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# $TiO_2$ coating types influencing the role of water vapor on the photocatalytic oxidation of methyl ethyl ketone in the gas phase

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## Abstract

Four $TiO_2$-based materials, named A, B, C and D, are used to investigate the influence of water vapor on the gas–solid adsorption and heterogeneous photocatalytic oxidation of gaseous methyl ethyl ketone (MEK). Two of the photocatalysts (A and B) are constituted of powdered $TiO_2$ deposited onto two different supports (ordinary glass and non-woven cellulose fibers). The other ones (C and D) are composed of a thin film of $TiO_2$ coated on glass substrates. The effect of water vapor on MEK initial conversion rates is studied for the four photocatalytic materials using the Langmuir–Hinshelwood model at the initial time. On the concentrations range where the model hypotheses are verified, adsorption constants $K$ and kinetics constants $k$ are calculated for experiments under both dry and humid atmosphere. When the relative humidity is increased, the evolution of these constants shows that water vapor acts differently depending on the form of deposited $TiO_2$ (powder and film).

*Keywords:* Photocatalysis; $TiO_2$; Powder; Film; Relative humidity; Methyl ethyl ketone

## 1. Introduction

Due to its stability and non-toxicity, $TiO_2$ has been extensively investigated for the photocatalytic degradation of a large variety of environmentally harmful organic compounds in gas or aqueous phase [1–4]. Photocatalytic degradation of air contaminants such as volatile organic compounds (VOC) has been studied over the last decades and more and more for applications to air treatment in habitable atmospheres [5–7].

Numerous studies dealt with the use of $TiO_2$-based photocatalysts in the form of powder or pellets [8,9]. This form of $TiO_2$ involves several technical problems, particularly because a step of filtration after the reaction is necessary. For this reason, supported $TiO_2$ was developed. Generally a thin layer of $TiO_2$ is coated on various substrates such as glass plates, silicon wafers, zeolites, ceramic membranes, activated carbon fiber for example [7,10–20].

The effect of humidity on the photochemical oxidation reaction in the gas phase has also been widely investigated because of its impact on the degradation rates [21]. The presence of water vapor has both inhibiting and activating capabilities on photocatalytic oxidation reactions of various VOC. Water vapor has been proved to react according to two main phenomena. On one hand, water molecules are transformed into hydroxyl radicals $OH^\bullet$ which are adsorbed at the titania surface, reacting as a hole trap ($h^+$). Hydroxyl radicals result from the dissociative chemisorption of water on the $Ti^{4+}$ sites [6]. On the other hand, as the concentration of water vapor increases, competitive adsorption occurs between pollutants and water molecules. The latter can be sorbed at the OH surface functional groups linked by

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hydrogen bonds as demonstrated by Greg and Sing (1984) and Raupp and Dumesic (1985) reported by Obee and Brown [6].

The first described phenomenon leads to increased reaction rates whereas the second involves a diminution of degradation rates [1,22].

More specific studies focusing on the photocatalytic degradation of VOC also noted a strong but contrasting influence of water vapor depending on the considered pollutant. The effect of water vapor can be globally positive, that is to say that there is an increase of reaction rates when augmenting the relative humidity. On the contrary, for some VOC, water vapor can have a general negative influence. Finally increasing the relative humidity can be first positive but after reaching a maximum can involve a decrease of reaction rates. Actually Peral and Ollis [23] demonstrated that the influence of 5% (1 g $m^{-3}$) of water in the feedstream varied strongly during the photocatalytic oxidation of acetone compared to 1-butanol, butyraldehyde or *m*-xylene over a bed of P25 $TiO_2$ (Degussa) in the powder form. They showed that the water concentration had no influence on the 1-butanol conversion rate but inhibited acetone oxidation. Kim and Hong [22] also proved that for an initial concentration of acetone of 0.7 g $m^{-3}$, an increase of the water vapor up to 15 g $m^{-3}$, inhibits the photocatalytic degradation. This tendency was not observed by Coronado et al. [24] for acetone and methyl isobutyl ketone oxidation using sol–gel $TiO_2$ thin films supported on glass rings.

Kim and Hong [22] showed that in the case of methanol and trichloroethylene using sol–gel $TiO_2$ coated inside Pyrex glass tubes, an increase of the water vapor concentration has first a positive effect on the degradation rate but after reaching a maximum involves a diminution. Similar observations were made by Obee and Brown [6] for the degradation of formaldehyde and by Peral and Ollis who showed that *m*-xylene conversion was enhanced by trace water addition but inhibited at higher water levels over P25 $TiO_2$, respectively, wash-coated on an alumina reticulate and forming a bed in the powder form [23].

Although the influence of pollutant characteristics has still to be enlightened, in the whole cases, the impact of the shape and nature of the titanium-based material is rarely discussed. In the current work, the influence of $TiO_2$ form (powder and film) on the effect of water vapor for the degradation of methyl ethyl ketone (MEK) in the gas phase is studied. MEK is taken as a typical molecule of indoor air pollutants [25]. Four $TiO_2$ supports are tested in a batch photocatalytic reactor at a fixed temperature. The influence of the initial contaminant concentrations is investigated at two levels of relative humidity. Experimental results are used to explain the mechanisms of adsorption and photocatalytic degradation of MEK over the photocatalysts when they are constituted of a film of $TiO_2$ and when they are made of powdered $TiO_2$. Attention particularly focuses on the different possible roles of humidity in function of the $TiO_2$ coating type.

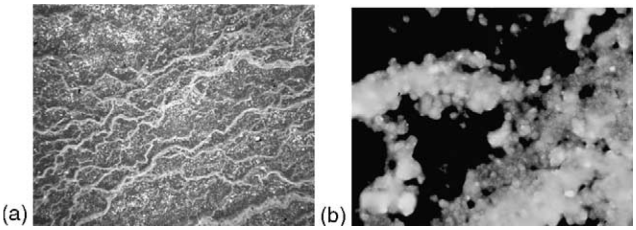

Fig. 1. Optical photomicrographs of top views of $TiO_2$ P25 Degussa deposited on microscopy glass slides: (a) 40× and (b) 1000×.

## 2. Experimental section

### 2.1. Catalysts

The four different $TiO_2$-based catalysts are named catalysts A, B, C and D. Characteristics and detailed observations are given for each of them.

Catalyst A is composed of powdered $TiO_2$ (P25 Degussa) deposited on optically transparent microscopy glass slides (76 mm × 26 mm) as described in a previous paper [19]. $TiO_2$ P25 Degussa is a mixture of anatase (70%) and rutile (30%) crystalline phases [26]. The average amount of $TiO_2$ deposited per glass support is of 6.3 mg, i.e. 3.2 g $m^{-2}$. Fig. 1 presents two optical photographs of this material (top view).

Looking at the optical microscopic observation (Fig. 1), $TiO_2$ grains are homogeneously distributed with some nanometer size aggregates.

Catalyst B is an industrial commercialized material, composed of mixed $TiO_2$ and $SiO_2$, with an atomic ratio Ti/Si equal to 2/3, deposited on a non-woven support (50 mm × 50 mm). This support is constituted of cellulose and synthetic fibers bound together with an organic mixture. Titanium dioxide is of anatase crystalline form and the amount of deposited $TiO_2$ is about 20 g $m^{-2}$ [27]. Fig. 2 shows the aspect of the impregnated fibrous support. Pictures are taken with an optical microscope.

Catalyst C is also an industrial material constituted of ordinary glass substrates (35 mm × 60 mm) coated with a thin transparent film of nanoparticles of crystallized $TiO_2$ over a silica layer to avoid the migration of $Na^+$ ions from the glass to the $TiO_2$ film. According to industrial information, the amount of deposited $TiO_2$ ranges from

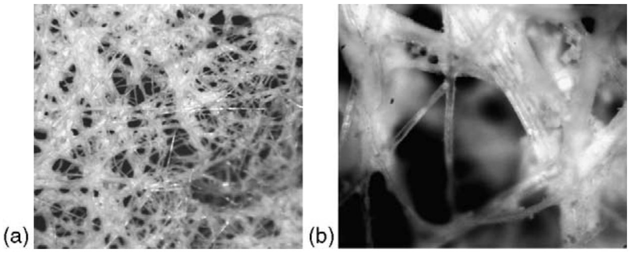

Fig. 2. Optical photomicrographs of the non-woven fibrous support impregnated with mixed $TiO_2/SiO_2$: (a) 40× and (b) 200×.