Comparison of different TiO₂ photocatalysts for the gas phase oxidation of volatile organic compounds

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Abstract Gas–solid photocatalyzed oxidation of air contaminants is being explored more and more for possible application to decontamination, purification and deodorization of enclosed atmospheres. Indoor air is characterized by a huge number of pollutants at low concentrations. Volatile organic compounds (VOC) represent the main indoor air pollutants category, and are of great concern since some of them can act negatively on human health. Several treatments exist to reduce VOC concentrations in gaseous effluents, but photocatalytic oxidation appears to be the most appropriate regarding indoor air specific constraints. It is then necessary to develop photocatalysts, which can possibly be used in an application such as indoor air-quality improvement. In the present work, three different TiO₂-based materials were studied and compared for the photocatalytic oxidation of a typical pollutant of indoor air: methyl ethyl ketone. Kinetic studies were performed for each material in dry and humid air conditions, and the Langmuir–Hinshelwood model was satisfactorily applied in almost every case. A second approach consisted of determining methyl ethyl ketone degradation by-products. Acetaldehyde was found to be the main gaseous intermediate, and could be taken into account in the general Langmuir–Hinshelwood modeling.

Keywords Degradation intermediates; indoor air treatment; methyl ethyl ketone; photocatalysis; supported TiO₂

Introduction

During the past several decades, indoor air pollution has become a public health concern. Indoor air quality (IAQ) is characterized by a huge number of pollutants, among which the main category is the one of volatile organic compounds (VOC) (Lee et al., 2002; Salthammer et al., 2002; Son et al., 2002). Actually, some VOC may induce nausea, irritations, asthma, sick building syndrome, and may cause cancers (Kim et al., 2001; Righi et al., 2002; Salthammer et al., 2002; Son et al., 2002; Meininghaus et al., 2003). Numerous treatments exist to reduce VOC concentrations in gaseous effluents, but photocatalytic oxidation appears to be the most appropriate regarding indoor air specific constraints (Pichat et al., 2000).

Photocatalytic degradation of air contaminants such as volatile organic compounds has been studied over the last decades, and encouraging results have been obtained (Peral and Ollis, 1992; Voronstov et al., 1997). Photocatalytic oxidation is based on the use of a light-activated semi-conductor to speed up VOC oxidation. A semiconductor is a compound which contains one or several crystalline phases and is able to release some electrons. It is characterized by a band gap of low energy (3.2 eV for TiO₂) between the valence band and the conduction band. When a semiconductor is irradiated with photons of the appropriate wavelength and energy, the band gap is exceeded and an electron is promoted from the valence band to the conduction band. The resultant electron-hole pair has a lifetime that enables it to participate in chemical reactions. The activation of TiO₂ by UV light (wavelength lower than 385 nm) can be written according to the equation below:
\[ \text{TiO}_2 + h\nu \rightarrow h^+ + e^- \]  

(1)

\( h^+ \) and \( e^- \) are powerful oxidizing and reductive agents respectively, which participate in oxidative and reductive reactions with \( \text{O}_2, \text{H}_2\text{O} \) and \( \text{OH}^- \). These reactions lead to the formation of highly reactive species such as superoxide and hydroxyl radicals. The latter oxidize VOC adsorbed on the catalyst surface. For the most part, final products of VOC photocatalytic oxidation are \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) (Peral et al., 1997; Zhao and Yang, 2003; Serpone et al., 1993). The strong oxidizing power of the photogenerated holes and electrons, and the chemical inertness and non-toxicity of \( \text{TiO}_2 \), make it a superior photocatalyst.

The present work aims to study three different \( \text{TiO}_2 \)-based photocatalysts for the photocatalytic oxidation of a typical indoor air pollutant: methyl ethyl ketone (MEK). A first part consists of summarizing the kinetic study results for each photocatalytic material with several operating conditions. The second part deals with determining methyl ethyl ketone degradation by-products by GC–MS quantitative analysis. The third part gives the results of the modeling of experimental data by the general Langmuir–Hinshelwood model.

**Experimental section**

**Catalysts**

Catalyst A is composed of \( \text{TiO}_2 \) thin films deposited on optically transparent microscopy glass slides (76 mm × 26 mm) using \( \text{TiO}_2 \) P25 Degussa (Raillard et al., 2004). The latter has a surface area of 50 m\(^2\) g\(^{-1}\), and is a mixture of anatase (70%) and rutile (30%) crystalline phases (Arabatzis et al., 2002). About 5 mg of \( \text{TiO}_2 \) was deposited per glass support, i.e. 2.5 g m\(^{-2}\).

Catalyst B is composed of mixed \( \text{TiO}_2 \) and \( \text{SiO}_2 \), with an atomic ratio Ti/Si equal to 2/3, deposited on a cellulose support (50 mm × 50 mm). The amount of titanium dioxide is about 20 g m\(^{-2}\).

Catalyst C is an industrial material comprising ordinary glass substrates (35 mm × 60 mm) coated with a thin transparent film of nanoparticles of crystallized \( \text{TiO}_2 \) in a silica binder. The amount of deposited \( \text{TiO}_2 \) is not known for this material.

**Measurement of the photocatalytic activity in gas phase**

Supported-\( \text{TiO}_2 \) samples were placed in a 12-L batch reactor. Irradiation was provided by a medium-pressure mercury lamp (Heraeus 700 W, \( \lambda_{\text{max}} = 365 \) nm). Experiments were performed under both dry (relative humidity (RH) between 0 and 7% at 30°C) and humid (RH of 30% at 30°C) atmospheric conditions. The gas was continuously mixed in the reactor with an all-Teflon pump. A gas chromatograph equipped with a flame ionization detector (AutoSystem XL, Perkin-Elmer) was used to follow methyl ethyl ketone concentration during kinetics, and a gas chromatograph equipped with a mass spectrometer (TurboMass Gold, Perkin-Elmer) was used to identify and quantify methyl ethyl ketone degradation by-products.

**Results and discussion**

**Kinetic study over the three photocatalysts**

Five initial concentrations were tested to perform the kinetic study over the three photocatalysts under dry and humid atmospheric conditions. Methyl ethyl ketone initial levels ranged from 0.6 to 6.0 g m\(^{-3}\).

In photocatalytic studies, the kinetics of degradation are generally represented by the Langmuir–Hinshelwood model at the initial time. The latter is defined by the following expression (Eq. (2)).
where \( r_0 \) is the initial reaction rate (g m\(^{-3}\) min\(^{-1}\)), \( k \) the reaction rate constant (g m\(^{-3}\) min\(^{-1}\)) and \( K \) the Langmuir adsorption constant (m\(^3\) g\(^{-1}\)). This expression is only valid at the initial time of the reaction when it can be assumed that no methyl ethyl ketone degradation by-products are already formed. In this study, initial reaction rates were calculated by modeling the kinetics slopes (MEK concentration versus irradiation time) by a third-order polynomial, and by deriving it at \( t = 0 \) \( (r_0 = -(dC/dt)|_{t=0}) \) and Langmuir–Hinshelwood parameters were calculated by least-squares analysis. The results are reported in Table 1 for the three photocatalysts at each level of relative humidity.

In both dry and humid atmospheric conditions the Langmuir–Hinshelwood model (Figure 2a) correctly describes the degradation kinetics of MEK. For catalysts A and B, the reaction rate constant \( k \) is higher under a humid atmosphere, even though it is lower for catalyst C. On the contrary, the Langmuir adsorption constant \( K \) is lower in humid air conditions for catalysts A and B, and is slightly higher for catalyst C. This may be explained by the different behaviors of water molecules, depending on the studied photocatalysts.

Actually, water vapor plays a double role in photocatalytic oxidation of organic pollutants. On one hand, water molecules can be adsorbed on the catalyst surface and occupy adsorption sites that become unavailable for pollutant adsorption. When water molecules have a good affinity with the photocatalyst adsorption sites, competitive adsorption between MEK and \( \text{H}_2\text{O} \) molecules on TiO\(_2\)-based catalysts takes place. On the other hand, water molecules can react with excited TiO\(_2\) to produce hydroxyl radicals (Sitkiewitz and Heller, 1996; Piscopo \textit{et al}., 2001; Kim \textit{et al}., 2002). Hydroxyl radicals are very oxidative compounds that can enhance the degradation of MEK.

Then it can be assumed that water molecules have a good affinity in term of adsorption with catalysts A and B, thus involving a decrease of Langmuir adsorption constants under a humid atmosphere. The higher value of reaction rate constants under a humid atmosphere for catalysts A and B may be explained by the formation of hydroxyl radicals. On the contrary, water molecules may be not only adsorbed but also condensed on to the catalyst surface. This may form a thin layer of water at the catalyst surface, also involving a fall in the photocatalytic reaction rate.

It appears to be difficult to compare the performances of the three photocatalysts using this method, because they do not have the same active surface area and the same TiO\(_2\) content. The mass of deposited TiO\(_2\) for catalyst C is not known, so it is more convenient to compare the three photocatalysts per surface unit. The so-called active surface corresponds to the one that is irradiated by the UV–visible lamp. The expressions of the photocatalytic degradation per surface area unit, derived from the Langmuir–Hinshelwood model, become:

\[
\frac{r_0}{K C_0} \quad \text{or} \quad \frac{1}{r_0} = \frac{1}{k K C_0} + \frac{1}{K} \quad \text{(3)}
\]

where \( r_0’ \) (g m\(^{-3}\) min\(^{-1}\) m\(^{-2}\)) is the initial reaction rate per surface area unit, \( k’ \) (g m\(^{-3}\) min\(^{-1}\) m\(^{-2}\)) the pseudo-Langmuir–Hinshelwood rate constant and \( K’ \) (m\(^3\) g\(^{-1}\)) the

### Table 1 Langmuir–Hinshelwood model parameters

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst A</th>
<th></th>
<th>Catalyst B</th>
<th></th>
<th>Catalyst C</th>
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<tbody>
<tr>
<td></td>
<td>Dry air</td>
<td>Humid air</td>
<td>Dry air</td>
<td>Humid air</td>
<td>Dry air</td>
</tr>
<tr>
<td>( k ) (g m(^{-3}) min(^{-1}))</td>
<td>0.0196</td>
<td>0.0482</td>
<td>0.0258</td>
<td>0.0339</td>
<td>0.0231</td>
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<tr>
<td>( K ) (m(^3) g(^{-1}))</td>
<td>0.524</td>
<td>0.137</td>
<td>0.950</td>
<td>0.478</td>
<td>0.129</td>
</tr>
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</table>

pseudo-Langmuir adsorption constant. The calculated values of $k'$ and $K'$ for the three photocatalysts at each level of relative humidity are given in Table 2.

In dry air conditions, the difference between $k'$ values is not important, although catalyst C presents the highest reaction rate. Under a humid atmosphere, $k'$ for catalyst A is about two times higher than for catalyst B and four times higher than for catalyst C. This means that water vapor has a strong influence on the methyl ethyl ketone degradation, and catalyst A gives the best performances with a relative humidity of 30% at 30°C and over a concentration range up to 6 g m$^{-3}$.

By consulting Figure 2b, conclusions can easily be drawn. It appears that for low initial

<table>
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<tr>
<th>Table 2</th>
<th>Langmuir–Hinshelwood model parameters per surface area unit</th>
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<tbody>
<tr>
<td>Catalyst A</td>
<td>Catalyst B</td>
</tr>
<tr>
<td>Dry air</td>
<td>Humid air</td>
</tr>
<tr>
<td>$k'$ (g m$^{-3}$ min$^{-1}$ m$^{-2}$)</td>
<td>4.948</td>
</tr>
<tr>
<td>$K'$ (m$^3$ g$^{-1}$)</td>
<td>0.524</td>
</tr>
</tbody>
</table>

Figure 2 Experimental points and the Langmuir–Hinshelwood model. (a) $r_0$ versus $C_0$. (b) $r'_0$ versus $C_0$
concentrations (less than 3 g m\(^{-3}\)), the best performances are obtained with catalyst B, whatever the relative humidity level.

For every initial MEK concentration, catalyst C offers the worst efficiency in term of MEK degradation. For catalyst A, there is an important difference in MEK photocatalytic degradation capacities varying with relative humidity. It may be thought that changing the ambient relative humidity would induce a variable efficiency of the photocatalyst in an everyday use of this catalyst for the improvement of IAQ. This aspect has to be considered when dealing with human health.

The efficiency of the catalysts should not be assessed only on MEK removal. Actually, another important aspect has to be considered. Photocatalytic oxidation of volatile organic compounds may lead to the formation of reaction intermediates. These by-products are potentially more dangerous to human health than the initial pollutants. They can differ from one photocatalyst to another and change with humidity conditions. In the present work, the by-products were identified and quantified for the three photocatalysts under dry and humid atmospheres by GC–MS analysis.

**MEK reaction intermediates**

In the photocatalytic oxidation of MEK under a dry or humid atmosphere, acetaldehyde was identified as the main intermediate gaseous product for the three photocatalysts. For catalysts A and B, the concentration of acetaldehyde first increased during experiments, and began to decrease when about 60% of initial methyl ethyl ketone amount were removed (Figure 3). For catalyst C, the concentration of acetaldehyde only increased during the experiment up to a MEK removal of about 60%, and would probably decrease after this point. Methyl formate (MF) was also detected for photocatalysts A and B under a dry atmosphere and for catalyst B only in humid atmospheric conditions. The concentration of MF reached a maximum of 7 mg m\(^{-3}\) (i.e. \(C_{MF}/C_{MEK0} = 0.1 \text{ mol}\%\)) for catalyst B under a humid atmosphere and a maximum of 130 mg m\(^{-3}\) (i.e. \(C_{MF}/C_{MEK0} = 2.7 \text{ mol}\%\)) for catalyst B and 94 mg m\(^{-3}\) (i.e. \(C_{MF}/C_{MEK0} = 1.8 \text{ mol}\%\)) for catalyst A under dry air. MF was not detected for methyl ethyl ketone photocatalytic oxidation over catalyst C, but would perhaps have been detected if experiments had been conducted over a longer irradiation time. Other by-products such as methanol and acetone were detected, but in very low concentrations, so that it was not possible to quantify them. They may have been simultaneously formed and consumed.

The conversion rate is expressed as \(f_i = C_i(t)/C_{imax}\), where \(C_i(t)\) is the product concentration at the time \(t\) and \(C_{imax}\) is the highest concentration reached during experiments. For methyl ethyl ketone, \(C_{max}\) corresponds to \(C_0\).

It is also possible to compare the production and consumption of acetaldehyde for the three photocatalysts by plotting the concentration of acetaldehyde in the gas phase divided by the active surface of photocatalyst (\(C_{acetaldehyde}/S\)) versus the amount of removed methyl ethyl ketone (1 – \(C_0/C_0\)) (Figure 4).

Figure 4 shows that catalysts A and B are equivalent in terms of acetaldehyde formation and degradation under a dry atmosphere. There is an important difference between experiments under dry and humid atmospheres. Mostly for catalysts A and B, the acetaldehyde concentrations are higher under humid atmospheres. Water vapor enhanced the appearance of acetaldehyde in the gas phase and reduced its consumption. It also enables the formation of methyl formate in the gas phase as a methyl ethyl ketone degradation by-product. To sum up, it can be said that catalyst A will give the best performances for the methyl ethyl ketone photocatalytic degradation in terms of initial pollutant removal (\(C_0\) ranging from 0 to 6 g m\(^{-3}\)), and a low degree of formation of by-products, which can also be degraded over this catalyst.
Figure 3 Time profiles of the methyl ethyl ketone, acetaldehyde and methyl formate conversion rates ($f_i$) for the photocatalytic oxidation of methyl ethyl ketone at $C_0 = 6 \text{ g m}^{-3}$ over catalyst A, catalyst B and catalyst C under dry and humid atmospheres.
Synthesizing a rate low

We now wish to develop rate laws for the photocatalytic degradation of MEK over the three photocatalysts under dry and humid atmospheres. The general Langmuir–Hinshelwood model can represent the rate law over the whole degradation time, considering that reaction intermediates and products are insignificant, by the following equation (Eq. (4)) (Sauer and Ollis, 1994; Zhao and Yang, 2003):

\[ r = \frac{kKC}{1 + KC} \]  

where \( r \) (g m\(^{-3}\) min\(^{-1}\)) is the reaction rate at time \( t \), \( k \) (g m\(^{-3}\) min\(^{-1}\)) the Langmuir–Hinshelwood rate constant and \( K \) (m\(^3\) g\(^{-1}\)) the Langmuir adsorption constant. This expression does not take possible reaction intermediates into account. Nevertheless, it seems obvious that reaction by-products will play an important role in the writing of the reaction rate law. The latter are entered in the equation in the adsorption term (Eq. (5)) (Fogler, 1992):

\[ r = \frac{kKC}{1 + KC + \sum K_i C_i} \]  

with \( K_i \) being the adsorption constant for by-product \( i \) and \( C_i \) the concentration of by-product \( i \) in the gas phase.

In the present work we only concentrate on acetaldehyde as a reaction intermediate with regard to its presence in every case, and because it was the main important by-product. As previously described, the relative humidity of the system was initially set to the desired value before beginning the photoreaction. The evolution of the humidity is not taken into account in the kinetic model employed. The model implicitly assumes that the concentration of water vapor remains unchanged during each experiment. In all cases, oxygen is present in a large excess. Consequently, its concentration can be considered invariable during the photocatalytic experiments. Oxygen concentration does not appear in the model equation. Moreover, the overall reaction is irreversible, and CO\(_2\) is assumed to be negligible. Then CO\(_2\) is not included in the model equation too.

The model equation is simply written (Eq. (6)):
with $K'$ being the acetaldehyde adsorption constant, $C'$ the acetaldehyde concentration, $K_e$ the water-vapor adsorption constant and $C_e$ the water vapor concentration (constant). The model constants are calculated from experimental data by multiple linear regressions. The constants are given in Table 3 for each catalyst. Figure 5 represents the difference between experimental and calculated data.

According to Figure 5, we assume that the Langmuir–Hinshelwood model is globally well-fitted. The difference between calculated and experimental data can be attributed to the fact that the model does not take methyl formate as a by-product into account and considers that the concentration of water vapor is constant during kinetics.

The model shows that catalyst B has the highest specific reaction rate constant. The methyl ethyl ketone adsorption constant is quite low for catalyst C and of the same order of magnitude for catalysts A and B. The water-vapor adsorption constant is very low for catalyst C, four times higher for catalyst B and 30 times higher for catalyst A. The acetaldehyde adsorption constant is the same order of magnitude for catalysts B and C and is three times higher for catalyst A. From these calculations, it appears that catalyst C seems to be the more efficient one in terms of the specific reaction rate constant. However, probably in relation to the low adsorption constants for this catalyst, the latter does not show better methyl ethyl ketone removal.

**Conclusion**

The photocatalytic degradation of methyl ethyl ketone over three TiO$_2$-based photocatalysts, as a function of the initial concentration and water vapor content, was investigated in a batch photoreactor. The kinetic results were simulated using the Langmuir–Hinshelwood model, so that reaction rate and Langmuir adsorption constants

### Table 3  Langmuir–Hinshelwood model parameters for the three photocatalysts

<table>
<thead>
<tr>
<th></th>
<th>Catalyst A</th>
<th>Catalyst B</th>
<th>Catalyst C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ (g m$^{-3}$ min$^{-1}$)</td>
<td>0.0213</td>
<td>0.0307</td>
<td>0.0275</td>
</tr>
<tr>
<td>$k[p]$ (g m$^{-3}$ min$^{-1}$ m$^{-2}$)</td>
<td>5.3897</td>
<td>6.1400</td>
<td>6.5476</td>
</tr>
<tr>
<td>$K$ (m$^3$ g$^{-1}$)</td>
<td>1.6427</td>
<td>1.2494</td>
<td>0.1139</td>
</tr>
<tr>
<td>$K[p]$ (m$^3$ g$^{-1}$)</td>
<td>6.9509</td>
<td>2.1737</td>
<td>2.5049</td>
</tr>
<tr>
<td>$K_e$ (m$^3$ g$^{-1}$)</td>
<td>0.1087</td>
<td>0.0153</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

**Figure 5** Calculated reaction rate versus experimental reaction rate for catalysts A, B and C.
could be calculated. The comparison of the materials was achieved by considering the geometric surface developed by each material leading to specific model constants. A second step consisted of determining methyl ethyl ketone degradation reaction intermediates for the three photocatalysts under dry and humid atmospheres. Acetaldehyde was found to be the main gaseous intermediate. Methyl formate was also detected for catalyst A in dry air, and for catalyst B in both dry and humid air. A rate law was determined for the three photocatalysts using the general Langmuir–Hinshelwood model and considering the role of acetaldehyde and water in the gas phase.

Catalysts A and B show the best performances in terms of methyl ethyl ketone removal for an initial concentration ranging from 0 to 6 g m$^{-3}$. Water vapor content has the strongest influence on catalyst A. The degradation rate is enhanced with a relative humidity of 30% at 30°C. Catalyst C seems to be efficient in term of a specific reaction rate constant: however, as a result of the low adsorption constants, the methyl ethyl ketone degradation is finally lower than that for both catalysts A and B. Finally, catalyst A is the most interesting photocatalyst regarding the formation and degradation of by-products when the relative humidity can be controlled.

References

