

Influence of the addition of M^{2+} (M: Co, Cu, Zn) on the properties and activity of Mo-TiO₂ photocatalysts for water remediation

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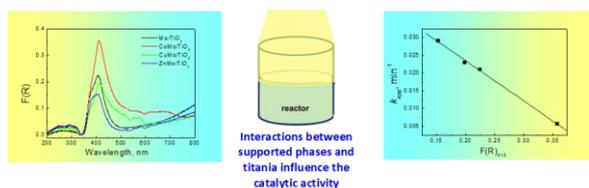
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Graphical abstract



Abstract

TiO₂ is the most effective photocatalyst, but it has low adsorption in the visible region. Many efforts have been done to improve its photocatalytic activity in the solar region. In this study we use Mo-oxo species supported on titania surface since it is well known that titania surface can disperse Mo oxo species through the development of intense interactions. The binary system was further modified with another metal ion M^{2+} (M: Co, Cu, Zn). These ions have different chemical properties, and they alter the physicochemical properties of the ternary system. The photocatalytic activity of the prepared catalysts was determined for the degradation of 0.5 mg L⁻¹ sulfamethoxazole under solar irradiation. It was found that the deposition of Mo has a detrimental effect on the activity of TiO₂ while the deposition of Zn or Cu can improve the activity of the ternary system. The sulfamethoxazole degradation follows first order kinetics, and the activity of the catalysts is well correlated with the interactions developed between support and supported phases.

Keywords: chemical hardness, photocatalyst, TiO₂, MoO₃, CoO, CuO, ZnO, ternary systems

1. Introduction

Although TiO₂ is probably the single most effective photocatalyst [Nakata, Fujishima, 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. WO₃ is a good candidate for doping titania, since it has a narrow band gap (about 2.8 eV), high acidity and combined with TiO₂ extends the visible adsorption spectrum. Finally, several studies have shown that the WO₃/TiO₂ system hinders the electron-hole recombination [Guo *et al.*, 2019]. Mo-oxo species is another interesting candidate for deposition onto TiO₂ surface, due to intense similarities between Mo-oxo and W-oxo species. The Mo-oxo species can interact with the surface -OH groups of TiO₂ and can form bi- and tri-substitute surface species. These inner sphere complexes can undergo partial 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 *et al.*, 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 TiO₂ results in a preferential, complete quenching of the lattice-electrons from the anatase phase. Using DR spectroscopy, it was found that loadings up to 1 at Mo/nm² can maximize the interactions with the titania surface.

It is interesting that both MoO₃ and WO₃ are n-type semiconductors like TiO₂. According to the above, it will be interesting to prepare Mo-TiO₂ photocatalysts with loading of 1 atom per nm² and then deposit another metal cation, with different properties [Mergenbayeva *et al.*, 2022] In order to select these cations, the chemical hardness of the solid oxides looks like a promising approach. Chemical hardness is closely related with the electron configuration of the oxides and their acid-base properties following Lewis theory, quantum chemical theory and DFT calculations. [Erdemir *et al.*, 2005]

Starting from 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, TiO₂ has an ionic potential of 5.8, while MoO₃ has ionic potentials of 8.9 [Erdemir *et al.*, 2005]. Two other important parameters for characterizing an oxide 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:

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

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

$$-\epsilon_{\text{HOMO}} = IP \text{ and } -\epsilon_{\text{LUMO}} = EA \quad (2)$$

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

The values of Φ , χ and η for different solid oxides can be found in [Erdemir *et al.*, 2005]; among them the values of the above parameters for TiO₂, MoO₃, CoO, CuO and ZnO are reported in Table 1.

Table 1. Quantum chemistry parameters of TiO₂, MoO₃, CoO, CuO and ZnO [Erdemir *et al.*, 2005]

Oxide	$\Phi/Z/r$	χ/eV	η/eV
TiO ₂	5.8	8.973	1.691
MoO ₃	8.9	9.493	2.044
CoO	2.7	7.465	1.558
CuO	2.4	7.874	0.710
ZnO	2.7	7.556	1.418

In this point it should be emphasized that the charge (Z) the ionic radius electronegativity and chemical hardness are closely related, as they take into account the electronic configuration of the oxide. Although the picture is rather simple for a single oxide, mixed oxides can be approached too. In this case the interactions between the two oxides and the coordination number can influence the number of transferred electrons probably in the interface between the different oxides. As a first approach the number of transferred electrons can be estimated from the equation (3)

$$\Delta N \approx \frac{(\chi_A - \chi_B)}{2(\chi_A + \chi_B)} \approx \frac{\Delta\chi}{2\Sigma\eta} \text{ or } \Delta N \approx \frac{(\mu_B - \mu_A)}{2(\eta_A + \eta_B)} \approx -\frac{\Delta\mu}{2\Sigma\eta} \quad (3)$$

Which means that the difference in electronegativity favors the number of transferred electrons, while the sum of the chemical hardness of the oxides resists the transfer.

This number is not the total change in electrons, but it is an approximate value for the orbital interactions and the strength of bonds [Parr *et al.*, 1983].

On the other hand, CoO and CuO oxides are p-type semiconductors, while ZnO is n-type like TiO₂ and MoO₃ [Moumen *et al.*, 2022; Park and Kolpak, 2018; Peelaers *et*

al., 2017; Chabri *et al.*, 2016; Anitha *et al.*, 2015]. 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 and to evaluate their difference in their photocatalytic activity, for the degradation of sulfamethoxazole under solar irradiation. Then the correlation with the discussed parameters was investigated.

2. Materials and methods

In this work, Mo/TiO₂ was prepared using commercial TiO₂ (Degussa P25) as a support with wet impregnation method and (NH₄)₆Mo₇O₂₄*6H₂O as Mo precursor compound. The catalyst was dried at 105°C for 2 h and calcined at 400°C for 2h. The prepared catalysts were 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/nm². Nitrate salts were used as precursors. The as-prepared catalysts were characterized by means of (i) diffuse reflectance spectroscopy (DRS) in a Cary 3 system, (ii) X-Ray diffraction (XRD), and (iii) point of zero charge determination. Details about the characterization of the samples can be found in [Papatheodorou *et al.*, 2022]. 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 [Kemmu *et al.*, 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 (TiO₂, Mo/TiO₂, or MMo/TiO₂ M: Co, Cu or Zn). 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 and 2, 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.

As it can be seen from Figure 1 the TiO₂ is the better photocatalyst for the degradation of SMX. The deposition of Mo species has detrimental effect on the activity of the catalyst. It can be attributed to the coverage of titania surface from Mo-oxo species. This behavior has also been reported in previous studies [Yang *et al.*, 2004; Di Paola *et al.*, 2002]. Also, the adsorption ability of the prepared catalysts is lower than that of the bare TiO₂. This is due to the surface coverage from Mo 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/TiO₂

sample shows the lower adsorption ability probably due to the higher hydrophobicity of MoO₃ phase and the high stability of the terminal O atoms in MoO₃ phase. Also, DFT calculations do not predict water dissociation on stoichiometric surface.

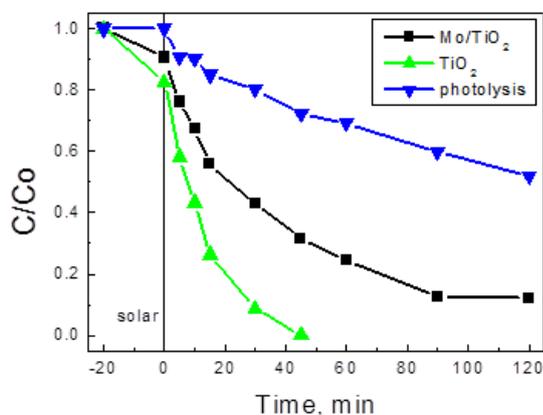


Figure 1. Degradation profile for the blank experiment, TiO₂, Mo/TiO₂.

This behavior has also been reported; generally, the doped catalysts exhibit recombination rates significantly higher than that of the support, which result to lower oxidation ability. Also, the Mo deposition can have some positive effects on the activity if the deposition is not surface but subsurface [Yang *et al.*, 2004]

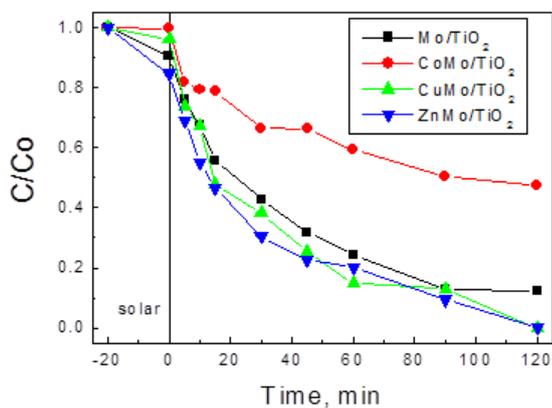


Figure 2. Degradation profile for the MMO/TiO₂ samples.

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 2. As it can be seen there is a big variation in the values of k_{app} , as a result of the differences in the degradation profiles. It should be noted that the CoMo/TiO₂ sample has the lowest value of k_{app} . The simultaneous presence of another transition metal, in the form of cation in this case, for the Mo/TiO₂ sample complicates the results. 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. To understand the observed differences in the activity the samples were characterized with different physicochemical techniques, like Diffuse Reflectance Spectrometry (DRS); to analyze the interactions of the supporting species and to determine the energy gap (E_g) of the catalysts, adsorption desorption isotherms of N₂; to determine the Specific Surface Area (SSA), mass titration method; to estimate the point of zero charge of the catalysts and powder X-Ray diffraction measurements to identified the possible crystal phases in the catalysts.

SSA determination: The values of SSA are reported in Table 2. As it can be seen there are not significant differences between the samples and almost the same with TiO₂. This is a first evidence that the deposition of Mo-oxo species can be achieved with high dispersion, while the subsequently deposition of M(II) cation is not alter the structural characteristics of the samples.

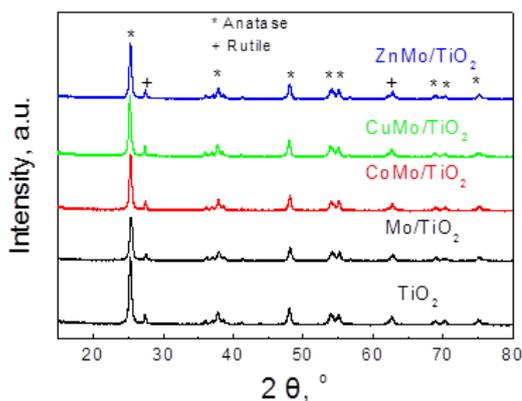


Figure 3. XRD patterns of the MMO/TiO₂ samples (M:Co,Cu or Zn).

XRD patterns: The XRD patters are presented in Figure 3 and confirm that there are not any significant changes in the structure of the catalysts. The only diffraction peaks that they can be observed are the peaks due to TiO₂. This is evidence that the calcination temperature during catalyst preparation is not high enough to cause changes in the crystal phase of TiO₂. The main diameter of the TiO₂ particles is not greatly affected, although it is rather bigger in the ternary systems and finally, the total crystallinity of the solid is reduced after the deposition of the M(II) cation, except in the case of CoMo/TiO₂, although the differences were not significant different.

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 after equilibration. Under these conditions, the measured pH approaches the pzc value of the mixed solid. The values are presented in Table

2. As it can be seen the deposition of the Mo-oxo species and the formation of supported MoO_3 after calcination lowers the pzc of the catalyst. This is expected since the MoO_3 phase have acidic character. In a recent work for the WO_3/TiO_2 system it was reported that the pzc of the catalyst is shifted in lower values than bare TiO_2 but significantly higher than the corresponding values of a mechanical mixture of WO_3 and TiO_2 of the same composition. The dispersion of WO_3 onto TiO_2 surface results in electron transfer and increases the surface electron density, which enhances the surface basicity of TiO_2 explaining the effect of higher pzc values. This is also expected for the $\text{MoO}_3/\text{TiO}_2$ system. [Tsatsos *et al.*, 2022].

Table 2. Point of zero charge, energy gap and k_{app} values of the catalysts

No	Catalyst	SSA (m^2g^{-1})	pzc	Eg (eV)	k_{app} (min^{-1})
1	TiO_2	54	6.2	3.09	0.074
2	Mo/TiO_2	54	4.9	2.87	0.021
3	CoMo/TiO_2	52	6.1	2.72	0.0056
4	CuMo/TiO_2	53	6.5	2.82	0.023
5	ZnMo/TiO_2	53	6.4	2.85	0.029

The pzc values of unsupported MO oxides exhibit the basic character of the oxides. Generally, the pzc values of CoO is reported around 9.0, while ZnO and CuO have values around 8.5 [Kosmulski, 2016]. Interestingly, although CoO seems to be more basic than ZnO and CuO, the pzc of the CoMo/TiO_2 is lower than the CuMo/TiO_2 and ZnMo/TiO_2 . This can be attributed to higher interaction of the Co^{2+} species with the $\text{MoO}_3/\text{TiO}_2$ surface. It should be noted that the deposition of Co(II) species on the Al_2O_3 follows second order kinetics and it was reported that a dimer $\text{Co}(\text{H}_2\text{O})_x\text{-O-Co}(\text{H}_2\text{O})_x$ ($x < 6$) complex is formed in the interfacial region during deposition [Ataloglou *et al.*, 2005].

Diffuse Reflectance Spectroscopy: The DR spectra of the catalysts studied with reference to PTFE disk are presented in Figure 4.

As it can be seen the $F(R)$ values for the Mo/TiO_2 and MMo/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 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 Mo – O – Ti bonds. These charge transfer phenomena are common in the systems, where a semiconductor is covered by a transition metal oxide, as in this case. Concerning the MMo/TiO_2 samples, no significant differences can be observed while the adsorption in visible region is low despite the black color of the CuO and CoO oxides, suggesting a rather good dispersion of the above oxides. Only the CoMo/TiO_2 sample, shifts the spectrum in the visible region in a more intense way.

The energy gap, E_g for the samples studied, can be calculated by the Tauc plot. The E_g can be found by extrapolation of the curve $(F(R) \text{ hv})^{1/2}$ against hv . The E_g

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 2 and the CoMo/TiO_2 sample has the lowest E_g among the samples, although this catalyst has the lowest activity among all. This is an evidence that the E_g is not the only factor affecting the photocatalytic performance of a supporting and the E_g is mainly determined from the interactions of the supported phase with the semiconductor who act as support.

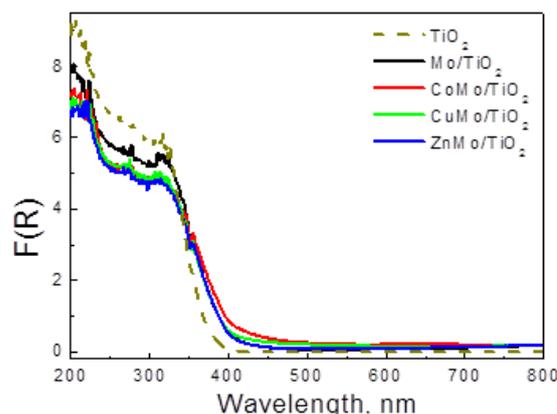


Figure 4. DR spectra of TiO_2 and the MMo/TiO_2 samples (M:Co, Cu or Zn), with PTFE as reference.

In order to investigate further the interactions of the supported phase the spectra were collected with TiO_2 as reference. These spectra are presented in Figure 5 and with the subtraction of the TiO_2 spectrum the influence of the supporting phases can be clearly observed on the adsorption spectra of the MMo/TiO_2 samples.

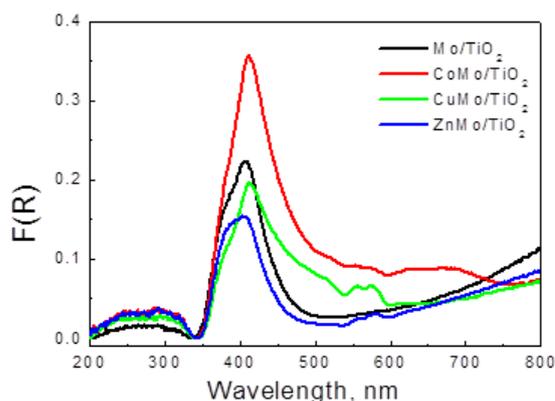


Figure 5. DR spectra of the MMo/TiO_2 samples (M:Co, Cu or Zn), with TiO_2 as reference.

They exhibit a rather intense peak centered at about 415 nm for all the samples, the CoMo/TiO_2 has the more intense peak, 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 some quantities of Co(III) in octahedral symmetry. This is

supported from the triplet center at about 580 nm and the shoulder at 680 nm.

Similar peaks have been reported for a variety of supported metal oxides on semiconductors [Vakros 2020; Papavasiliou *et al.*, 2018; Nikolova *et al.*, 2007; Stamatis *et al.*, 2007]. The above is characteristic of the charge transfer phenomena between the supported Mo phase and titania surface through oxygen bond Mo-O-Ti and how the presence of another cation affects them. Taking into account the detrimental effect of the supported Mo phase on the activity of TiO₂ these interactions are not favorable for the photocatalytic process. Although these interactions are favorable for achieving good dispersion consume surface groups and alter the electronic density of the titania, as it was shown for the WO₃/TiO₂ system [Tsatsos *et al.*, 2022]. The deposition of Co increases the peak and thus it is expected to hinder the activity. On the other hand the presence of Zn and Cu lowers the peak and it is expected to enhance the activity. The above are confirmed from the catalytic activity results in a quantitative way, taking as measurement of the activity the values of k_{app} . Indeed, the correlation between the absorbance of the samples in 415 nm and the k_{app} values is linear, as it can be seen in Figure 6.

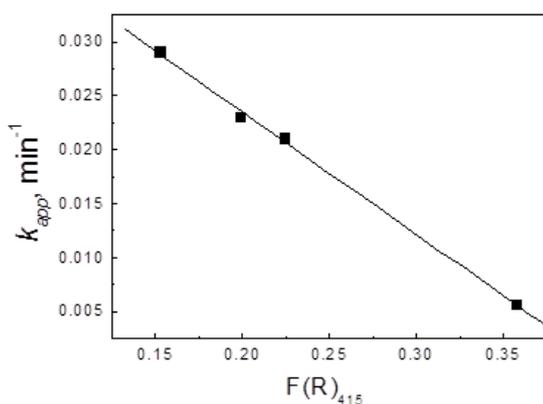


Figure 6. Linear dependence of the k_{app} values with the absorbance of each catalyst in 415 nm.

One other interesting correlation can be achieved for the ternary catalysts using again the k_{app} values as measurement of the activity and the ΔN , the number of transferred electron calculated from the equation (3) combine the MoO₃ as oxide 1 with CoO, CuO and ZnO as oxide 2. It can be supported that the charge transfer between Mo and Ti is the determining factor for the activity of the catalyst and the second supported metal alters these interactions. In order to determine the ΔN , we have to take into consideration that the atomic ratio between Mo and either M is 2:1, while for the Co it can be argued that the value is 4:1 since Co(II) ions have the tendency to form dimer in the interfacial region [Ataloglou *et al.*, 2005]. Thus, the calculated value of ΔN is different from the stoichiometric MO – MoO₃ mixed oxides, since μ and η are molecular and not orbital properties [Erdemir *et al.*, 2005]. The correlation is linear (Figure 7), revealing the importance of the interactions

between the supported phases and the influence of the electronic configuration and the properties of the individual oxides. At this point it should be noted that this is a first try to correlate the reactivity of a ternary system with properties like electronegativity or chemical hardness. The catalytic reaction is also important, since different processes may demand high interactions to achieve better yield. Also, the adsorption of the reactant can alter significantly the electronic configuration of the catalyst. All these parameters increase the difficulty for a more solid approach.

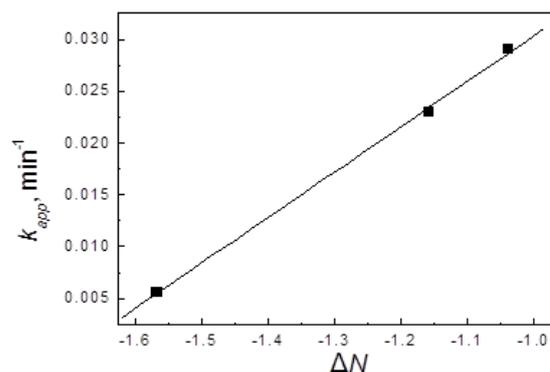


Figure 7. Linear dependence of the k_{app} values with the number of transferred electrons ΔN .

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 TiO₂. This is due to the interactions between titania surface and supported molybdena phase through the charge transfer phenomena of the Mo – O – Ti formed. The above bonds are responsible for the high dispersion of MoO₃ phase and the detrimental effect on the photocatalytic activity. The charge transfer phenomena can be detected with diffuse reflectance spectroscopy. The deposition of M(II) ions on the Mo/TiO₂ system can alter the physicochemical characteristics of the ternary system and the interactions between Mo and TiO₂. The observed differences in the activity can be approached with properties like electronegativity or chemical hardness of the individual oxides. Among Co, Cu and Zn metal ions only Co is not a good dopant for the binary system, probably due to its low chemical hardness, the tendency to form dimers in the interfacial region and the p-type semiconducting nature. The other two metal ions are possible candidates for the binary MoO₃/TiO₂ system or similar systems.

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