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Enhance effect of Nd(III) doping TiO_2 thin film on the photocatalytic degradation of 2-chlorophenol in Wastewater Effluent

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1. Introduction

The aim of this study is to investigate the photocatalytic behavior of Nd(III) doped on the surface of supported TiO_2 catalysts prepared by the MOCVD method.

In this paper, wet chemical methods and nanostructuring titania preparation method were also used for the synthesis of TiO_2 and TiO_2 thin films doped with Nd(III), and 2-CP have been photodecomposed using the thin films under air cooling and air saturation at both batch and continuous flowing system. The photocatalytic efficiencies for these thin films coated on the surface of various kinds of supports such as stainless steel cloth(SS), quartz glass tube(QGT), and silica gel(SG) were also investigated and compared with those of TiO_2 powder.

2. Matrials and Methods

2.1 Materials: TiO_2(P25), stainless steel cloth(SS), TIP, neodymium(III) acetylacetonate, silica gel(DavisilTM, 250-400㎛).

2.2 Preparation of Nd(III) doped TiO_2 thin films: The hot-wall low-pressure reactor setup of TiO_2 thin film by CVD method was discussed in the paper reported previously(Li, 2001).

2.3 Thin film characterization: Structure characterization; XRD; Rigaku D-Max B, The Nd(III) concentration on the surface of the TiO_2/Support; XPS Model ESCA 750, observation of surface morphology; SEM-AMRAY 1810 Model

2.4 Photoreactor and light source: A bench-scale photoreactor system consisted of a cylindrical pyrex-glass cell with the size of 20 cm, in diameter and 30 cm, in hight inside-coated with mirror. And the UV lamp having the resource of 100 W Hg lamp(Ace Glass Inc.) was immersed into the solution with air cooling jacket(Jung, 2001).

2.5 Procedure and analysis: ①HPLC(HP-1100m) equipped with UV detector ② TOC Analyzer(T-D, DC-190 ③ IC(Dionex Bio LC Chromatography) equipped with

ECD ④ GC-MS equipped with a HP-5971 mass selective detector

3. Results and discussion

The locations of (101), (004), (200), (105) and (211) diffraction peaks show that the film is polycrystalline structure TiO_2 stoichiometry with an antase type. Nd concentration of the Nd-TiO_2-SS tin film was measured to be 1.0 wt% by XPS.

The results exhibited that activities of the photodegradation for 2-CP have been enhanced in the order of Nd(III)-TiO_2-QGT>TiO_2-QGT as the same support ,and SS>QGT as a support. Especially, 99% of 2-CP has been destructed within 60 min when neodymiumize TiO_2 thin films coated on the surface of SS was used as a photocatalyst.

The binding energy of the 4d electron at 122.0 eV indicates that the Nd(III) is in the metallic state since O is absent in the reaction system. The main photoreaction in this system as follows;

$$TiO_2 + h \rightarrow e^-(cb) + h^+(VB) \quad (1)$$

$$Nd^{3+} + 3e \rightarrow Nd \quad (2)$$

This finding suggests that the reaction occurs via the L-H mechanism and the quantity of Nd(III) loaded can be controlled by t.

All of the chlorinated intermediates were destroyed within 90 minutes in the batch experiment. The formation of chloride ions is slower than the degradation of 2-CP. For example, about 85% of 2-CP have been degraded but 75% of chloride ions have been observed after 40 minutes of photooxidation using Nd-TiO_2-SS/UV system

The results indicate that the identified organic acids with unsaturated carbon-carbon bonds(i.e., muconic acids and maleic acid) have very low concentrations compared to the compounds with saturated carbon-carbon bonds(i.e., tartaric acid, oxalic acid, glyoxalic acid)(Table 1).

Results from regression analysis for the Nd-TiO_2-SS thin film show that rate constant(k) is 3.52×10^{-3} mM/min and the adsorption coefficient(K) is 6.43 mM^{-1}.

Table 2 and 3 gives the pseudo first order rate constants(k, mole/min) and half period($t_{1/2}$, mole/min) for 2-CP photodegradation(k_{2CP}), chloride-production(k_{cl}) and total carbon dioxide-generation($k_{\Sigma CO2}$) in the presence of UV alone and the photocatalysis plus UV like to the Nd-TiO_2-SS, Nd-TiO_2-QGT, TiO_2-SS thin film and P25 powder, respectively under batch experiment .

Table 1. Major mass spectra and HPLC data* of photodegradation of 2-CP.

PT(min)	intermediate	R.T.(min)	m/z	Quantity(%)
0-60	2-chlorophenol	12.5	128	82.5
10-60	catechol	10.2	110	0.4
5-120	2-chlorocatechol	14.8	144	6.8
5-70	4-chlororesocinol	15.2	144	0.6
5-120	chlorohydroquinone	15.6	144	12.1
5-210	glyoxylic acid	6.92	74.0	46.4
40-210	succinic acid	9.03	100	16.2
5-150	maleic acid	5.12	116	0.3
5-40	acetic acid	10.1	103	6.6
5-150	oxalic acid	8.61	90.5	3.2

* Eluent : 1.0% H_3PO_4 (f= 0.1mL/min) for organic acids and 2-chlorocathechol
PT; Photooxidation time(min), RT; Retention time(min)

Table 2. Summary of kinetic results(k) of photodegradation of 2-CP.

	Nd-TiO_2-SS	Nd-TiO_2-QGT	P25	UV-alone	TiO_2-SS
2CP	3.52×10^{-3}	2.94×10^{-3}	2.28×10^{-3}	1.35×10^{-4}	2.54×10^{-3}
Cl	1.74×10^{-3}	1.49×10^{-3}	1.16×10^{-3}	1.26×10^{-4}	1.31×10^{-3}
CO_2	7.62×10^{-4}	6.01×10^{4}	5.18×10^{-4}	$> 10^{-6}$	5.38×10^{-4}

Table 3. Summary of half period($t_{1/2}$) of photodegradation of 2-CP.

	Nd-TiO_2-SS	Nd-TiO_2-QGT	P25	UV-alone	TiO2-SS
2CP	20	24	38	456	28
Cl^-	35	43	61	500	52
CO_2	126	140	163	-	145

*TiO2-SS(CVD,40 φ ㎠, 37 ㎛), TiO_2-QGT(40.84 φ ㎠)

4. Conclusion

Results indicate that Nd(III) doping improves the photodegradation of 2-CP. Among all supporting materials studied, SS(37㎛) appears to be the best support. An optimal amount of doping material at 1.0%(w/w) of TiO_2 -substrate thin film gives the best photodegration of 2-CP.

References

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