

## M/TiO<sub>2</sub> photocatalysts for the abatement of pollutants in gaseous and liquid effluents

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*M/TiO<sub>2</sub> photocatalysts have been prepared and their application to two different reactions, decomposition of acetic acid in liquid phase to produce CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> and propene oxidation in gas phase to CO<sub>2</sub> and H<sub>2</sub>O, has been studied, paying attention to low cost metals (Cu, Cr, Ni and Co). P25 TiO<sub>2</sub> submitted to the same treatment has been used as reference. Cu/P25 is the best performing photocatalyst amongst those containing metals for both reactions, and works particularly better than P25 for acetic acid decomposition. However, for low concentration propene oxidation P25 performs better than any of the M/TiO<sub>2</sub> photocatalysts. There are significant differences between the activities of the different M/P25 catalysts, although the relative activity order for both tests is the same: Cu > Ni > Co ≥ Cr.*

### 1. Scope

The organic matter which contaminates water is transformed into acetic acid, and this difficult-to-remove pollutant can be photocatalytically decomposed to produce biogas and hydrogen<sup>1</sup>. On the other hand, propene is a gas phase indoor pollutant because it is an important component of tobacco smoke<sup>2</sup> and, as well, it can be removed by photocatalytic oxidation. With the purpose of finding active catalysts for these processes, different metals have been added to TiO<sub>2</sub> to improve its photoresponse to visible light and to reduce the recombination of photogenerated electrons and holes<sup>3</sup>. Thus, this work deals with the preparation of M/TiO<sub>2</sub> photocatalysts in which low cost metals (Cu, Cr, Ni and Co) have been used.

### 2. Results and discussion

M/TiO<sub>2</sub> (M=Cu, Co, Cr and Ni) catalysts have been prepared by the impregnation of Evonik Aeroxide TiO<sub>2</sub> P25 with aqueous solutions of the metal nitrates (5 ml/g) of the appropriate concentration to have 1 wt. % metal loading. In each case the suspension was kept at 80 °C for 24 h to evaporate the solvent. Afterwards, the samples were treated in Ar at 350 °C for 1 h. TiO<sub>2</sub> P25 was submitted to the same thermal treatment and used as reference. The obtained photocatalysts were characterized by gas adsorption (N<sub>2</sub> and CO<sub>2</sub> at -196 °C and 0 °C, respectively, Autosorb-6B (Quantachrome), XRD (Miniflex II Rigaku) and SEM (JEOL JSM-840). The photodecomposition of acetic acid was performed using 350 mg catalyst, 250 ml of a 1 M aqueous acetic acid solution and a 365 nm mercury lamp for 12 h; the produced CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> were quantified by mass spectrometry. Propene oxidation was carried out using 110 mg catalyst, a flow of 100 ppmv propene in air stream (30 ml/min or 60 ml/min) and a 365 nm UV-A lamp; the outlet gas was continuously analyzed by mass spectrometry.

The characterization of the photocatalysts shows that most properties of all M/TiO<sub>2</sub> catalysts are similar to those of P25: BET surface areas around 60 m<sup>2</sup>/g, about 88% crystalline phase (76% anatase and 12% rutile) and anatase crystallite size around 19 nm. However, they have quite different colour, which can lead to differences in optical and, hence, photocatalytic performance (Figure 1).

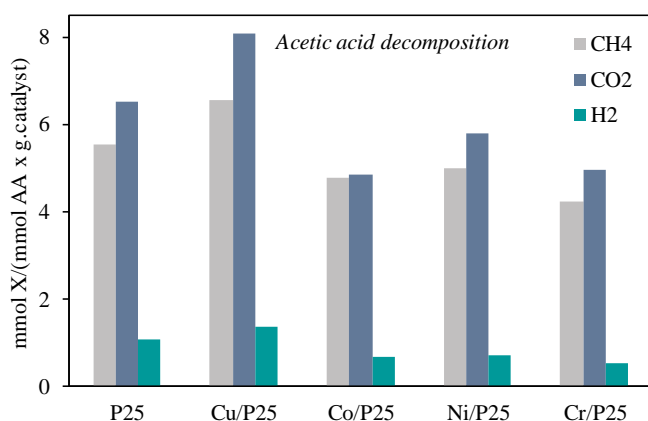


Figure 1. P25 and M/P25 samples.

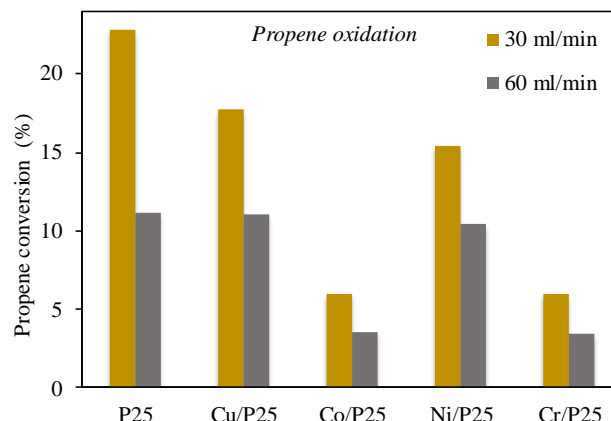
Figure 2 shows the photocatalytic activity of the prepared samples in the acetic acid decomposition. It can be observed that Cu/P25 is the best performing material but, excepting this sample, the metal containing samples are less active than P25. Thus, Cu improves the photocatalytic activity of P25. The amounts of biogas and hydrogen produced with Cu/P25 catalyst are about 37% higher than those produced with P25, which is remarkable considering the low Cu loading, 1 wt. %.

Regarding propene oxidation (Figure 3), in all cases the metal incorporated to P25 has a negative influence on the photocatalytic activity of TiO<sub>2</sub> and P25 shows the best photocatalytic performance.

In both reactions, the activity order of the different M/P25 catalysts is the same: Cu > Ni > Co ≥ Cr, although the relative differences in activity between catalysts are quite different in the two processes. This means that the optical properties, influenced by the incorporated metal (Figure 1), play a different role in the different reactions. It should be mentioned that, excepting copper, the metals tested do not provide the advantages expected, but the activity of Cu/P25 in propene oxidation is nearly three times larger than that of Cr/P25 and, in the challenging process of acetic acid decomposition, Cu/P25 catalyst is more active than P25, which constitutes a promising result. The positive role of Cu might be related to a decrease in the band gap according to the literature<sup>3,4</sup>. Further research is needed to understand how some properties of TiO<sub>2</sub> are modified by the different metals and the advantages of copper over the other metals, and also to develop, if possible, other Cu/TiO<sub>2</sub> catalyst with higher activity.



**Figure 2.** Methane, CO<sub>2</sub> and H<sub>2</sub> obtained in the photocatalytic conversion of acetic acid.



**Figure 3.** Propene conversion (at 30 and 60 ml/min) for the synthesized M/TiO<sub>2</sub> samples.

### 3. Conclusions

Different M/TiO<sub>2</sub> (M=Cu, Co, Cr and Ni) photocatalysts have been prepared and tested in two different reactions: acetic acid decomposition in solution and gas phase propene oxidation. The metal incorporated has some effect on the colour of the photocatalyst, and therefore on its performance. The catalytic activity trend of the M/P25 samples is the same in both reactions: Cu/TiO<sub>2</sub> > Ni/ TiO<sub>2</sub> > Co/ TiO<sub>2</sub> ≈ Cr/ TiO<sub>2</sub>, but there are significant differences between the catalytic activities in the two processes. It must be pointed out that Cu/P25 is more active than P25 for acetic acid decomposition. However, P25 shows the best activity for propene oxidation. Further research is being performed to understand the advantages of copper over the other metals and the different role of metals in both reactions.

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