Photocatalytic Dehydrogenation of Aqueous Methanol Solution by Naked and Platinized TiO₂ Nanoparticles†

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Nanosized titanium dioxide particles (Hombikat UV 100) doped with different percentages of platinum metal was prepared by photodeposition method. Crystallite size and photocatalytic activity was characterized by X-ray diffraction and ultraviolet-visible light spectroscopy, spontaneously. Spectrophotometer measurements have been used to determine the concentration of formed formaldehyde following Nash method at a wavelength 412 nm. Doped titanium dioxide was found more active than naked one in the existence of oxygen gas. However, naked titanium dioxide was found inactive in the existence of nitrogen gas and the suspension of aqueous methanol solution was converted to grey colour indicating the consuming of titanium dioxide lattice oxygen. The effect of loading of platinum on titanium dioxide was studied in the range 0.25-1 %. Platinized titanium dioxide with a loading of 0.5 wt % of platinum appeared to be the most active photocatalyst in the selective partial dehydrogenation of methanol. Photocatalytic dehydrogenation was made over the temperature range 278-298 K, using UVA radiation. Activation energies for formaldehyde formation were found identical on naked and platinized Hombikat (23 ± 1 kJ mol⁻¹). The identical activation energy for the photocatalytic dehydrogenation of aqueous methanol solution over platinized and naked titanium dioxide in the presence of oxygen is believed to be associated with the transport of photoelectrons through the catalyst to the adsorbed oxygen or metal on the surface of titanium dioxide.

Key Words: Titanium dioxide, Platinized titanium dioxide, Methanol, Photocatalytic dehydrogenation, Activation energy.

INTRODUCTION

Heterogeneous photocatalysis plays a crucial role in converted the light's energy to chemical energy[1,2]. The requirements of this process are summarized with finding the semiconductors (photocatalysts), which have a suitable band gaps range between (1.4-3.9) eV[3].

In photocatalysis process, there are three important steps occur when the semiconductor absorbs the photons, which have energy equal to or higher than the band gap. These are: 1) Creation of electron - hole pairs in the bulk by promoting the photoelectron from the valence band to conductive band and leaving a photohole in valance band. 2) Reaction of formed electron and hole with chemical species on the surface of semiconductor. 3) Recombination of electron and hole to liberate heat (this process will inhibit the rate of photoreaction). The first two steps are essentially depended on the electronic and structural properties of semiconductors thereby the recombination process will decrease with increase the crystallinity of semiconductor[4-6].

The modification of the surface could be occurred by three different methods, the first is depended on photosensitized of the semiconductor by dye either with precipitated it on surface that called regenerative dye semiconductor/visible light system or with dissolved the dye in solution that called nonregenerative dye semiconductor/visible light system into visible light region by excitation the dye with absorbed photons thereby librated the photoelectrons on dye surface then injected into semiconductor[3,7], the second method included the coupling for two or more types of semiconductors with each other that lead to increase the lifetime of holes by injecting the electrons into the conductive band for other semiconductor and produced a semiconductor works into visible region instead of UV region[7-9] while the third method employs noble metals like (Pt, Au, Pd, Ag…) which doped on semiconductor surface that will format of a Schottky barrier, the advantage of this method due to accelerate the photoreaction by trapping of the photoelectron and photohole (photogenerated charge carriers) because metals act as sink for electrons that will increase the lifetime of hole therefore the recombination process will depress[10-16].

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The aim of this work was focused on photocatalytic dehydrogenation of aqueous solution of methanol. The formation of formaldehyde was determined by employing Nash method at a wavelength 412 nm after photocatalytic reaction with naked and paltanized TiO_2 UV 100 with finding O_2.

EXPERIMENTAL

Titanium dioxide type Hombikate UV 100 was supplied from Sachtleben (Germany) consists of 100 % anatase with surface area more than 250 g/cm^2 and the average diameter of the primary particles ranged 5-10 nm was employed throughout all experiments. Different percentages of Pt were doped on titanium dioxide particles by photodeposition method[11,17] under UV-A light by a Philips Hg lamp (90 W).

In all experiments, naked TiO_2 or platinized titanium dioxide was suspended in 100 cm^3 of 40 mM methanol type absolute HPLC was supplied by Biosolve using a magnetic stirrer. At interval times; 2 cm^3 of reaction mixture was collected in a test tube and centrifuged (4000 rpm, 15 min) in an 800 B centrifuge. The filtrated solution was carefully removed by a syringe to new test tube and centrifuged again to remove the fine particles of naked TiO_2 and Pt doped TiO_2 at the same speed and period of time. The rate of reaction was measured with using a spectrophotometer measurements by following Nash method to determine the concentration of produced formaldehyde at a wavelength 412 nm[18,19].

RESULTS AND DISCUSSION

Preliminary experiments: A series of experiments had been done in Fig. 1. In absence of UV light (dark reaction) under O_2 or N_2 the reaction was never ocurred becuse no electron-hole pairs formed, while in absence the catalyst (photolysis process) the results showes a negative test for formaldehyde formation.
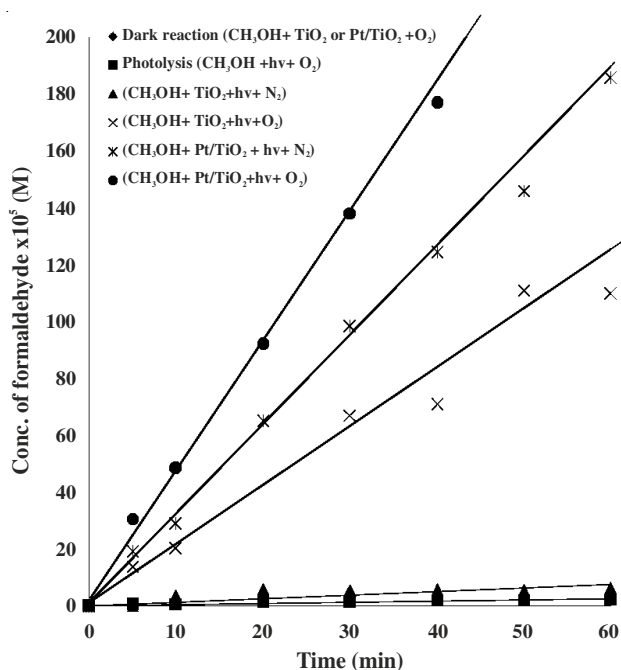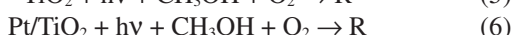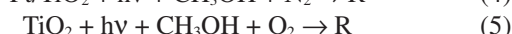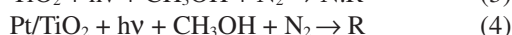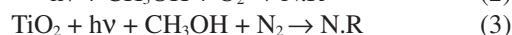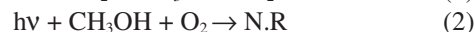

Fig. 1. Effect types of current gases, at cat. dose of TiO_2 and Pt/TiO_2 equal 200 and 175 mg/100 mL respectively. T = 298.15 K, CH_3OH conc. = 40 mM

In the photocatalytic reaction with purged a N_2 gas in solution, the gray colloid solution was apperanced that indicated to consume the lattice oxygen of TiO_2[11] and no reaction was produced.

The photocatalytic reaction with using a methanol, TiO_2, oxygen and UV light was occured because they are an essential parameters for the photooxidation that enhanced the formation electron-hole pairs, which play a vital role for pushing the photoreaction.

While when using Pt doped TiO_2 nanopartical instead of nacked TiO_2 the efficiency of reaction under N_2 was raising because Pt is act as a sink of photoelectrons that will increase the life time of photoholes and raise the effeciency of photodegradation of methanol. The maximum efficiency of reaction was occured under O_2 that beyond to react the O_2 with photoelectrons and produced in the ending a hydroxyl radical and inhibited the recombination process[11,20].

Equations explain the effect of different parameters on the photocatalytic dehydrogenation of methanol (R refered to the occurance of the reaction while N.R. was no- reaction occured).

$$TiO_2 \text{ or } Pt/TiO_2 + CH_3OH + O_2 \rightarrow N.R \quad (1)$$
$$h\nu + CH_3OH + O_2 \rightarrow N.R \quad (2)$$
$$TiO_2 + h\nu + CH_3OH + N_2 \rightarrow N.R \quad (3)$$
$$Pt/TiO_2 + h\nu + CH_3OH + N_2 \rightarrow R \quad (4)$$
$$TiO_2 + h\nu + CH_3OH + O_2 \rightarrow R \quad (5)$$
$$Pt/TiO_2 + h\nu + CH_3OH + O_2 \rightarrow R \quad (6)$$

Characterization of Pt doped TiO_2: From the X-ray diffraction patterns spectra, the crystallite sizes of undoped and Pt doped TiO_2 were calculated by aiding with the more stable peaks, which have a Miller indicates equal (101) and substituted all the information in Scherrer's equation[20,21].

$$D = \frac{k.\lambda}{B.Cos\ \theta} \quad (7)$$

where: D is a crystallite size, k is a Scherrer's constant (0.89), λ is wavelength of the X-ray radiation (0.15418 nm for CuK_α), B is the full width half maximum (FWHM) intensity and θ is a diffraction (Bragg) angle.

The peaks which have a Miller indicates equal (004) is boarding that refer to doped Pt on TiO_2 is real[22] at 2θ regain started from 35° to 45°.

Table-1 shows, the values of crystallite sizes, which calculated by Scherrer's equation that ranged into a metallic nanoparticals range.

TABLE-1 CALCULATION CRYSTALLITE SIZE OF UNDOPED TiO_2 AND pt DOPED TiO_2		
Crystal components	Pt (wt %)	Crystallite size (nm)
TiO_2 Hombikate (UV 100)	0.00	8.326
$Pt-TiO_2$	0.25	9.099
$Pt-TiO_2$	0.50	9. 326
$Pt-TiO_2$	0.75	8. 447
$Pt-TiO_2$	1.00	7. 541

From Fig. 2, the small amounts of Pt doped on TiO_2 surface will increase the charge carrier space distance (CCSD) therefore the recombination process reduces[23], then increases in crystallite sizes. According to the following equations[24].
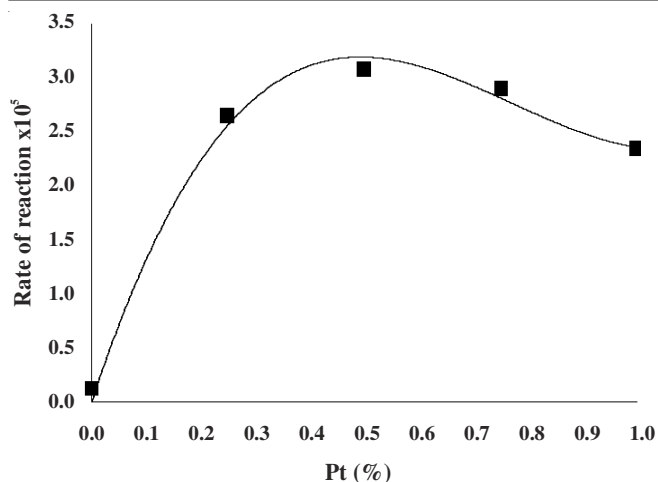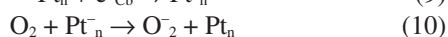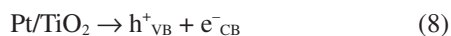
Fig. 2. Relation between rate of reaction and percent of Pt on TiO$_2$, at cat. dose of Pt/TiO$_2$ equal 175 mg/100 mL, pH = 6, T = 298. 15 K, CH$_3$OH conc. = 40 mM, N$_2$

$$Pt/TiO_2 \rightarrow h^+{}_{VB} + e^-{}_{CB} \quad (8)$$
$$Pt_n + e^-{}_{Cb} \rightarrow Pt^-{}_n \quad (9)$$
$$O_2 + Pt^-{}_n \rightarrow O^-{}_2 + Pt_n \quad (10)$$

After 0.5 (Pt) % doped TiO$_2$ the reaction is inhibited with increase the loading of Pt that refereed to increase of recombination process by capturing of electrons with charged centrals (h$^+$)[24]

$$Pt^-{}_n + h^+{}_{VB} \rightarrow Pt_n \quad (11)$$

The increasing of the amount of metal, which give a depth of grey colour that will shield the light to reach of TiO$_2$ and the excitation of electrons to conductive band was depressed[25].

Effect of catalyst mass: Fig. 3 shows the effect of naked TiO$_2$ and Pt doped TiO$_2$ concentrations on photoreaction for oxidation of methanol solution. The rates of reaction were found to be directly proportional to catalyst concentrations that beyond to increase of active sites on surface of catalyst at ranged (50-200) mg/100 mL. At higher catalyst concentrations after 200 mg/100 mL the reaction rates were decreased that indicated to occur of screening effect[26].
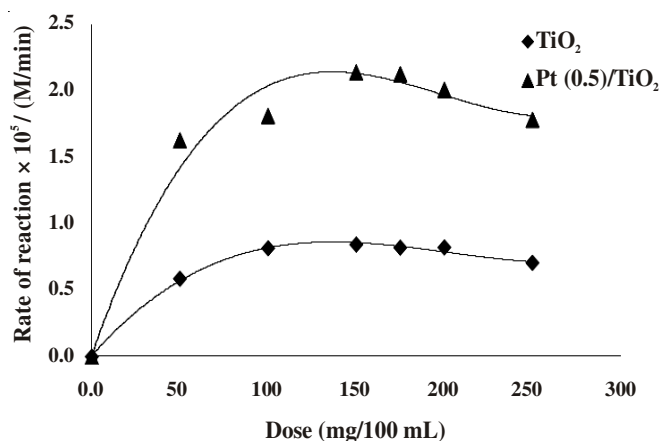

Fig. 3. Effect of catalyst mass on the rate of reaction. cat. dose = 50-250 mg/100 mL, T = 298.15 K, CH$_3$OH conc. = 40 mM, O$_2$

Effect the pH of solution on reaction: Fig. 4 shows, that the pH of solution plays a crucial role in increase or decrease the rate of photoreaction. That depended on the ionization state of TiO$_2$ surface, by the following equations[27]:
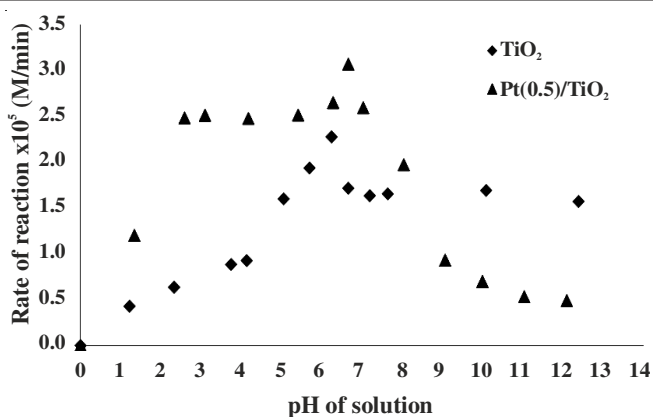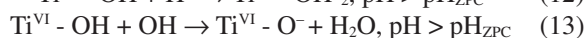

Fig. 4. Effect the pH of solution on the rate of reaction. cat. dose of TiO$_2$ and Pt/TiO$_2$ equal 200 and 175 mg/100 mL respectively. pH = 1-12, T = 298.15 K, CH$_3$OH conc. = 40 mM, O$_2$

$$Ti^{VI} - OH + H^+ \rightarrow Ti^{VI} - OH^+{}_2, \ pH > pH_{ZPC} \quad (12)$$
$$Ti^{VI} - OH + OH \rightarrow Ti^{VI} - O^- + H_2O, \ pH > pH_{ZPC} \quad (13)$$

where, pH$_{ZPC}$ (pH of zero point charge) represents the pH value at which the coverage of H$^+$ equals the coverage of OH$^-$ on surface of catalyst.

At pH less than 6.2 (pH$_{ZPC}$) of TiO$_2$ UV 100 the surface become positively charged that increase to the electrostatic repulsion between the charge of surface and the hydronium cation (H$_3$O$^+$) and decease the adsorption of it on the surface, whereas at pH more than 6.2 the surface become negatively charged that cause increasing in the electrostatic repulsion between the charge of surface of catalyst and the lone pair electron donor of oxygen atom in methanol molecule thereby the adsorption process of methanol molecule inhibits, hence the recombination process increase, because the number of scavenger in valance band will decrease[27].

The maximum rate of reaction by using Pt doped TiO$_2$ is producing at pH equal 6.5 this value lies in the range of pH$_{ZPC}$ 5.8-6.8[28].

Effect of temperature: The plotted results in Fig. 5 indicated that the apparent activation energy for the photocatalytic dehydrogenation was calculated at temperature range 278-298 K by Arrhenius plot. In photocatalytic reaction, the apparent activation energy deals with the promoted the photoelectrons from the valance band to the conductive band of catalyst[29,30]. The calculated values of apparent activation energy on naked and platinized TiO$_2$ are low (23 ± 1 kJ mol^{-1}). The identical activation energy for the photocatalytic dehydrogenation of aqueous methanol solution over platinized and naked titanium dioxide in the presence of oxygen is believed to be associated with the transport of photoelectrons through the catalyst to the adsorbed oxygen on the surface[31].

Suggested photocatalytic mechanism for naked and Pt doped TiO$_2$: In general, when the photon of light fills on the colloid solution, which contain methanol with catalyst either TiO$_2$ or Pt/TiO$_2$ the photohole and photoelectron were created, then the photohole and photoelectron input in serious of reactions according the following equations[31-33]:

Photoexcitation
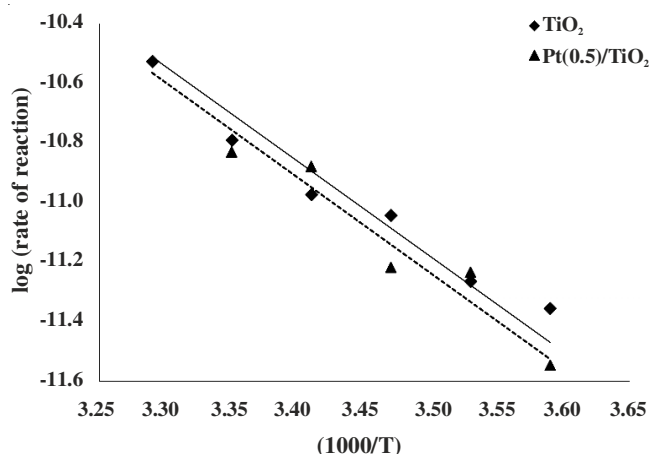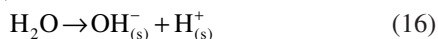
$$TiO_2 \ or \ M/TiO_2 + hv \rightarrow (h^+ - e^-) \ (exciton) \quad (14)$$

$$(h^+ - e^-) \rightarrow h^+ + e^- \quad (15)$$
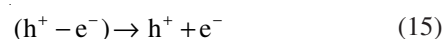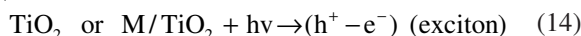
Fig. 5. Arrhenius plot for photodehydrogenation of methanol solution on TiO$_2$ and Pt/TiO$_2$ at (278-298) K

### Ionization of water

$$H_2O \rightarrow OH^-_{(s)} + H^+_{(s)} \qquad (16)$$

Charge carrier trapping: 1) Photoelectron is collected by platinum crystallites which act as snick of it ; and oxygen gas is reacted with photoelectron to produce a super oxide anion (O$_2^-$).

$$Pt_n + e^-_{Cb} \rightarrow Pt_n^- \qquad (17)$$
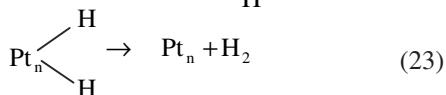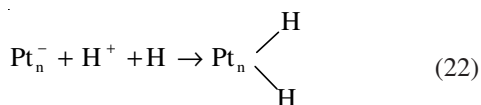
$$O_2 + e^-_{Cb} \rightarrow O_2^- \qquad (18)$$

2) Photohole is migrated to the surface of catalyst and reacted with the adsorbed hydroxyl ion to generate a hydroxyl radical; and reacted him with the adsorbed alcohol molecule to produce a hydrogen ion and CH$_2$OH species.

$$OH^-_{(s)} + h^+_{VB} \rightarrow {}^\cdot OH_{(s)} \qquad (19)$$

$$CH_3OH + h^+_{VB} \rightarrow {}^\cdot CH_2OH + H^+ \qquad (20)$$
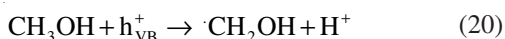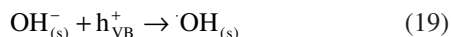
then, the generated hydroxyl radical reacts with alcohol.

$$\cdot OH_{(s)} + \overset{H}{\underset{H}{\diagdown}}CHOH \rightarrow \overset{H}{\underset{H}{\diagdown}}C^\cdot OH + H_2O \qquad (21)$$
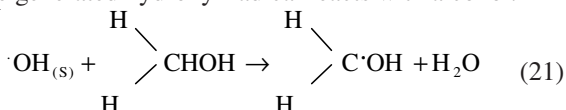
Generation of hydrogen: The platinum crystallite converts the protons to hydrogen atoms during reverse hydrogen spillover.
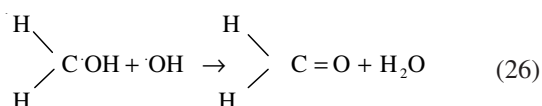
$$Pt_n^- + H^+ + H \rightarrow Pt_n\overset{H}{\underset{H}{\diagup}}\diagdown \qquad (22)$$

$$Pt_n\overset{H}{\diagup}\underset{H}{\diagdown} \rightarrow Pt_n + H_2 \qquad (23)$$

or, the half amount of hydrogen maybe librated by depending on H$^+$ from equation (20).

$$Pt_n^- + H^+ \rightarrow Pt_n - H \qquad (24)$$
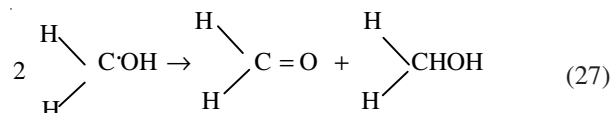
$$Pt_n - H \rightarrow Pt_n + \frac{1}{2}H_2 \qquad (25)$$
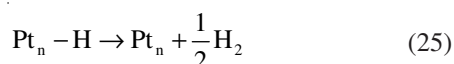
Formation of formaldehyde: This process is performed by three reactions:

1) Methoxyl radical reacts with hydroxyl radical.

$$\overset{H}{\underset{H}{\diagdown}}C^\cdot OH + {}^\cdot OH \rightarrow \overset{H}{\underset{H}{\diagdown}}C = O + H_2O \qquad (26)$$

2) Two methoxyl radicals react together:

$$2\,\overset{H}{\underset{H}{\diagdown}}C^\cdot OH \rightarrow \overset{H}{\underset{H}{\diagdown}}C = O + \overset{H}{\underset{H}{\diagdown}}CHOH \qquad (27)$$

3) Methoxyl radical dissociates to form hydrogen atom and formaldehyde molecule.

$$\overset{H}{\underset{H}{\diagdown}}C^\cdot OH \rightarrow \overset{H}{\underset{H}{\diagdown}}C = O + H \qquad (28)$$
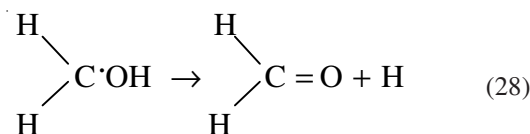
Conclusion

The efficiency of photocatalytic reaction of aqueous methanol solution was studied by using with or without Pt doped TiO$_2$ nanoparticales. The rate of reaction was measured with using a spectrophotometer measurements by following Nash method to determine the concentration of produced formaldehyde at a wavelength 412 nm. The crystallite size values were found between 7.541 and 9.326 nm.

Some important parameters in photocatalytic dehydrogenation of methanol solution like: loading of Pt on TiO$_2$, the concentration of mass, pH of solution and effect of temperature to calculate the activation energy for naked and Pt doped TiO$_2$ nanoparticales spontaneously. The best loading of platinum on titanium dioxide was 0.5 wt % that gives a high activity in dehydrogenation of methanol, while the increased of loading will shield the light.

The pH of solution plays a strong role in increasing the activity of reaction, so all catalysts have a certain range of zero point charge a round pH equal 6 thereby if the pH more or less these values that will decrease the rate of reaction.

Activation energies for formed formaldehyde were calculated at the temperature range 278-298 K by using Arrhenius equation for naked and platinized Hombikat UV 100 (23 ± 1 kJ mol^{-1}). The activation energy values for the photocatalytic dehydrogenation of aqueous methanol solution over platinized and naked titanium dioxide in the presence of oxygen is small that beyond to be associated with the transport of photoelectrons through the catalyst to the adsorbed oxygen on the surface and oxidation part from the produced formaldehyde to formic acid.

The recombination process was inhabited by using Pt doped titanium dioxide, that cause an increasing the separation between photoelectron and photohole.

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