Cu/TiO$_2$ Photocatalysts for the Conversion of Acetic Acid into Biogas and Hydrogen

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In the present study Cu/TiO$_2$ photocatalysts with different Cu loadings (0.5, 1 and 10 wt. %) have been prepared by sol-gel method and compared with pure TiO$_2$ and a commercial TiO$_2$ catalyst. They have been characterized by adsorption-desorption isotherms, X-ray diffraction and XPS and they have been tested in the photocatalytic decomposition of acetic acid in aqueous solution. The amount of CH$_4$, CO$_2$ and H$_2$ produced were measured by mass spectrometry. The results show that the incorporation of copper improves the catalytic properties of TiO$_2$ and that the highest activity is achieved with the sample containing 0.5 wt. % of copper.

Background

Photocatalytic treatment of waste waters could lead to the production of biogas, an attractive energy resource because it is environmentally friendly and economically feasible.

TiO$_2$ is one of the most investigated photocatalysts due to its advantages: stability against photocorrosion, low-cost and suitable band gap. However, its wide band gap leads to a poor light absorption and a rapid recombination of electron-hole pairs, which results in low photocatalytic activity [1]. In order to improve the photoefficiency of the electronic process, as well as the response into the visible part of the spectrum, TiO$_2$ doping with transition metals, such as copper, seems an interesting alternative that has recently become object of interest.

This study focuses on the preparation of Cu/TiO$_2$ catalysts by the sol-gel method for the photocatalytic degradation of acetic acid in aqueous solution. The effect of the Cu loading and the properties of the Cu/TiO$_2$ photocatalysts have been investigated and their activities have been compared with those of a synthesized pure TiO$_2$ sample and of a commercial TiO$_2$ photocatalyst (P25 from Evonik).

Objectives

The aim of this work is to prepare Cu/TiO$_2$ photocatalysts with different Cu loadings and to study their catalytic behaviour in the photocatalytic degradation of acetic acid to obtain biogas and hydrogen.

Methods

Cu/TiO$_2$ catalysts were prepared by sol-gel method according to the following procedure: titanium tetraisopropoxide (TTIP) was mixed with glacial acetic acid (AcAc) at 0°C. Afterwards, distilled water with the required amount of Cu(NO$_3$)$_2$ previously dissolved (to obtain 0.5, 1 and 10 wt. % Cu) was added dropwise under vigorous stirring. The TTIP:AcAc:H$_2$O molar ratio was 1:10:350. The mixture was stirred for 1 h and then it was ultrasonicated for 30 min, stirred again for 5 h, heat treated at 70°C for 12 h and dried at 100°C. The obtained solid material was crushed and, finally, heat treated at 500°C in Ar atmosphere.

A TiO$_2$ sample was also prepared following the same procedure, but avoiding the incorporation of Cu(NO$_3$)$_2$ during the synthesis. Characterization was carried out by gas adsorption, XRD and XPS.

The catalytic activity tests were perfomed in the following conditions: 1M acetic acid aqueous solution, a mercury lamp of 365 nm wavelength and 12 h reaction time. The reaction products, primarily CH$_4$, CO$_2$ and H$_2$, have been quantified by mass spectrometry.

Results

Table 1 shows characterization data of the samples prepared and studied, and includes BET surface areas determined by N$_2$ adsorption isotherms (-196°C). It can be observed that the BET surface area of the synthesized TiO$_2$ is larger than that of P25 material. Comparing different samples prepared by in situ method, an increased
copper loading leads to a decrease in the adsorption capacity.

Results of XRD analysis show that all the prepared samples are crystalline and their diffraction peaks correspond to anatase phase. The calculated crystal sizes are compiled in Table 1. It must be remarked that the crystal size of all synthesized samples is smaller than that for commercial P25 (composed of 75% anatase and 25% rutile [2]). Moreover, the introduction of copper slightly increases the anatase crystal size of these materials: the larger the copper percentage, the larger the anatase crystal size.

| Table 1. Main parameters obtained from the textural and structural characterization. |
|----------------|----------------|----------------|
| Sample         | $S_{\text{BET}}$ (m$^2$/g) | Crystal size$^a$ (nm) | Cu enrichment$^b$ |
| P25            | 60             | 22.01           | -                |
| TiO$_2$        | 139            | 8.25            | -                |
| Cu/TiO$_2$ is0.5 | 153           | 8.41            | 2.1              |
| Cu/TiO$_2$ is1  | 150            | 8.90            | 1.5              |
| Cu/TiO$_2$ is10 | 130            | 9.72            | 1.3              |

$^a$Anatase crystal size
$^b$Cu surface enrichment calculated from XPS as the ratio between Cu/(Cu+Ti)$_{\text{sup}}$ and Cu/(Cu+Ti)$_{\text{num}}$

The XPS Cu 2p$_{1/2}$ results reveal the presence of copper in two different oxidation states. In the three samples about 70% Cu(I) and 30% Cu(II) are present. Cu surface enrichment has also been calculated (see data in Table 1).

Figure 1 shows the amounts of CH$_4$, CO$_2$ and H$_2$ produced by the different photocatalysts. The synthesized TiO$_2$ is more active than P25, in agreement with its larger surface area and smaller crystal size. The presence of copper shows a positive effect, as the Cu/TiO$_2$ samples are more active than pure TiO$_2$. Regarding copper loading, data of Figure 1 show that an increase in the copper content leads to a reduction in the amount of CO$_2$ and CH$_4$ produced.

These results are not easy to be explained, but the decrease in activity with Cu loading increase can be connected with the decrease in surface area and increase in crystal size, and also with the decrease of copper surface enrichment.

An effect of the Cu content on the band gap energy, as reported by other authors [3,4], can not be discarded, but it has not determined yet in our work.

Conclusions

The presence of copper in Cu/TiO$_2$ photocatalysts significantly favours their catalytic efficiency, being more interesting those prepared with a low copper loading, 0.5 wt. %.

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References
1. □ Oral  ☒ Poster

2. I apply for student SPEA9 grant to cover my accommodation costs in Strasbourg:  ☒ Yes  □ No

3. Chosen topics by order of preference
   Topic 1: Water treatment
   Topic 2: Environmental reactions
   Topic 3: Photocatalytic hybrid systems

4. Special Issues of SPEA 9
   Contribution to Special Issues of SPEA 9?  ☒ Yes  □ No  Journal name: Catalysis Today

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   Keywords: Photocatalysis, TiO₂, copper, degradation, acetic acid, biogas.