Influence of the addition of M^{2+} (M: Co, Cu, Zn) on the properties and activity of W-TiO$_2$ and Mo-TiO$_2$ photocatalysts for water remediation

Mergenbayeva S., [1] Poulopoulos S., [1]* Grilla E., [2] Vakros J.,[2] and Mantzavinos D. [2]

[1] Department of Chemical and Materials Engineering, School of Engineering and Digital Sciences, Nazarbayev University, 53 Kabanbay batyr ave., Nur-Sultan

[2] Department of Chemical Engineering, University of Patras, , GR-26504 Patras

*corresponding author:
e-mail: stavros.poulopoulos@nu.edu.kz

Abstract: In this study, ternary systems of M1M2TiO$_2$ (M1:Co, Cu, Zn) M2 (WO$_3$, MoO$_3$) were prepared and tested for the photocatalytic degradation of sulfamethoxazole. It was found that W-oxo species can be used without significant alteration of the TiO$_2$ activity, while only Cu is a possible candidate for the ternary system either due to its chemical hardness and/or its p-type semiconducting nature.
Keywords: TiO$_2$, WO$_3$, SMX

1. Introduction

Although TiO$_2$ is probably the single most effective photocatalyst (Nakata, 2012) used for water remediation, its main disadvantage is the low adsorption in the visible region. To overcome this problem, several strategies have been followed, including the deposition of oxo-anions on titania surface. Generally, the deposition of W-oxo species was found to have a positive action onto photocatalytic activity of titania. WO$_3$ is a good candidate for doping titania, since it has a narrow band gap (about 2.8 eV), high acidity and combined with TiO$_2$ extends the visible adsorption spectrum. Finally, several studies have shown that the WO$_3$/TiO$_2$ system hinders the electron–hole recombination (Guo, 2019).

Mo-oxy species is another interesting candidate for deposition onto TiO$_2$ surface. The Mo-oxo species can interact with the surface –OH groups of TiO$_2$ and can form bi- and tri- substitute surface species. These inner sphere complexes can undergo reduction during calcination, even under an oxidative atmosphere, by forming Mo(V) oxo species. This can be done only when a covalent bond is formed between titania surface and molybdenum phase. This interaction has been detected with diffuse reflectance (DR), Raman and EPR spectroscopy (Panagiotou, 2010). Mo(V) species are exclusively formed on the anatase phase and during irradiation the electrons formed are highly reduced, while the holes are significantly increased. Specifically, only electrons from rutile can be detected while the interaction of Mo with TiO$_2$ results in a preferential, complete quenching of the lattice-electrons from the anatase phase. Using DR spectroscopy, loadings up to 1 at Mo/nm^2 can maximize the interactions with the titania surface. This value is close to the one for W species in basic solutions of tungstate ions. Also, both Mo- and W-oxo species can interact with terminal and bridging surface O groups.

According to the above, it will be interesting to prepare W-TiO$_2$ and Mo-TiO$_2$ photocatalysts with loading of 1 atom per nm^2 and then deposit another metal cation, with different properties. In order to select these cations, one has to take in mind that TiO$_2$ has an ionic potential of 5.8, while MoO$_3$ and WO$_3$ have ionic potentials of 8.9 and 8.8, respectively. The ionic potential, φ, which is defined as the ratio of electric charge to the radius of ion, measures charge density on the surface of ion. Two other important parameters are the chemical potential and the chemical hardness. Chemical potential, μ, measures the escaping tendency of an electron cloud, while chemical hardness, η, determines the resistance of the species to lose electrons. By definition, these two parameters are closely related since:

$$-\mu = \chi = (IP + EA) / 2 \text{ and } \eta = (IP - EA) / 2 \qquad (1)$$

where IP is the ionization potential, EA is the electron affinity of the system and χ is the electronegativity. Within the validity of Koopmans' theorem, the frontier orbital energies are given by

$$-\varepsilon_{HOMO} = IP \text{ and } -\varepsilon_{LUMO} = EA \qquad (2)$$

where HOMO is the highest occupied molecular orbital, and LUMO the lowest unoccupied orbital.

So, it is interesting to test Co(II), Cu(II) and Zn(II) ions since these ions have different values of φ, μ and η, i.e. (2.7, 7.485, 1.558) for CoO, (4.0, 7.874, 0.710) for CuO and (2.7, 7.556, 1.418) for ZnO.

2. Experimental

In this work, two base photocatalysts, namely Mo/TiO$_2$ and W/TiO$_2$ were prepared using commercial TiO$_2$ (Degussa P25) as a support with wet impregnation

method and the active species were W(VI) or Mo(VI) oxoanions, respectively. The two base catalysts were then used to prepare ternary systems by dry impregnation. The third cation deposited was either Co(II), Cu(II) or Zn(II) with the surface concentration of the M(II) ion set to 0.5 at/nm^2. The as-prepared catalysts were characterized by means of (i) diffuse reflectance spectroscopy (DRS), (ii) X–Ray diffraction (XRD), and (iii) point of zero charge determination. Catalytic activity was evaluated using solar irradiation and sulfamethoxazole (SMX at 0.5 mg/L in pure water) as the probe molecule. SMX is an antibiotic drug, which has been consistently detected in surface waters, ground waters and domestic wastewaters, with the latter being the most common anthropogenic source of antibiotics release in the environment (Kemmou, 2018). The irradiation source was an Oriel LCS-100 solar simulator using a 100 W xenon, ozone-free lamp. The incident intensity was measured by actinometry and was found equal to 7.3 10^{-7} einstein/(L.s).

3. Results and discussion

The oxidation mechanism involves the irradiation of the catalyst (TiO$_2$, or M1M2/TiO$_2$ M1: Co,Cu or Zn and M2: Mo or W). During irradiation the production of holes and electrons occurs. These species can oxidize the organic pollutant, SMX, and degrade it.

The results are presented in Figures 1–3, where the degradation of SMX is depicted as the change of its normalized concentration over time. Time zero corresponds to the beginning of irradiation, while the negative time interval (–20 to 0) refers to the dark adsorption phase.
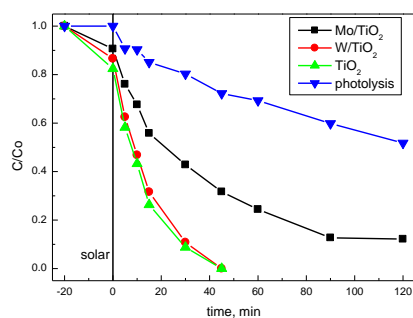

Figure 1. Degradation profile for the blank experiment, TiO$_2$, Mo/TiO$_2$ and W/TiO$_2$

As can be seen from Figure 1, the degradation is the combined result of the irradiation and the presence of the catalyst since direct SMX photolysis is rather limited. On the other hand, the presence of Mo–oxo species clearly hinders the degradation process in contrast with the W–oxo species, where the same or even better activity can be obtained. This behavior has also been reported in previous studies (Yang, 2004; Di Paola, 2002). The adsorption ability of the prepared catalysts is lower than that of the bare TiO$_2$. This is due to the surface coverage from Mo and W oxo species. This coverage decreases the surface sites available for the adsorption, since it is well-known that the deposition of the oxo anions occurs on the surface –OH groups. The Mo/TiO$_2$ sample shows the lower adsorption ability although the atomic radius of

Mo atoms is lower than W. The difference can be the result of the higher hydrophobicity of MoO$_3$ phase due to the high stability of the terminal O atoms in MoO$_3$ phase. Also, DFT calculations do not predict water dissociation on stoichiometric surface.
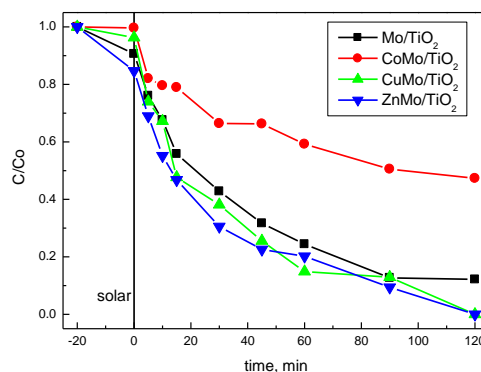

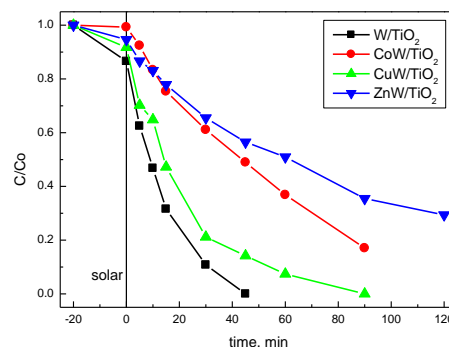**Figure 2.** Degradation profile for the M1Mo/TiO$_2$ samples.

Figure 3. Degradation profile for the M1W/TiO$_2$ samples.

The simultaneous presence of another transition metal, in the form of cation in this case, complicates the results. For the Mo/TiO$_2$ case, both improvement and hindering of the activity can be observed. Cu and Zn enhance the activity, while Co has a significantly negative effect, both in degradation and adsorption processes. On the other hand, Zn has a positive effect on both processes, while Cu has negative effect on adsorption but increases the degradation ability especially in longer time intervals. For the M1W/TiO$_2$ catalysts, there are some differences. Zn and Co decrease significantly the degradation ability. As for Cu, the detrimental effect is lower although still measurable. All three transition metal ions also decrease the adsorption ability of the catalyst.

The process can kinetically be described as a pseudo first order reaction. In this respect, the ln(C/Co) ratio should have a linear dependence with time. The slope of this linear fit is equal to –k_{app}, the apparent kinetic constant. The values of k_{app} are presented in Table 1.

Point of zero charge

The point of zero charge, pzc, of the prepared catalysts was measured with the mass titration method. A suspension of about 10%w/w was prepared and the pH value was measured. Under these conditions, the

measured pH approaches the pzc value of the mixed solid. The values are presented in Table 1.

Table 1. Point of zero charge, energy gap and k_{app} values of the catalysts.

No	Catalyst	pzc	Eg (eV)	k_{app} (min^{-1})
1	TiO_2	6.2	3.09	0.074
2	Mo/TiO_2	4.9	2.87	0.021
3	W/TiO_2	6.6	2.92	0.070
4	$CoMo/TiO_2$	6.1	2.72	0.0056
5	$CuMo/TiO_2$	6.5	2.82	0.029
6	$ZnMo/TiO_2$	6.4	2.85	0.029
7	CoW/TiO_2	6.1	2.87	0.0098
8	CuW/TiO_2	6.3	2.85	0.042
9	ZnW/TiO_2	5.8	2.86	0.019

Diffuse Reflectance Spectroscopy

The DR spectra of the catalysts studied with reference to PTFE disk are presented in Figures 4–6.
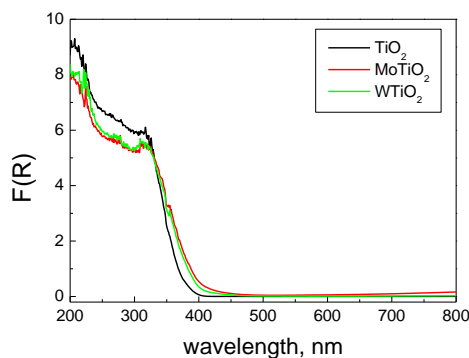
Figure 4. DR spectra of the TiO_2, Mo/TiO_2 and W/TiO_2 samples.

As can be seen in Figure 4, the F(R) values for the Mo/TiO_2 and W/TiO_2 are lower in the UV region ($\lambda < 350$ nm) than the bare TiO_2. This is the result of the surface coverage with the MoO_3 and WO_3 phase. On the other hand, the adsorption on near UV region (350 – 450 nm) is higher for the supported samples. This is the result of charge transfer phenomena between the M2 – O – Ti bonds (M2: Mo or W). These charge transfer phenomena are common in the systems, where a semiconductor is covered by a transition metal oxide, as in this case.

As can also be seen, these interactions are rather higher in the case of Mo/TiO_2, since the F(R), an analogue to absorbance, is more intense for this sample, while the surface coverage seems to be a little smaller in the case of W/TiO_2 as the F(R) is higher in the UV region. This is in accordance with the XRD results where crystallites of WO_3 were detected.

Concerning the M1Mo/TiO_2 samples, no significant differences can be observed (Figure 5). The coverage of the TiO_2 is higher, while for $CoMo/TiO_2$ the absorption in the near UV region is higher, suggesting more intense interactions with the Co phase.
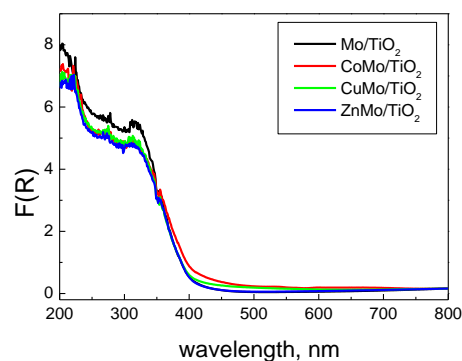
Figure 5. DR spectra of the M1Mo/TiO_2 samples (M1:Co,Cu or Zn).

The absorbance in the visible region is small for the $CoMo/TiO_2$ and $CuMo/TiO_2$ samples, despite the black color of the corresponding bulk oxides due to the small quantity of the Co and Cu phase. This may suggest that the above oxides are rather well dispersed on the surface of the catalyst.
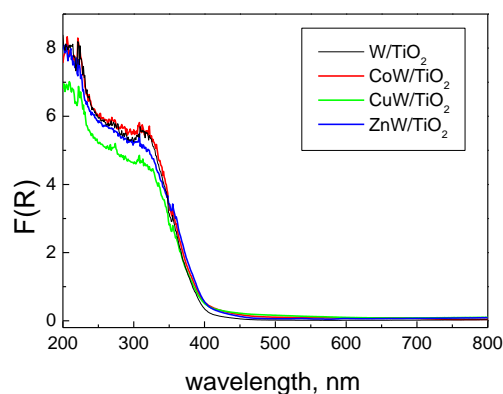
Figure 6. DR spectra of the M1W/TiO_2 samples (M1:Co,Cu or Zn).

The M1W/TiO_2 samples exhibit similar behavior (Figure 6). Only the CuW/TiO_2 sample has smaller absorption in UV region.

In order to investigate further the interactions of the supported phase the spectra were collected with TiO_2 as reference. These spectra are not presented here. They exhibit a rather intense peak centered at about 400 nm for all the samples, M1Mo/TiO_2 and M1W/TiO_2 .In the case of M1Mo/TiO_2, the CoMoTiO$_2$ has the more intense peaks, while no shift of the peak center is observed. Moreover, the absorbance in the visible region can be detected for Co and Cu samples. This is due to the black color of the corresponding oxides and, in the case of Co, the oxide seems to be closer to Co_3O_4 enriched with Co(III) in octahedral symmetry. This is supported from the triplet center at about 580 nm and the shoulder at 680 nm. The spectra of the M1W/TiO_2 samples show significant differences. Besides the absorbance in the visible region for the Co and Cu sample, the main peak at about 400 nm is shifted at higher wavelengths. This may be related to the lower Eg values of these two oxides

or the fact that these oxides are p–type semiconductors, in contrast to the TiO_2, MoO_3, WO_3 and ZnO, which are n–type. The $ZnMo/TiO_2$ sample has a spectrum similar if not identical to Mo/TiO_2 pointing out that no interactions with TiO_2 occur.

The energy gap, Eg for the samples studied, can be calculated by the Tauc plot (Figure 7). The Eg can be found by extrapolation of the curve $(F(R) h\nu)^{1/2}$ against hν. The Eg value is the value of vertical segment of the plot to intersect on x–axis where y–axis is zero. The values are presented in Table 1.
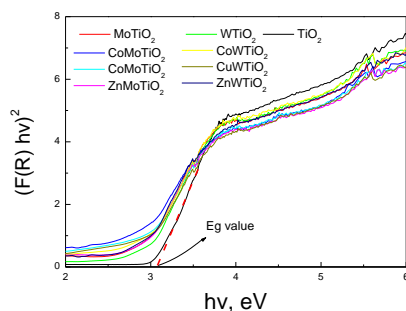

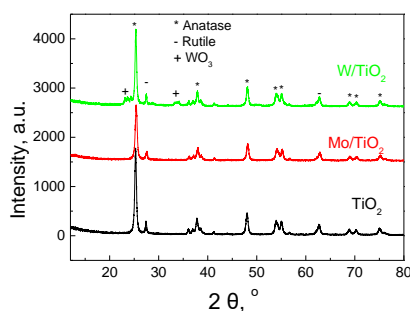**Figure 7**. Tauc plot for the samples studied.

X–Ray Diffraction Analysis

Figure 8. XRD patterns of the TiO_2, Mo/TiO_2 and W/TiO_2 samples.

The XRD patterns of the TiO_2, Mo/TiO_2 and W/TiO_2 samples are presented in Figure 8. As can be seen, the main crystallite phase of TiO_2 is the anatase phase. Although TiO_2 P25 has about 20% rutile only the peak at 27.5^o can be clearly seen. The deposition of Mo phase does not form new XRD peaks. This is a first evidence that Mo phase is well dispersed on the titania surface. On the other hand, the deposition of W–phase forms new peaks corresponding to WO_3 phase.

The XRD patterns for the $M1Mo/TiO_2$ and $M1W/TiO_2$ do not exhibit any new peaks corresponding to the M1O oxides, probably due to the low quantities of the second metal. Also, no significant differences can be observed after the deposition of the second transition metal cation in the corresponding peaks of titania, although the mean crystallite diameter is slightly increased after the second deposition and the total crystallinity of the solid is reduced (Table 2).

Table 2. Mean particle diameter and crystallinity of the prepared catalysts

No	Catalyst	Mean d (Å)	% crystallinity
1	TiO_2	218	80.1
2	Mo/TiO_2	195	79.4
3	W/TiO_2	249	76.8
4	$CoMo/TiO_2$	241	81.2
5	$CuMo/TiO_2$	248	78.7
6	$ZnMo/TiO_2$	240	77.7
7	CoW/TiO_2	251	72.3
8	CuW/TiO_2	252	74.0
9	ZnW/TiO_2	247	75.1

4. Conclusions

From the above study, it was found that the deposition of Mo-oxo species has generally a detrimental effect on the photocatalytic activity of TiO_2, while the W-oxo species can have positive effect after having carefully regulated the surface concentration. The deposition of M(II) ions on the $Mo(W)/TiO_2$ system can alter the physicochemical characteristics of the ternary system. Only Cu is a possible dopant for the binary system, probably due to its low chemical hardness and the p-type semiconducting nature. In any case, the net effect can be case-specific, thus requiring careful selection of experimental conditions.

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