

Photocatalysis of Metal Tungstates Molybdates

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ABSTRACT

The metal elements are capable of yielding a large diversity of oxide compounds. These materials have a tendency to attain a lot of structural geometries having an electronic structure showing insulator, semiconductor or metallic character. It is observed that photocatalytic properties are found in the metal tungstates having formula MWO_4 . These materials are widely used in super capacitors. Manganese tungstate ($MnWO_4$) is observed to be very sensitive to humidity and magnetism. Hence, it can be used as humidity sensor and photocatalyst. The current article highlights the photocatalysis of metal tungstates molybdates.

1. Introduction

$MnWO_4$ gets crystallized in the wolframite structure having a monoclinic space group with each cell including 2 Mn^{2+} ions.

The figure 1(a) shows the crystal structure of $MnWO_4$ and Figure 1(b) shows the elliptical spiral spin structure in AF_2 phase of $MnWO_4$

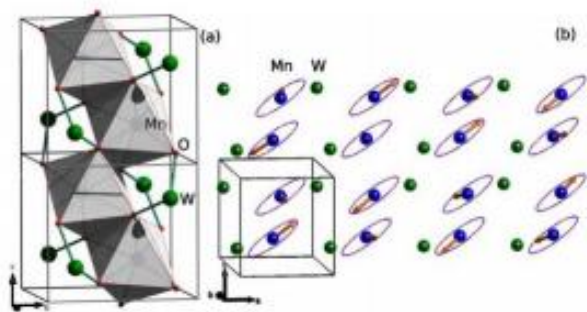


Figure 1(a) Crystal structure of $MnWO_4$ and (b) elliptical spiral spin structure in AF_2 phase of $MnWO_4$

It is observed that $CuWO_4$ is a ternary oxide semiconductors that attracts extensive consideration due to showing scientific characteristics like ionic conductivity, ferroelasticity and photocatalytic.

The following figure shows the crystal structure of $CuWO_4$, the green, blue and red balls represent Cu, W and O atoms, respectively.

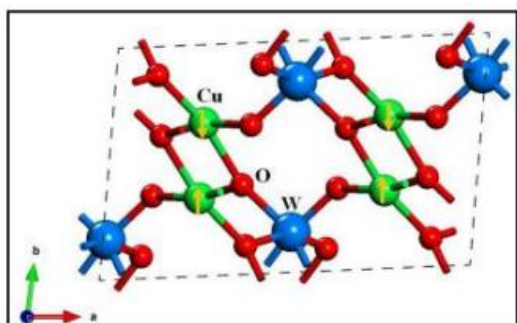


Figure 2: The crystal structure of $CuWO_4$, the green, blue and red balls represent Cu, W and O atoms, respectively

$ZnWO_4$ has attracted a great deal of research attention due to its wide physical and chemical properties. Among which the photocatalytic properties have been extensively investigated due to its unique combination of physical and chemical properties, in terms of molecular and electronic versatility, reactivity, and stability, make us have reason to believe it may be a promising photocatalyst. $ZnWO_4$ with different morphologies has been prepared, including porous $ZnWO_4$ films, nanorods, nanoparticles, etc. It was believed that the difference in catalytic activities among these different morphologies of $ZnWO_4$ was mainly caused by their crystallinity and surface area. The photocatalytic activity of $ZnWO_4$ was influenced by many properties like porous structure, crystal growth orientation, OHdefects, ion doping and synergetic effect of enhancing catalytic activity in degrading dyes combining electro-oxidation with photocatalysis.

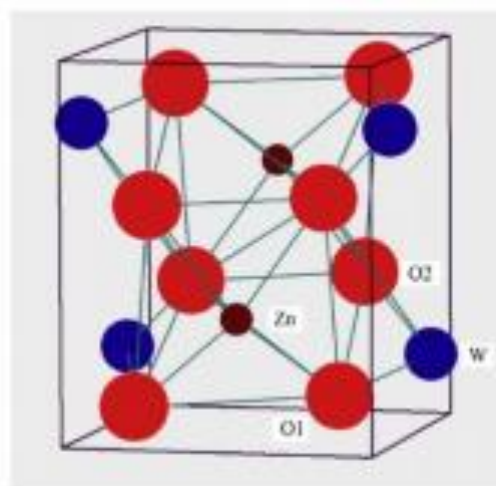


Fig. 3: Crystal structure of zinc tungstate, $ZnWO_4$

2. Photocatalysis of Metal Tungstates Molybdates

The usage of nanoparticles as electrochemical sensors can decrease overpotential of many analytically important electrochemical reactions, and even realize the reversibility of some redox reactions, which are irreversible at common unmodified electrodes. For example, highly sensitive nitric oxide (NO) microsensor was developed by the modification of

a platinum microelectrode with gold nanoparticles in which the nanoparticles catalyze the electrochemical oxidation of NO with an overpotential decrease of about 250 mV.

During the photocatalytic process, the irradiation of photocatalyst with visible or ultraviolet radiation activates the catalyst and establishes a redox environment in the aqueous solution. Here, the photocatalyst act as sensitizers for light induced redox process due to their electronic structure, which is characterized by a filled valence band and an empty conduction band.

The photocatalyst absorbs the photons with energies equal to or higher than its band gap energy or threshold energy. Each photons of the irradiated light hits an electron in the occupied valence band of the semiconductor, and can elevate the electron to the unoccupied conduction band. This leads to the formation of conduction band electrons and valence band holes. This process is generally called as the electron-hole pair creation. The photocatalytic activity depends on the ability of catalyst to create electronhole pair. These charge carriers may take different paths. First, they can get trapped, either in shallow traps (ST) or deep traps (DT). Second, they can recombine, nonradiatively or radiatively, dissipating the input energy as heat. Finally, they can react with electron donors or acceptors adsorbed on the surface of the photocatalyst.

Photocatalytic reactions are extremely complex processes involving many participants namely water, organic substrate, catalyst, light and oxygen. Hence, it is clear that operational parameters may affect the photocatalytic efficiency. The rate of photocatalytic process are known to be affected by several operation conditions including pH of the medium, amount of catalyst, substrate concentration, light intensity, temperature and oxygen pressure. Also, physical and chemical intrinsic properties of the photocatalyst may affect its photoefficiency.

The photocatalytic rate increases with an increase in the amount of catalyst, as this translates into an increase in the number of available active sites. However, when the amount of catalyst is increased beyond an optimum amount, the increase in the number of active sites is offset by a decrease in the penetration depth of visible or UV radiation. This is due to the higher opacity of the suspension and scattering effects by the catalyst particles. This leads to a decrease in the number of 'active' sites and therefore reduction in the degradation rate. It has been found that the optimal catalyst dosage is dependent on the light intensity. For higher light intensity, the optimal catalyst loading should be high.

3. Discussion

Transition metal molybdates ($AMoO_4$, A =Mn, Cu, Zn, Bi, Ag) have attracted a great deal of attention due to its unique physical and chemical properties which make them attractive and promising material. A transition metal with high catalytic activity, has attracted great interest and attention in various fields. Different molybdates are usually formed during the interaction of molybdenum and other materials or during nuclear fuel reprocessing. Since oxygen vacancies have been reported to exist in various molybdates, the application

prospects of molybdates as catalysts are attractive in many fields. Molybdates can also work as additives in steels and corrosion resistant alloys in mining and metallurgy industries, as well as improving the peeling strength of aluminum-polymer (A/P) composites used in packing, automobile, and aerospace industries.

Copper molybdate ($CuMoO_4$) exhibits two polymorphs at atmospheric pressure, the α form with Mo located in a tetrahedral environment (stable form) and the γ form with Mo located in an octahedral environment (metastable form). This oxide appears as a true horn of numerous note-worthy properties: it is thermochromic, trisochromic and piezochromic since it exhibits a phase transition associated with a color change from green to brown. This first order transition is accompanied by a strong change of volume and an anisotropic splitting of grains and occurs according to a dominocascade kinetics. Moreover, the temperatures/pressures of transition are adjustable by chemical doping.

Zinc molybdate ($ZnMoO_4$) has attracted increasing attention due to its various applications in photoluminescence, for humidity sensors, in photocatalysis, as pigments for anticorrosive paints or for battery materials. All these properties are intimately related to its semiconducting behavior.

Silver molybdates have received considerable attention due to their great importance for potential applications in electrocatalysts, photocatalyst, optical devices etc. Particularly, the exploration of new results with structural complexity will be a primary task. Ag_2MoO_4 possess polymorphism. This oxide is able to exhibit a (α -phase) tetragonal structure or (β - phase) cubic structure, depending on the pressure used in the synthesis process.

Nanohybrids are the materials having more than one phase and at least one of the phases should have one dimension less than 100 nm. This definition includes mesoporous materials, colloids, copolymers, organic-inorganic hybrid materials and multiphase nanostructures etc., The physical and chemical properties like electronic, mechanical, thermal, optical, electrochemical, and catalytic properties are strikingly different from that of the component materials.

During the last few decades, conducting polymers have been gathering a great interest in various fields by providing the opportunity of combining the electrical properties of a semiconductor and metals with the traditional advantages of conventional polymers such as easy and low cost preparation and fabrication.

Copolymerization, the main motivation for preparing copolymer composites lies in the possibility that these materials overcome the limitation of the rareness of new conjugated p-bond-containing monomers. It is believed that copolymerization of a pair of monomers will lead to an increase in the number of conductive polymers that can be made from the same set of monomers.

4. Conclusion

The overall photocatalytic degradation process is not too sensitive to temperature. The degradation rate dependency on temperature is reflected by the low activation energy (5–20 kJ mol⁻¹) compared with ordinary thermal reactions. Due to photonic activation, the photocatalytic systems do not require

heating and can operate at room temperature. This absence of heating is very attractive for processes carried out in aqueous medium, especially for water purification, because there is no need to waste energy in heating water, which has a high heat capacity.

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