SHORT COMMUNICATION

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Influence of Metals and Reduced Oxygen Species on the Photooxidation of 2-Propanol with a Cesium Peroxidotitanate Complex

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The mechanism of the photocatalytic degradation of 2-propanol under anaerobic condition was investigated in the presence of the novel cesium peroxidotitanate complex Cs$_2$(NH$_4$)$_2$[Ti$_4$(O$_2$)$_4$([Hcit]$_2$)(cit))$_2$Cl$_2$. This complex contains two different kinds of peroxido units. Two peroxido groups bind to the titanium atom in a side-on σ-fashion, the other peroxido units are directly bonded to the titanium and cesium atoms. These bridging peroxido groups are responsible for the inhibited activity in the photooxidation in contrast to what was found in previous studies about unbridged peroxidotitanate complexes. The decelerated oxidation of the alcohol is useful for the determination of the mechanism during the photocatalytic oxidation process. Therefore, ESI mass spectrometry and $^{13}$C NMR spectroscopy were applied to obtain a deeper insight into the mechanism in the alcohol oxidation. Furthermore, an influence of the metal salt (Cs vs. Li) with respect of the photocatalysis was detected. The cesium peroxido complex shows significant results in the photochemical oxidation of 2-propanol to acetone. More than 50 % acetone was obtained without detection of any side products. The conversion yield from 2-propanol to acetone was monitored by $^1$H and $^{13}$C NMR spectroscopy and by Raman spectroscopy. The catalytic activity is not limited to 2-propanol; 1-phenylethanol could also be oxidized by 1. An intermediate of the photooxidation could be isolated and was characterized.

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Introduction

In recent decades, much attention has been focused on developing measures to convert organic pollutants into nontoxic compounds.[1] Among these detoxification techniques, semiconductor photocatalytic oxidation (PCO) has been developed.[2,3] A complete understanding of the photocatalytic mechanism on the surface of the photocatalyst is still in the early stages. In the case of the photocatalytic oxidation of 2-propanol under UV irradiation, products like acetone, mesityl oxide, CO$_2$ and propene are reported in different yields, depending on the modified titania and the reaction conditions.[4,5] In many cases, these TiO$_2$ catalysts are modified with metal salts during the synthesis in order to reduce the bandgap energy of the resulting photocatalyst.[6,7] For the excitation of such a photocatalyst like TiO$_2$, energy in the UV-light region is necessary.[9] No reaction occurs without UV irradiation because the frequency of the light has to be higher than the bandgap energy of the semiconductor. The bandgap for pure anatase TiO$_2$ is 3.2 eV, such that its absorption edge occurs below 400 nm.[9] Different metal-doped titania systems were used in the PCO, such as alkali and noble metals. They show high activity in different oxidation processes.[10] The reduction of molecular oxygen during the photocatalytic process taking place on the surface of TiO$_2$ particles, is important for the PCO of organic pollutants.[11] To investigate the role of reduced oxygen in the photooxidation of alcohols, we transfer the situation from the catalyst surface to a molecular level. By applying a model approach, we have synthesized a well-defined oxidotitanate complex modified by different kinds of peroxido units and cesium ions. We have previously reported that different metal-containing peroxidotitanate complexes show high activity in the photooxidation of 2-propanol, whereas similar complexes without any peroxido units did not show any activity in the PCO.[12] The influence of alkali metals as promoting species in the catalysis is well known.[13] Cs-doped titania systems play an important role in different oxidation processes. Catalytic measurements demonstrated that cesium is a strong promoter of the activity and selectivity in the oxidation of o-xylene to phthalic anhydride by V/Ti/O catalysts.[14] We decided therefore to incorporate cesium instead of lithium in the structure of supramolecular peroxidotitanate complexes. The complex contains two different peroxido units. Two peroxido groups bind to the titanium atom in a side-on σ-fashion, the other peroxido units form bridges between titanium and cesium atoms. In contrast to our previous studies, this coordination seems to be essential for an inhibited oxidation activity and therefore more adequate to study the mechanism and the role of reduced oxygen species in the alcohol oxidation under photochemical conditions.

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