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Comparison the Efficiency of Ir doped-TiO_2 Nanostructure as Risk-Reduction Materials for Toluene and n-Hexane

Van Thi Thanh Ho[1,*], Dung Hung Chau[2], Ngan Thi Thanh Nguyen[2], Khang Le Huy[2]

[1]Ho Chi Minh City University of Natural Resources and Environment (HCMUNRE), Ho Chi Minh City 700000, Vietnam;
[2]Ho Chi Minh City University of Technology, Ho Chi Minh City 700000, Vietnam; Vietnam National University-Ho Chi Minh City, Ho Chi Minh City 700000, Vietnam
*****Correspondence: httvan@hcmunre.edu.vn

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***Abstract*— *We have studied comparison the efficiency of Ir doped-TiO_2 nanostructure as risk-reduction materials for toluene and n-hexane. In particular, the most attractive advantages of our Ir doped-TiO_2 may be a high efficiency of VOCs treatment as well as the different mechanism of Ir doped-TiO_2 Risk-Reduction Materials between n-hexane and toluene organic compounds treatment have been studied in work. The study results show that there is a significant difference in the maximum achievable efficiency of toluene and n-hexane organic compounds degradation using Ir-TiO_2 photocatalyst. The photocatalytic material has the highest toluene treatment efficiency at 97.50 % which is much higher than that for n-hexane compound (60.03%). This outcome may be due to the difference in the structure of these two organic compounds. According to the scheme proposed by Montelio's research group [63], the alkane, after meeting the free hydroxyl radical OH·, will be cleaved into alkyl radicals; the OH· radicals are essentially electrophilic. In the case of alkanes, they will attack the stable cationic carbon-forming site on the secondary carbons. Due to the conjugation effect of the aromatic ring and the methyl radical in the toluene, the H of the ring will become flexible; therefore, toluene will be more easily decomposed.*

I. INTRODUCTION

Indoor air quality is the air quality within and around buildings and structures and an important determinant of population health and well-being.1,2 One of the sources of indoor air pollution is volatile organic compounds (VOCs), which originate from various sources and are the major cause of sick house syndrome. VOCs are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. Photocatalytic oxidation over semiconductors is regarded as a promising approach for environmental remediation. Titanium dioxide (TiO_2) is a popular photocatalyst for environmental remediation because of abundance and low material cost, outstanding chemical and photochemical stability, and high capacity for photooxidation [15–17]. However, the application of TiO_2 photocatalyst material is still limited because of the short range of wavelength affected and the low adsorption capacity of solar and indoor radiations (less than 5%) because the band gap of TiO_2 has relatively high energy (anatase TiO_2, ~3.2 eV) [5-6]. To solve this issue, the method of doping metals into TiO_2 lattice structure is considered as the sufficient approach to narrow the band gap [7-8] and decline the rate of recombination of electrons and holes, thus improve the photocatalytical efficiency of TiO_2. M. Hinojosa-Reyes et al. [13] used the perlite granules coated with In-doped TiO_2 photocatalyst to decompose ethylbenzene gas [13]. The In-doped TiO_2 materials, containing 1.0 and 5.0 wt% of In doped, are synthesized by sol-gel method from Titanium (IV) isopropoxide and Inidium (III) acetylacetonate precusors, then heated at in 4 hours. The products showed that 5.0 wt% In-doped TiO_2/perlite photocatalyst has the ethylbenzene degradation efficiency of ~25% in 40 minutes, higher than the efficiencies of TiO_2 (P25) photocatalyst with ~15%. However, the result also showed that 5 wt% In-doped TiO2 photocatalyst has the band gap of 3.32 eV, which is higher than the band gap of commercial TiO2 (P25) photocatalyst (3.26 eV). This is also the limit of the In-doped TiO_2 photocatalyst in visible light region. Haibao Huang et al. [15] investigated a series of transition metals (Mn, Co, Cu, Ni, Fe) doping into the TiO_2 network to improve the benzene decomposition under vacuum ultraviolet (VUV) irradiation. M-doped TiO_2 photocatalysts (M = Mn, Co, Cu, Ni, Fe) were synthesized by the sol-gel method and calcined at 550°C for 4 hours. The particle size range of the resulting photocatalyst material has about 10-40 nm, and the specific surface area is < 50 m^2/g. The results show that the Mn-doped material has the highest benzene decomposition efficiency (~58.0%) and ozone in the range of investigated materials. However, previous work has only focused on the treatment of acetone [10,12], ethylbenzene [13], xylene [11]; few researchers have addressed the problems of the n-hexane and toluene organic compounds treatment.

In the present study, we have studied comparison the efficiency of Ir doped-TiO_2 nanostructure as risk-reduction materials for toluene and n-hexane. In particular, the most attractive advantages of our Ir doped-TiO_2 may be a high efficiency of VOCs treatment as well as the different mechanism of Ir doped-TiO_2 Risk-Reduction Materials between n-hexane and toluene organic compounds treatment have been studied in work.

II. MATERIALS AND EXPERIMENTS

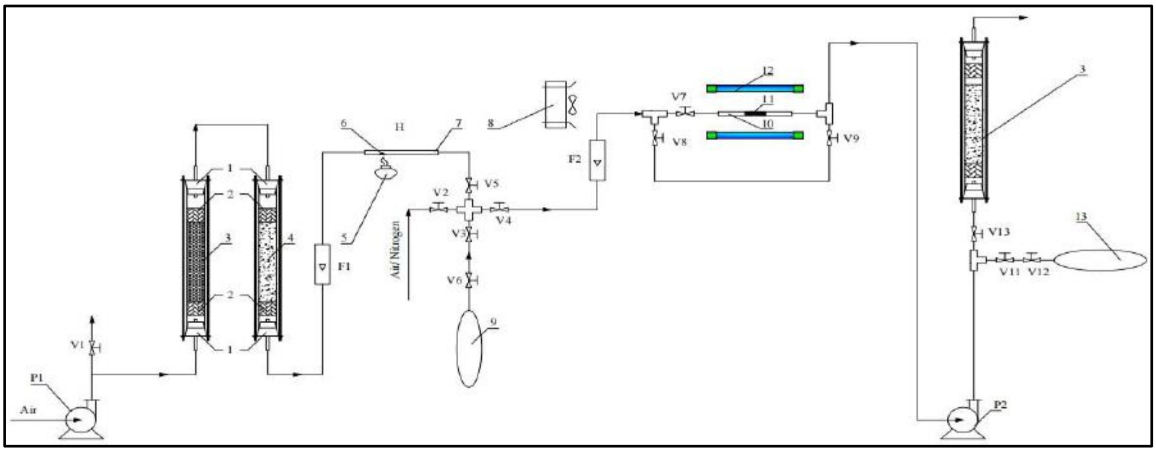
2.1 Materials

NO	Chemical	Symbol	Origin	Purity
1	Iridium trichloride hydrate	$IrCl_3.xH_2O$	Sigma Aldrich	99.9%
2	Titanium (IV) tetrachloride	$TiCl_4$	Aladdin	99.0%
3	Hydrochloric acid	HCl	Pháp	36.4%
4	Toluene	$C_6H_5CH_3$	Sigma Aldrich	99.9%
5	n-hexane	C_6H_{12}	Sigma Aldrich	99%

2.2 Experiments

The Ir-doped TiO_2 photocatalyst is synthesized followed our previous work[Ref.s]

The Ir-doped TiO_2 photocatalyst is used to decompose VOCs (toluene and n-hexan) by the system and process in the **Fig 1**



1- Rubber cap; 2- Glasswool; 3- Silicagel; 4- Activated Carbon; 5- Alcohol burner; 6- Sample drop; 7- Glassy tube; 8- Cooling fan; 9- Airbag containing inlet gas; 10- Reaction tube; 11- Photocatalyst; 12- UV light; 13- Air bag containing outlet gas

P1: Pumping air in; P2:Withdrawing air out; F1: Flow meter for inlet gas; F2: Flow meter for gas passing through photocatalyst;

Fig 1: Schematic diagram of toluene and n – hexane treatment system using nano Ir-doped TiO_2 photocatalyst in laboratory

The degradation reaction of toluene ($C_6H_5CH_3$) and n-hexane (C_6H_{12}) on the newly synthesized Ir-doped TiO_2 nano photocatalysts were carried out on a specially built treatment system. Toluene/n-hexane's concentrations were measured before and after blowing through the catalyst sample to investigate the catalytic activity of the photocatalysts. Experiment by following these steps:

- Fasten the airbag containing inlet gas to the connection position with valve V3, open valve V6 (airbag valve), set the flowmeter F1 to 1 liter/min, lock all valves. After that, stuff glass wool into the glassy tube, drop a sample (consisting of 0.02 mL toluene/n-hexane and V mL distilled water) into the sample dropper tube, heat the sample dropper tube to evaporate toluene and n-hexane.
- Open valves V5 and V3, turn on pump P1, start the timer simultaneously; collect air within 3 minutes to fill the airbag, lock the V6 airbag valve, turn off the pump and the alcohol burner, lock the remaining valves.
- Stuff 0.1g of the synthesized photocatalyst into the reaction tube, divide the amount of catalyst into three equal segments alternating with glass wool samples so that the photocatalyst is evenly distributed on the column. Turn on the radiator fan, UV light, let the light oww for 10 minutes before operating to ensure that the emitted radiation is stable, fasten the airbag to the connection position with valve V11, open valve V12 of the airbag
- Adjust the air suction pump P2 and flowmeter F2 at the investigated flow rate F, attach the airbag containing the inlet sample to the connection position V3, open valve V3, V4, V7, and V11 (valves V5, V6, V8, V9, and V13 are locked).
- Turn on pump P2, open valve V6, start the timer simultaneously, collect air for a period of time t (minutes) to be investigated with the set flow rate until the airbag reaches the appropriate tension. Lock valve V12, V11, remove the gas sample's airbag, turn off pump P2, and turn off the UV lamp.
- After gas collection, cleaning the system, glass tubes containing sample drops and catalyst column; lock valve V3, open valve V2, and V13 to blow air into the system, then close all valves to prepare for the next experiment.
- The airbag containing the outlet sample is characterized by gas chromatographic analysis to determine the concentration of toluene or n-hexane.

III. RESULTS AND DISCUSSION

3.1 Effect of Ir-doped ratio to toluene decomposing efficiency:

Table 3.1: Experiments analyze the effect of Iridium ratio on toluene decomposing efficiency

No.	**Iridium ratio** *(%)*	**Droplet volume Toluene** *(mL)*	**Droplet volume H_2O** *(mL)*	**Measured humidity** *(%)*	**Airflow rate through the catalyst** *(mL/min)*	**Gas collection time** *(min)*
1	0.5				200	15.25
2	1.0				200	15.42
3	1.5				200	15.23

Table 3.2: Gas chromatography results of determining toluene concentrations, corresponding with 0.5%; 1.0%; 1.5% Ir-doped TiO_2

No.	**Iridium ratio** *(%)*	**Toluene concentration before the reaction** C_o *(mg/m³)*	**Toluene concentration after the reaction** C_m *(mg/m³)*	**Decomposing efficiency** *H (%)*
1	0.5	1901	1361	28.04
2	1.0		887	53.34
3	1.5		47.5	97.50

Table 3.1-3.2 shows the concentration of toluene in the gas sample before and after Ir-doped TiO_2 catalyst treatment at different Iridium doping ratios. The investigated reaction was carried out with the condition that 0.02 ml toluene and 0.11 ml H_2O were added to the gas sample, respectively (corresponding to the measured air humidity in the gas sample of 73%). The airflow through the catalyst was 200 mL/min, and the gas sample was collected for 15 min to

fill the TEDLAR BAG 3L airbag. After completing the experiment and conducting gas chromatographic analysis, determine the concentration of toluene in the catalyst samples 0.5%; 1.0%; 1.5% Ir-doped TiO_2 is 1361 mg/m3 respectively; 887 mg/m3 and 47.5 mg/m3 respectively, with a decomposition efficiency of 28.04%; 53.34% and 97.5%. It can be seen that the decomposition efficiency of 97.5% when using the photocatalyst with an Iridium doping percentage of 1.5% is quite ideal and higher than previous studies on toluene treatment by photocatalyst. With the above results, the Iridium doping ratio of the catalyst plays a decisive role in the toluene treatment ability of the material. The 1.5% Ir-doped TiO_2 catalyst gives a much higher efficiency than the remaining catalyst samples.

3.2 Effect of Ir-doped ratio on n-hexane decomposing efficiency:

Table 3.3: The experimental parameters in analyzing the effect of Ir-doped ratio on n-hexane decomposing efficiency

No.	**Ir ratio** *(%)*	**Droplet volume n-hexane** *(mL)*	**Droplet volume H_2O** *(mL)*	**Measured humidity** *(%)*	**Airflow rate through the catalyst** *(mL/min)*	**Air collection time** *(min)*
1	0.5	0.02	0.11	~72	200	15.80
2	1.0				200	15.28
3	1.5				200	15.23

Table 3.4: Gas chromatography results of determining n-hexane concentrations, corresponding with 0.5%; 1.0%; 1.5% Ir-doped TiO_2

No.	**Iridium ratio** *(%)*	**N-hexane concentration before the reaction** *C_o (mg/m^3)*	**N-hexane concentration after the reaction** *C_m (mg/m^3)*	**Decomposing efficiency** *H (%)*
1	0.5	10591	4534	57.18
2	1.0		4616	56.42
3	1.5		4799	54.68

Table 3.3-3.4 shows the concentration of toluene in the gas sample before and after Ir-doped TiO_2 catalyst treatment at different Iridium doping ratios. The investigated reaction was carried out with the condition that the sample drops of 0.02 mL n-hexane and 0.11 mL H_2O added to the gas sample were 0.02 mL and 0.11 mL, respectively (corresponding to the measured air humidity in the gas sample being 72%). The airflow through the catalyst was 200 mL/min, and the gas sample was collected for 15 min to fill the TEDLAR BAG 3L airbag. After completing the experiment and conducting gas chromatographic analysis, determine the concentration of n-hexane in the catalyst samples 0.5%; 1.0%; 1.5% Ir-doped TiO_2 is 4534 mg/m3 respectively; 4616 mg/m3 and 4799 mg/m3, respectively, with a decomposition efficiency of 57.18%; 56.42% and 54.68%, the difference is not significant. It can be seen that the ratio of Iridium has but not much influence on the n-hexane decomposition efficiency of the catalyst. With a saturated hydrocarbon compound and difficult to decompose like n-hexane, the yield greater than 50% is relatively high. Unlike toluene treatment, with n-hexane, the 0.5% Ir-doped TiO_2 catalyst sample was more efficient (57.18%) than the two other rates.

3.3 Analyze and explain toluene and n-hexane decomposing mechanism of nano Ir-doped TiO_2 photocatalyst:

The obtained experimental results show a big difference in the maximum achievable efficiency of toluene and n-hexane decomposition using Ir-doped TiO_2 photocatalyst and the degradation efficiency variation trend. The photocatalytic material has the highest toluene treatment efficiency at 97.50%, much higher than the n-hexane's (60.03%). This outcome may be due to the difference in the structure of these two organic compounds. According to the scheme proposed by Montelio's research group [17], the alkane, after meeting the free hydroxyl radical OH·, will be cleaved into alkyl radicals; the OH· radicals are essentially electrophilic. In the case of alkanes, they will attack the stable cationic carbon-forming site on the secondary carbons. Due to the conjugation effect of the aromatic ring and the methyl radical in the toluene, the H of the ring will become flexible; therefore, toluene will be more easily decomposed.

Interestingly, the experimental results show that when increasing the Ir ratio from 0.5% to 1.5%, the toluene treatment efficiency increases sharply while n-hexane decreases slightly. As mentioned, metal ions in the structure of the catalytic material can act as traps to increase the lifetime of electrons and holes, leading to an increase in the reaction efficiency, which can be seen in the case of toluene treatment. However, according to equation (2.20), the OH· radicals can recombine with the metal center M (in the case of this thesis is Ir) and eliminate both OH· agent and electron – limiting the production of reducing agent $O_2^{\bullet -}$. In addition, according to the scheme proposed by Monteiro, the formed alkyl radical can create a ketone or an aldehyde [17]; some previous studies have also shown that in the presence of O_2, the ketone can produce more OH^-. The OH^- radicals after receiving holes from the first catalyst layer will form OH•, and in large quantities, the OH• will recombine with the metal centers in the later layers before reaching the n-hexane. The reaction of acetone with O_2 to give a hydroxyl can be depicted by equation (4.1):

$CH_3COCH_3 + O^- \rightarrow CH_3COCH_2\bullet + OH^-$ (4.1)

If the metal ratio in the photocatalyst is too low, it will not be enough to prevent recombination. At the same time, the distance between metal centers will be too far to effectively transfer electrons/holes to redox agents. Otherwise, the presence of many metal ions that strongly reduce the bandgap energy can also increase the recombination capacity and decrease the yield so that there's an optimal metal ratio. However, in the case of n-hexane, the interference of OH· changes the yield of n-hexane differently from toluene's degradation yield. In conclusion, each processed organic compound will have a different optimal denaturing metal ratio; the cause may be due to the by-products generated and their interaction with redox agents.

The mechanism of treatment of toxic compounds toluene/n-hexane in the air using Ir-doped TiO_2 photocatalyst materials is proposed as follows:

Electron separation process:

Electron and hole pairs would be produced whenever the sample material was irradiated with an appropriate light source. These electrons and holes would be the main oxidizing agents, but they moved freely in the lattice and easily recombined with each other:

$Ir\text{-}(TiO_2) \xrightarrow{vis-h\upsilon} e_{cb}^{-} + h_{vb}^{+}$

Electron trap process:

In making Ir-doped TiO_2 materials, Ir^{3+} ions were converted into Ir^{4+} and replaced in positions of Ti^{4+} ions in the crystal lattice, causing defects in the lattice. From the obtained results, based on the electron trapping and displacement mechanism proposed by Choi et al., the role of Ir in the Ir-doped TiO_2 crystal lattice was described as follows:

Electron trap center: $Ir^{4+} + e_{cb}^{-} \rightarrow Ir^{3+}$ (4.2)

Hole trap center: $Ir^{4+} + h_{vb}^{+} \rightarrow Ir^{5+}$ (4.3)

Electron transfer process:

After trapping the electron pairs, Ir metal would transfer electrons to the redox participating agents O_2 and OH^-:

$Ir^{5+} + OH^- \rightarrow OH\bullet$ (4.4)

$Ir^{3+} + O_2 \rightarrow O_2^{\bullet -}$ (4.5)

Due to the ability to trap both electrons and holes, the treatment efficiency of Ir-doped TiO_2 catalyst was higher than other M-doped TiO_2 catalysts. If only one of the two were trapped, the reaction efficiency would be low because the charges dissociate from the trap and move to the phase interface. The trap mechanism helped prevent the recombination of electrons and holes, increasing the lifetime of photogenerated electrons, thereby improving catalytic efficiency. The water molecule adsorbed on the catalyst reacts with the hole, produces a hydroxyl radical, and oxidizes the organic compound. Photochemical reactions have been shown to depend on the production of hydroxy molecules [18],[19]. Oxygen is essential for photochemical reactions to occur. Usually, the rate of organic matter decomposition increases with oxygen concentration [20]. The treatment mechanism for organic compounds such as toluene and n-hexane by Iridium modified TiO_2 photocatalyst could be summarized in Fig 2.

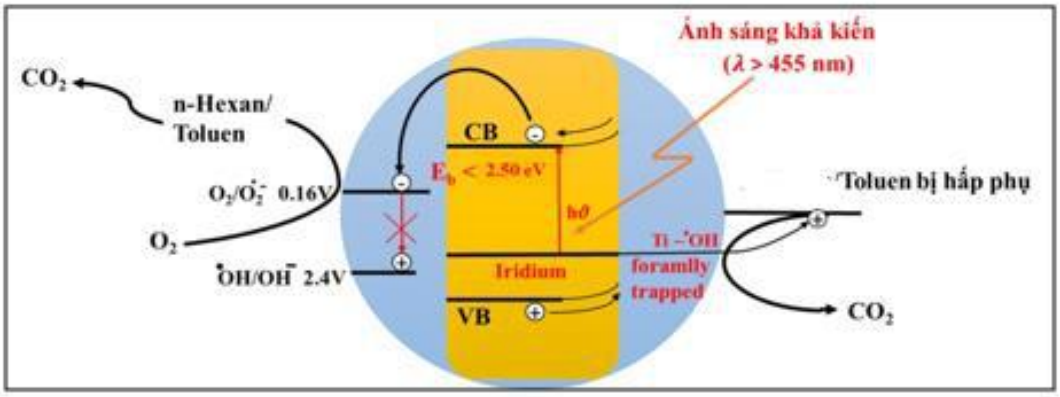


Fig 2: A proposed mechanism to degrade toxic volatile organic compounds using Ir-doped TiO_2 nano-sized photocatalyst

IV. CONCLUSIONS

The comparison the Efficiency of Ir doped-TiO2 Nanostructure as Risk-Reduction Materials for Toluene and n-Hexane is studied in this work. The study results show that there is a big difference in the maximum achievable efficiency of toluene and n-hexane organic compounds degradation using Ir-TiO_2 photocatalyst as well as the tendency to change the efficiency of the organic compounds. decomposition rate. The photocatalytic material has the highest toluene treatment efficiency at 97.50% which is much higher than that for n-hexane compound with 60.03%. The reason for this may be due to the difference in structure of these two organic compounds. The research results open up a new research direction on the application of Ir doped TiO_2 photocatalyst materials in the effective treatment of VOCs with a simple process.

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