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# Increase of CO photocatalytic oxidation rate over anatase $TiO_2$ particles by adsorbed water at moderate coverages: The role of peroxide species

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ABSTRACT

Effect of water coverage on photocatalytic activities of CO oxidation was investigated on two $TiO_2$ samples: Hombikat UV 100 and Degussa P25. Surprisingly, the initial rate for CO photocatalytic oxidation over both $TiO_2$ samples shows the extreme dependence with maximum with the increase of water coverage from zero (for fully dehydrated $TiO_2$ samples) to one monolayer. The maximum of CO photooxidation rate was at ~0.5 monolayer of adsorbed water for both $TiO_2$ samples, wherein the catalytic activity was higher for $TiO_2$ Hombikat UV 100 than $TiO_2$ Degussa P25. It was concluded that the role of water is more complex than just a competition for adsorption sites between $H_2O$ and CO, and with moderate $H_2O$ coverages the positive influence of adsorbed water on CO photooxidation rate occurs. Different mechanisms of CO photooxidation on a fully dehydroxylated and partially hydrated $TiO_2$ with participation of different oxidizing species generated under UV-irradiation were suggested.

## 1. Introduction

Photocatalytic oxidation by titanium dioxide has attracted much interest in recent decades since it is useful for the transformation and decomposition of organic compounds under mild conditions [1–6]. Nevertheless, the number of fundamental issues is still unclear. Furthermore, some of them take the central place in the photocatalytic science. For the long period of time the mechanism of oxidation by hole-mediated OH-radicals was dominating. According to this mechanism, holes react with OH-groups of catalyst or adsorbed water and produce very active OH-radicals while electrons are captured by $O_2$ and become minor participants of reactions [5,7]. However, in the past years conventional mechanism has been critically reconsidered [8,9]. A number of papers has shown that during interaction of holes with OH-groups and water OH-radicals are formed only in a small extent [9,10] and the products of $O_2$ photoreduction could be sufficiently active in oxidation processes [9,11,12]. For correct consideration of these processes it appears to be very important to achieve understanding of the role of adsorbed water. Especially in respect that presence of water is unavoidable in practical implementations and catalyst behavior under these conditions can greatly differ from the well-studied but idealized catalyst behavior without adsorbed water.

Examination of the simplest molecules interaction with catalyst in the presence of adsorbed water both in the dark and under illumination appears to be one of the easiest ways to achieve this understanding. Despite much has been done previously one can observe that the interest in these studies notably revive [13–16].

The photocatalytic oxidation of CO using $TiO_2$ has been studied by many scientists as the CO oxidation is one of the simplest reactions to study surface-catalyzed reactions and the total reaction can be divided into a few elementary steps [17–20]. It has been found that only $TiO_2$ samples containing specific oxygen vacancy sites produced from annealing the surface in vacuum in the temperature range of 400–900 K or $Ar^+$ sputtering exhibit activity for the CO photooxidation [20,21]. But it is hard to imagine that oxygen vacancies would remain under near-ambient conditions under which photocatalytic purifying devices usually run. Really, recent research of Petrik and Kimmel shows that at temperatures above 250 K oxygen vacancies of $TiO_2$ almost completely react with water [22].

Few studies of CO photocatalytic oxidation under near ambient conditions have demonstrated that moisture significantly retards CO oxidation process (noble metal doping improves the situation [23]), inhibition of CO adsorption in the presence of water vapor was found to be the cause [24–27]. On the contrary, suppressing number of organic substances have an extremal dependence of their photocatalytic oxidation rates on water pressure with

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optimal $H_2O$ concentration at ambient temperature laying in 5–25% room humidity, according to a substance with corresponding water coverages $1 \div 2$ monolayers [28].

Generalizing the studies of CO photooxidation on titanium oxide in the published literature, it can be said that two extreme cases are considered: 1) CO photooxidation in dry oxygen on $TiO_2$ pretreated at high temperatures of 400–900 K (mostly thorough physicochemical investigations) and 2) CO photooxidation under highly humidified, near-ambient conditions (mostly environmental catalysis investigations). There are no data on CO photooxidation on $TiO_2$ in the presence of small coverages of adsorbed water, despite this information is crucial to establish the limits of applicability of the previously revealed regularities.

The aim of this work is to study the influence of the adsorbed water at different coverages on the CO photooxidation on $TiO_2$ both from the viewpoints of reaction rate and active species. We demonstrate that the activity of CO photooxidation on $TiO_2$ surprisingly shows the extreme dependence with maximum with the increase of water coverage from zero (for fully dehydrated $TiO_2$ samples) to one monolayer with maximum at ~0.5 monolayer of adsorbed water. We suggest adsorbed water contributes to formation and stabilization of intermediate peroxo-species that speed up CO photocatalytic oxidation.

## 2. Experimental section

### 2.1. Materials and characterization

Two commercial $TiO_2$ samples: Degussa P25 (~80% anatase and ~20% rutile) and Hombikat UV 100 (100% anatase) were compared for their photoactivity in CO oxidation. These samples will hereafter be referred to as $TiO_2$-D and $TiO_2$-H, respectively. Specific BET surface areas of $TiO_2$-D and $TiO_2$-H were 50 $m^2/g$ and 350 $m^2/g$, respectively.

As a pretreatment, the $TiO_2$ samples were photoirradiated for 2 days in air to decompose the organic impurities adsorbed on $TiO_2$ surface. Before spectral and catalytic measurements, samples were pressed and crashed to obtain the particles with dimensions of 0.3–0.5 mm. Then samples (~300 mg) were placed into a tubular quartz part of reactor equipped with quartz and $CaF_2$ windows for UV-illumination and DRIFT measurements, respectively (Fig. 1A) and then were heated at certain temperature under vacuum.

### 2.2. DRIFT spectroscopic experiment

After the required pretreatment the samples were characterized by DRIFT spectra at room temperature. DRIFT spectra were recorded with a Nicolet “Impact 410” FT-IR spectrometer equipped with a homemade diffuse reflectance attachment. $CaF_2$ powder was used for background measurements. Spectra with 4 $cm^{-1}$ resolution were processed with OMNIC software. For all spectra, the reflectance with respect to $CaF_2$ was converted into Kubelka-Munk units.

### 2.3. Thermogravimetry

The weight loss of $TiO_2$ powder over a temperature range of 25–800 °C was monitored by TGA with a SDT Q-600 (TA Instruments). The heating rate was 5 °C $min^{-1}$ and dry air flow rate of 100 $cm^3$ $min^{-1}$.

### 2.4. Catalytic measurements

Catalytic measurements were carried out in a closed system, connected to a vacuum system, at ambient temperature. The system for catalytic experiments is shown on Fig. 1B. The glass reactor (Fig. 1A) of volume $V_3 = 35$ $cm^3$ with the quartz windows (diameter, 2.5 cm) for UV-irradiation was connected to an electron impact ionization mass-spectrometer XT100(M) (Extorr, Inc) with an electron multiplier. The total volume of the system for catalytic experiments ($V_{cat}$) was 91.7 $cm^3$. The volume $V_{cat}$ is equal to sum volumes $V_2 + V_3$ denoted in Fig. 1B.

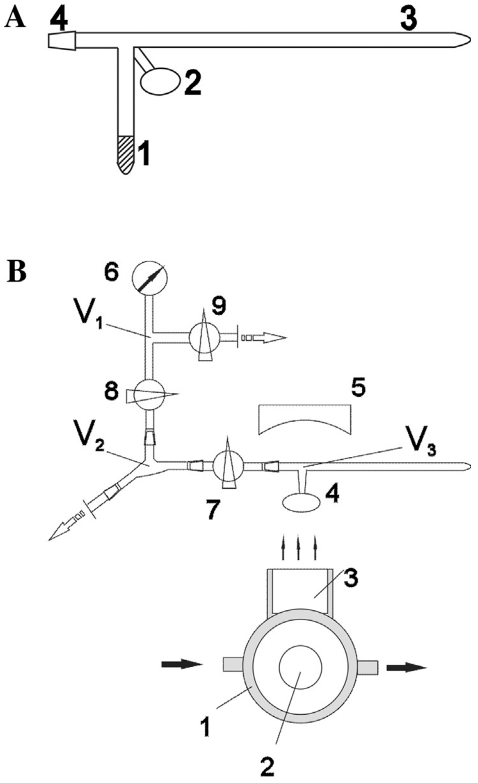

**Fig. 1.** (A) Glass reactor: 1—$CaF_2$ windows for DRIFT measurements, 2—quartz windows for UV-illumination, 3—tubular quartz part for pretreatment, 4—connection to vacuum system. (B) The general scheme of system for catalytic experiments: 1—metal lamp holder with water cooling, 2—DRL-400 (400 W) high-pressure arc mercury lamp, 3—quartz prism filled with distilled water, 4—reactor, 5—mirror, 6—vacuum pressure gauge, 7–9—vacuum valves; $V_1$, $V_2$, $V_3$—calibrated volumes.

The gas mixture of CO and $O_2$ (1:1, 10 Torr total pressure, typically) was used for photocatalytic oxidation reactions. Before reaction CO and $O_2$ gases were dried by passing through a liquid nitrogen trap.

The samples were placed in the part of reactor with quartz windows (Fig. 1A-2) and irradiated at ambient temperature by full light of a DRL-400 (400 W) high-pressure arc mercury lamp without an external glass flask through a water filter to reduce heating of the samples. The intensity of UV-irradiation was 75 mW/$cm^2$ with predominant band at 365 nm. The geometric area under UV-irradiation was 4.2 $cm^2$. We defined it as “working area” ($S_w$). This value corresponds to the front and back surfaces of quartz windows filled with the granules of $TiO_2$. A mirror was used to illuminate the back surface. The internal distance between the surfaces was ~1.0 mm.

The removal of CO by photooxidation and the production of $CO_2$ were monitored with the mass-spectrometer. Initial rates were calculated according the formula:

$$W = \frac{\Delta N_{CO}}{S_w \cdot \Delta t},$$

where $\Delta N_{CO}$ and $\Delta t$ are the number of removed CO molecules in $V_{cat}$ and the time interval of 10% conversion, respectively.