



Photocatalytic Oxidation of Formaldehyde in ZnO or SiO₂ Suspensions

GUANGSHUN HOU^{1,*}, YINGJIE LI², XUCHENG PANG¹ and DADONG SHAO³

¹Institute of Resources and Environment, Henan Polytechnic University, Jiaozuo, Henan Province, P.R. China

²Department of Physics and Chemistry, Henan Polytechnic University, Jiaozuo, Henan Province, P.R. China

³Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, 230031, Hefei, P.R. China

*Corresponding author: E-mail: guangshunhou@eyou.com

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Photocatalytic oxidation of formaldehyde in K₂SO₄ solution using ZnO or SiO₂ as catalyst under ambient condition is studied. The effects of UV illumination time, catalyst (ZnO or SiO₂) content (m/V), HCHO initial concentration, pH and K₂SO₄ concentration on the photocatalytic oxidation of HCHO are determined. The presence of SiO₂ (1.0 g/L) can increase the photocatalytic oxidation of HCHO (2.0 × 10⁻² g/L) from 7.1 to 19.2 % after illumination time of 24 h. The photocatalytic oxidation of HCHO is dependent on pH value, but independent of ionic strength. The results are important for the application of sand (SiO₂) in the treatment of HCHO pollution in eutrophic environment and for the evaluation of the removal of organic pollutants by photocatalytic oxidation in the natural environment.

Key Words: Formaldehyde, SiO₂, ZnO, Photocatalytic oxidation, Formic acid.

INTRODUCTION

Formaldehyde is a common compound, which is widely used in medicine, industry and aquaculture industry, *etc.*¹⁻⁴ and is frequently found in wastewaters and waste gases causing environmental pollution. Formaldehyde is regarded as a very toxic agent with severe negative action on living organisms in the environment¹⁻³. Due to the increasing concern about formaldehyde pollution, the abatement of its emission is of significant practical interest at low temperature, especially at room temperature under natural environmental conditions^{5,6}. A number of studies related to the removal of formaldehyde have been carried out using activated carbon, aluminum oxide and ceramic materials *etc.* as adsorbents^{5,7}. Generally, adsorbents can only successfully eliminate formaldehyde for a short period due to the limited removal capacities of the adsorbents.

Photocatalytic method is a promising air purification technology for trace contaminant degradation because a broad range of organic pollutants can be completely mineralized to environmentally harmless compounds such as CO₂ and H₂O at room temperature and atmospheric pressure^{5,7,8}. Among various semiconductor photocatalysts, TiO₂ and ZnO have been proved to be the active catalyst and have been widely investigated. The removal of formaldehyde using TiO₂ as catalyst has been widely investigated^{4,8,9}. However, the data available in literatures about the removal of formaldehyde using ZnO as catalyst are still relatively fragmented and scarce. Sand is widely distributed in natural environment, such as in riverbeds,

in dunes and in coastal deposits. Kormann, *et al.*¹⁰ reported that hydrogen peroxide was generated by illumination of aqueous suspensions of semiconducting minerals, such as TiO₂, ZnO and also of desert sand. Although SiO₂ is inert as catalyst in most reactions, many reactions can process on SiO₂, such as partial oxidation of CH₃OH to formaldehyde^{11,12}, selective oxidation of propane¹³ and intramolecular dehydration of *N*-(2-hydroxyethyl)-2-pyrrolidone¹⁴. Thereby, study of SiO₂ as a catalyst is important and critical to understand the photocatalytic oxidation of organic pollutants in the natural environment because SiO₂ may act as the catalyst. SiO₂ can adsorb a certain amount of ultraviolet (UV) light and can be excited in the range of 200-500 nm¹⁵⁻¹⁷. Gallais *et al.*¹⁸ observed the luminescence of SiO₂ excited by a 244 nm pump beam. Positive oxide charge can be induced in SiO₂ and the ionizing radiation can create electron hole pairs in SiO₂^{19,20}. It is reasonable that SiO₂ can be a kind of natural catalyst in the environment.

However, to the best of our knowledge, investigations on SiO₂ as catalyst are still scarce. Thereby, knowledge of the photocatalytic activity of SiO₂ is critical to understand the photocatalytic oxidation of organic pollutants in the presence of SiO₂ in the natural environment. The purposes of this paper are: 1) to investigate the photocatalytic oxidation of formaldehyde by using SiO₂ and ZnO as catalyst; 2) to determine the intermediary compounds in the photocatalytic oxidation of formaldehyde; and 3) to study the photocatalytic oxidation of

formaldehyde as a function of SiO₂ or ZnO mass content, pH, illumination time and ionic strength.

EXPERIMENTAL

All chemical reagents Zn(NO₃)₂·6H₂O, Na₂CO₃, NaOH, K₂SO₄, H₂SO₄, H₃PO₄, NH₃·H₂O, KOH, SiO₂, formaldehyde, acetic acid, ammonium acetate and acetylacetone were purchased in analytical purity and used without any purification in the experiments. All solutions are prepared with Milli-Q water under ambient conditions.

Preparation of ZnO by homogeneous precipitation

method: 80 mL 0.5 mol/L NaOH aqueous solution was added dropwise into 40 mL 0.5 mol/L Zn(NO₃)₂ aqueous solution under vigorous stirring and then 50 mL 0.5 mol/L Na₂CO₃ solution and a certain volume of water was added. The mixture was kept at 60 °C for 30 min before filtration. The derived slurry was washed thoroughly with Milli-Q water after filtration and dried in oven at 95 °C for 24 h. The sample was calcined at 350 °C for 3 h in the end and thus ZnO was obtained.

SiO₂ was gently crushed and sieved to < 74 μm and then purified by 0.1 mol/L HNO₃ leaching overnight. At last, SiO₂ was washed thoroughly with Milli-Q water until the filtrate was neutral and dried at 110 °C for 2 days in the end.

In the experiments, the UV illumination was achieved by using a 20 W UV sterilization strip lamp. The primary illumination of the lamp was emitted at 253.7 nm. The lamp was 3 cm above the polyethylene tubes in the experiments.

All the experiments were carried out at T = 20 ± 1 °C in ambient conditions. The stock solution of catalyst (5.0 g/L), formaldehyde (0.10 g/L) and K₂SO₄ (0.40 mol/L) were added in polyethylene test tubes to achieve the desired concentrations of different components. The pH values of the suspension were adjusted by adding negligible volumes (herein about 10-50 μL for each tube) of 0.1 or 0.01 M H₂SO₄ or KOH. After the suspensions had been shaken for 24 h under UV illumination, the solid and liquid phases were separated by centrifugation (BECKMAN COULTER 64R) at 7500 rpm for 20 min at temperature controlled to 20 °C.

ZnO dissolves in acidic²¹ and basic²² solutions due to the less noble decomposition potential of ZnO than the equilibrium potential of H₂O/O₂ and ZnO may transfer electrons to the photo-generated holes and dissolve in acidic or basic solutions²². Thereby, the solution containing ZnO or SiO₂ were adjusted to pH 8.0 ± 0.1 to restrain the dissolution of ZnO.

The concentration of formaldehyde was analyzed by acetylacetone spectrophotometric method at wavelength 414 nm. All the experimental data were the average of duplicate determinations and the average uncertainties of the data were < 5 %. The removal percentage (%) of formaldehyde is calculated from the difference between the initial concentration (C₀) and the final one (C_{final}) of formaldehyde in solution using the following equation:

$$\text{Removal (\%)} = \frac{C_{\text{removal}}}{C_0} \times 100 \% = \frac{C_0 - C_{\text{final}}}{C_0} \times 100 \% \quad (1)$$

RESULTS AND DISCUSSION

Fourier transform infrared spectra of ZnO and SiO₂:

The characterization of SiO₂ by FTIR (Fig. 1) is recorded using

a Bruker EQUINOX55 spectrometer in KBr pellet at T = 20 ± 1 °C. As can be seen from Fig. 1, in the FTIR spectrum of SiO₂, the stretching vibration of H-O-H (*ca.* 3430 cm⁻¹, 1625 cm⁻¹), the asymmetric stretching vibrational of Si-O-Si (*ca.* 1090 cm⁻¹), symmetric stretching of bulk Si-O-Si (*ca.* 790 cm⁻¹), bending vibration of O-Si-O bond (*ca.* 694 cm⁻¹), bending modes of bulk Si-O-Si (*ca.* 460 cm⁻¹) can be identified and the CO₂ atmospheric peak (*ca.* 2364 cm⁻¹), respectively²³⁻²⁶.

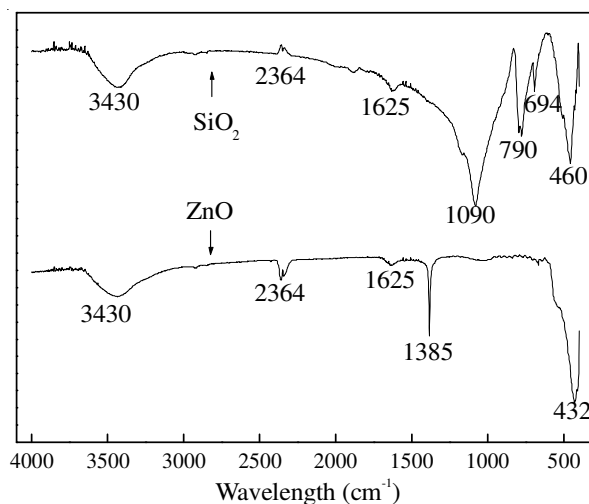


Fig. 1. Fourier transform infrared spectra of SiO₂ and ZnO

In the FTIR spectrum of ZnO, the stretching vibration of H-O-H (*ca.* 3430 cm⁻¹, 1625 cm⁻¹), the typical IR absorption peak of ZnO (*ca.* 432 cm⁻¹), the CO₂ atmospheric peak (*ca.* 2364 cm⁻¹) and the absorbed CO₂ absorption bands (*ca.* 1385 cm⁻¹) can be identified, respectively^{25,27-30}.

Effect of UV illumination time: Formaldehyde in aqueous solution exists mainly in the hydrated form as methylene glycol³¹⁻³³ and the methylene glycol exists predominantly in its ionized form in basic solution³¹:



SiO₂ contains physico-adsorbed water, surface hydroxyl groups and siloxane functionality³⁴⁻³⁶. The hydroxyl groups exist as single, *geminal* and hydrogen-bonded forms on the surfaces of SiO₂³⁶. Okumura *et al.*,³⁷ reported that the point of zero charge (PZC) of SiO₂ is around pH 2 and SiO₂ surface carries negative charge at pH > 2. Therefore, the sorption of formaldehyde on SiO₂ is difficult. Herein we found that the sorption of formaldehyde on ZnO and SiO₂ was negligible in our experiments and formaldehyde could not be oxidized in dark condition. Thereby, the removal of formaldehyde was carried out only under UV illumination.

Photocatalytic oxidation of formaldehyde at T = 20 ± 1 °C as a function of UV illumination time is shown in Fig. 2. As can be seen from Fig. 2, the removal of formaldehyde in ZnO and SiO₂ suspensions increased with the increasing of UV illumination time. After the suspension was illuminated for 24 h, the removal of formaldehyde was *ca.* 62.8 % in ZnO suspension and *ca.* 19.2 % in SiO₂ suspension.

It is worthy to note that SiO₂ is widely distributed in the natural environment. Although the photocatalytic activity of SiO₂ is much lower than that of ZnO, SiO₂ is still considered as a

potential material in the elimination of environmental pollution. The results are interesting to understand the photocatalytic oxidation of organic materials in the natural environment. The natural elimination of organic pollutants in the environment may be partly attributed to the photocatalytic activity by SiO₂.

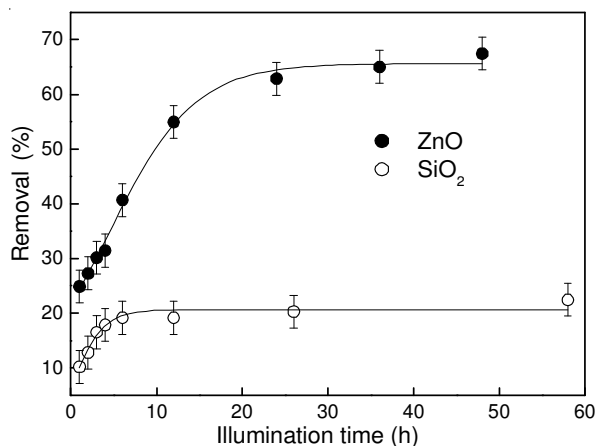


Fig. 2. Effect of UV illumination time on the removal of formaldehyde in ZnO and SiO₂ suspensions. C[HCHO]_(initial) = 2.0 × 10⁻² g/L, catalyst (ZnO or SiO₂) content (m/V) = 1.0 g/L, C[K₂SO₄] = 0.09 mol/L, pH = 8.0 ± 0.1

Effect of catalyst content: Photocatalytic oxidation of formaldehyde at T = 20 ± 1 °C as a function of catalyst content is shown in Fig. 3. As can be seen from Fig. 3, the removal of formaldehyde is only ca. 7.1 % in the solution without catalyst after illumination time of 24 h. The removal of formaldehyde increases with the increasing of SiO₂ and ZnO content in the suspensions. As catalyst content increases from 0.2 to 2.0 g/L, the removal percentage of formaldehyde from solution increases from ca. 20.9 % to ca. 66.1 % in ZnO suspension and from ca. 10.0 % to ca. 20.1 % in SiO₂ suspension. It is necessary to notice that the content of SiO₂ is only 2.0 g/L and the removal of formaldehyde achieves to ca. 20.1 %. As can be seen from Figs. 2 and 3, it is reasonable that the widely distributed sand (SiO₂) can improve the elimination of organic pollutants (such as formaldehyde) under illumination in the environment.

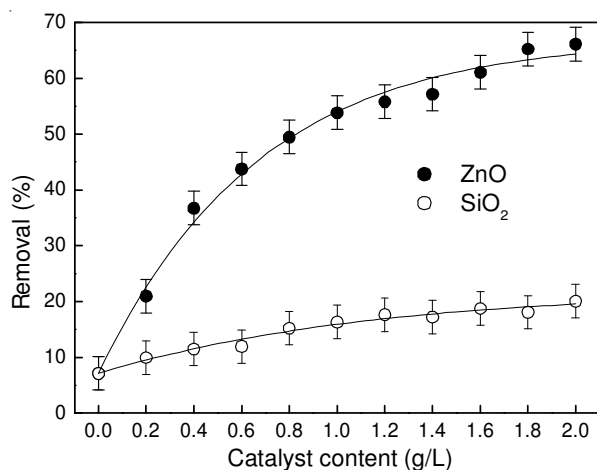


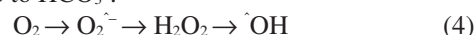
Fig. 3. Effect of catalyst contents on the removal of formaldehyde. C[HCHO]_(initial) = 2.0 × 10⁻² g/L, C[K₂SO₄] = 0.09 mol/L, pH = 8.0 ± 0.1, illumination time : 24 h

Determination of intermediate compounds: The intermediate compounds in the photocatalytic oxidation of formaldehyde is analyzed by using high performance liquid chromatography on Agilent 1100 series HPLC, using Agilent C₁₈ column (250 mm × 4.6 mm, 5 μm) and 2.00 × 10⁻² mol/L H₃PO₄ (pH = 2.0, adjusted by NH₄OH) as mobile phase (1.5 mL/min) at room temperature. The detection is made at the wavelength of 210 nm.

During the photocatalytic oxidation of formaldehyde to CO₂, formaldehyde is oxidized to the final product *via* an intermediate formation³⁸. Formate acid (HCOO⁻) is the most commonly intermediary compound from the conversion of formaldehyde by photocatalytic oxidation in aqueous phase and gaseous phase^{9,31,39,40}. The oxidation of the HCOO⁻ is the rate determining step of the overall path^{33,38}. Thus, the yield of HCOO⁻ is also an important parameter to indicate the photocatalytic oxidation of formaldehyde⁹.

The intermediary compound determined by HPLC in the photocatalytic oxidation of formaldehyde is shown in Fig. 4A. As can be seen from Fig. 4A, only carbonate and formate (intermediary compound) were detected by HPLC analysis in photocatalytic oxidation of formaldehyde. The peak areas of HCOO⁻ in HPLC derived from the system containing ZnO and from the system containing SiO₂ was about 3:1, which was quite close the ratio of the removal percentage of formaldehyde in ZnO and SiO₂ suspensions, respectively (*i.e.*, 62.8 %: 19.2 % ≈ 3: 1). The amounts of HCOO⁻ detected by HPLC analysis was quite consistent with the removal percentage of formaldehyde in ZnO and SiO₂ suspensions, which indicated that HCOO⁻ is one important intermediary compound in the photocatalytic oxidation of formaldehyde. Silva *et al.*¹ observed that HCOO⁻ can be completely oxidized. It is worthy to note that the addition of SiO₂ increases the concentration of HCOO⁻ in solution, which is in agreement with the photocatalytic oxidation of formaldehyde in SiO₂ suspension.

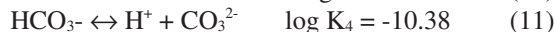
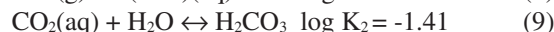
From the HPLC analysis, it is clear that HCOO⁻ is one of the intermediate compounds in the photocatalytic oxidation of formaldehyde to HCO₃⁻:



The net oxidation equation of formaldehyde to HCO₃⁻ is:



HCO₃⁻ was also detected in the HPLC analysis, the presence of HCO₃⁻ was attributed to the dissolution of CO₂ in solution. The dissolution equilibrium constant of gaseous CO₂ in solution⁴¹:



As can be seen from Fig. 1, ca. 62.8 % of formaldehyde (2.0 × 10⁻² g/L) was oxidized in ZnO suspension (1.0 g/L, pH = 8.0 ± 0.1) after illuminated for 24 h. If the formaldehyde (ca. 62.8 %) was oxidized to CO₂ entirely, about 4 × 10⁻⁴ mol/L CO₂ would be produced. Therefore, the calculation of partial pressure of CO₂ (g) and the concentration of H₂CO₃, CO₂ (aq), HCO₃⁻ and CO₃²⁻ at different pH value was proceeded assuming the carbonate concentration of 4.0 × 10⁻⁴ mol/L.

According to the dissolution constants of eqns.(8)-(11), the relative concentrations of different species are shown in Fig. 4B. The relative concentrations of H₂CO₃ at different initial concentrations of NaHCO₃ are listed in Table-1 as a comparison⁴¹. From Fig. 4B, it is clear that the final production of CO₂ in the photocatalytic oxidation of formaldehyde mainly exists in CO₂ (aq) and HCO₃⁻ forms at pH = 8.0 ± 0.1. Therefore, the species of CO₂ was simply expressed as HCO₃⁻, irrespective of other species in suspension.

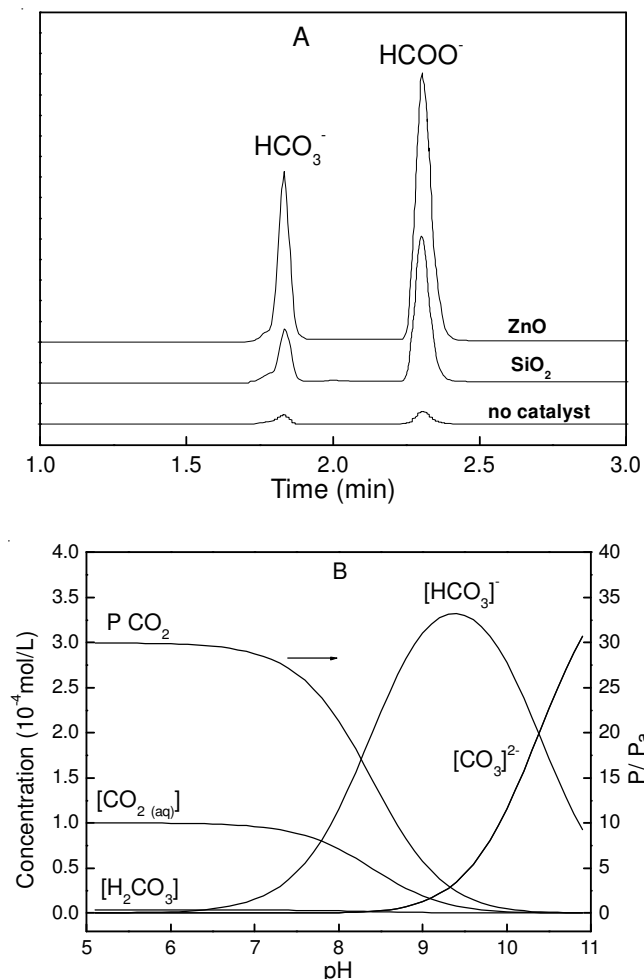


Fig. 4. Evaluation of intermediary compounds. A: C[HCHO]_(initial) = 2.0 × 10⁻² g/L, C[K₂SO₄] = 0.09 mol/L, pH = 8.0 ± 0.1, illumination time: 24 h. B: the calculation of partial pressure of CO₂ (g) and the concentration of CO₂ (aq), H₂CO₃, HCO₃⁻ and CO₃²⁻ in 4.0 × 10⁻⁴ mol/L carbonate solution at different pH value

TABLE-1
CALCULATED CONCENTRATION OF H₂CO₃ AND
CORRESPONDING PARTIAL PRESSURE OF CO₂ IN
SOLUTIONS PREPARED WITH NaHCO₃ (Oter *et al.*⁴¹)

Total NaHCO ₃ (mol L ⁻¹)	[H ₂ CO ₃] (mol L ⁻¹)	PCO ₂ in RTILs (atm)
2 × 10 ²⁶	1.95 × 10 ²⁷	5.02 × 10 ²⁶
2 × 10 ²⁵	6.97 × 10 ²⁷	1.79 × 10 ²⁵
2 × 10 ²⁴	2.79 × 10 ²⁶	7.17 × 10 ²⁵
2 × 10 ²³	2.33 × 10 ²⁵	5.98 × 10 ²⁴
2 × 10 ²²	1.86 × 10 ²⁴	4.78 × 10 ²³

*RTILs: room temperature ionic liquids

Removal efficiency of formaldehyde at different formaldehyde initial concentration: Photocatalytic oxidation of

formaldehyde at T = 20 ± 1 °C at different formaldehyde initial concentrations is shown in Fig. 5A. One can see that the removal of formaldehyde in ZnO suspension is much higher than that of formaldehyde in SiO₂ suspension. As can be seen from Fig. 5A and 5B, the removal of formaldehyde from solution without catalyst is quite low. When the final concentration of formaldehyde achieves *ca.* 21.8 mg/L in the solution without catalyst, the removal of formaldehyde is only *ca.* 2.2 mg/L. ZnO has a very high capacity in the removal of formaldehyde from solution. As the final concentration of formaldehyde increases from 0.76 mg/L to 17.4 mg/L, the removal of formaldehyde increases from 3.2 mg/L to 22.6 mg/L.

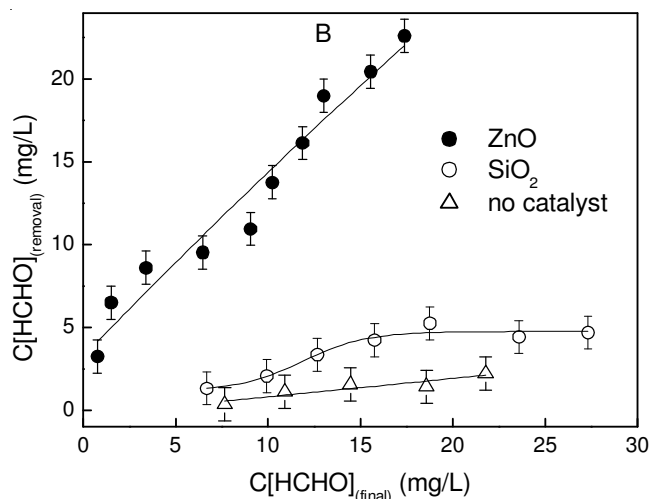


Fig. 5. Removal of formaldehyde (HCHO) at different HCHO initial concentration. m/V = 1.0 g/L, C[K₂SO₄] = 0.09 mol/L, pH = 8.0 ± 0.1, illumination time: 24 h

The presence of SiO₂ in solution can increase the removal of formaldehyde comparing to the solution without catalyst. As the final concentration of formaldehyde increases from 6.7 mg/L to 15.8 mg/L, the removal of formaldehyde increases from 1.3 mg/L to 4.2 mg/L (Fig. 5B). Then the amount of formaldehyde removal maintains level with further increasing of formaldehyde final concentration.

Due to the toxicity of formaldehyde, wastewaters which contain high concentrations (800-1500 ppm) of formaldehyde are difficult to be treated by conventional processes (such as biological process) because formaldehyde can inhibit microbial activity and causes the death of microbe¹⁻³. Photocatalytic oxidation of formaldehyde is considered as one of the potential methods in the elimination of formaldehyde pollution in the environment, especially at high concentrations.

Effect of pH: Photocatalytic oxidation of formaldehyde at T = 20 ± 1 °C as a function of pH is shown in Fig. 6. Herein, the removal of formaldehyde in ZnO suspension as a function of pH is carried out only in pH 8-11. As can be seen from Fig. 6, the removal of formaldehyde increases from 53.8 % to 95.3 % rapidly when pH value increases from 8.1 to 11.1 in ZnO suspension. The increase of pH values improves the removal of formaldehyde in SiO₂ suspension and in the solution without catalyst. The removal of formaldehyde increases from 14.6 % to 16.8 % at pH increasing from 4.2 to 10.9 in SiO₂ suspension and increases from 6.7 % to 10.2 % with the

increasing of pH from 4.9 to 11.1 in the solution without catalyst. The removal of formaldehyde in SiO₂ suspension is lower than that of formaldehyde in ZnO suspension.

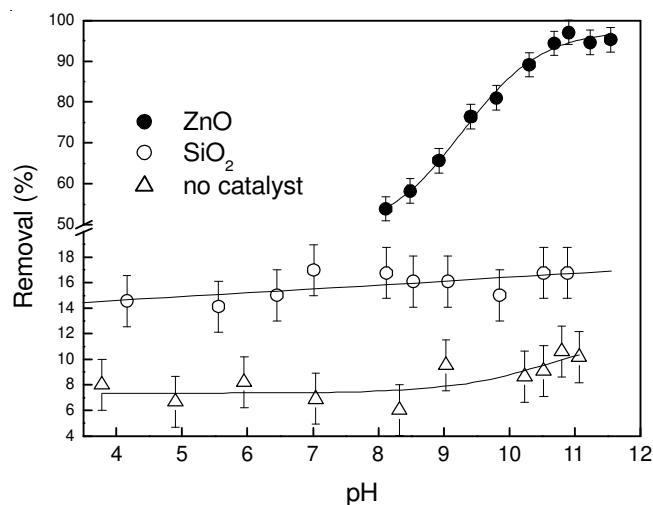


Fig. 6. Effect of pH value on the removal of HCHO. $C[\text{HCHO}]_{(\text{initial})} = 2.0 \times 10^{-2}$ g/L, $m/V = 1.0$ g/L, $C[\text{K}_2\text{SO}_4] = 0.09$ mol/L, illumination time: 24 h

Effect of ionic strength: Photocatalytic oxidation of formaldehyde at $T = 20 \pm 1$ °C as a function of K_2SO_4 concentrations ranged from 0.018 mol/L to 0.180 mol/L are investigated. The removal of formaldehyde is (63 ± 3) % in ZnO suspension and (19 ± 3) % in SiO₂ suspension. We do not find that the photocatalytic oxidation of formaldehyde increases with the increasing of ionic strength under our experimental conditions. It suggests that ionic strength in solution has unnoticeable influence on the photocatalytic oxidation of formaldehyde.

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