehyde, and acetaldehyde, guidelines for indoor chemicals by the Ministry of Health, Labor and Welfare are set. Here, set initial value of the concentration of toluene is the 260mg/m<sup>3</sup>, which is the guideline value, and the maximum amount of parabiotoxic aldehyde when decompose by 50% is used, the amount of the by-product is 0.69 $\mu\text{g}/\text{m}^3$  formaldehyde and 1.60 $\mu\text{g}/\text{m}^3$  acetaldehyde when used in previous experiments. These values were divided into the guidelines value and the total was compared. As shown in Table 2, the risk mitigation as a decompose of toluene is 0.5 while the risk increase due to the production of parabiotoxic aldehyde is 0.04.

Although decomposition intermediates are produced, the total amount reduces risk from 1.0 to 0.54.