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Chapter

Arsenomolybdates for Photocatalytic Degradation of Organic Dyes

Zhi-Feng Zhao

Abstract

Polyoxometalates (POMs) have fascinating structures and promising properties. The arsenomolybdates, as an important branch of POMs, are outstanding photocatalysts for organic dyes. In this work, we selected organic dyes to evaluate the photocatalytic activity of arsenomolybdates under UV light, containing compared with photocatalytic activity of different structural arsenomolybdates, stability, and the photocatalytic reaction mechanism of arsenomolybdates as photocatalyst. The arsenomolybdates may be used to as environmental photocatalysts for the degrading of organic dyes and solving the problem of environmental pollution.

Keywords: arsenomolybdates, photocatalyst, photocatalytic activity, organic dyes, UV light

1. Introduction

POMs is one of the most outstanding materials in modern chemistry, as the metal-oxide clusters with abundant structures and interesting properties [1–6], which render them to potential applications in electrochemistry [7, 8], photochemistry [9, 10], catalytic fields [11, 12], and so on (**Figure 1**). Chalkley reported the photoredox conversion of $H_3[PW_{12}O_{40}]$ into a reduced POM by photoirradiation with UV light in the presence of 2-propanol as a reducing reagent in 1952 [13]. Hill et al. started systematic investigation of photoredox catalysis using POMs in the 1980s [14]. Accordingly, POMs photocatalysis has been applied to a wide range of reactions, including H_2 evolution, O_2 evolution, CO_2 reduction, metal reduction, and the degradation of organic pollutants and dyes [15–20].

POMs are subdivided into isopolyoxometalates, which feature addenda metal and oxygen atoms, and heteropolyoxometalates, where a central heteroatom provides added structural stabilization and enables reactivity tuning [21]. In recent years, the research of POMs is mainly focused on heteropolyoxometalates. The arsenomolybdates are essential member of the heteropolymolybdates family [22], because of the redox properties of Mo and As atoms. The discoveries of many excellent articles on arsenomolybdates for ferromagnetic, antitumor activity, electrocatalysis properties, and lithium-ion battery performance have been reported in the last years [23–26]. However, there is no stress and discuss on the progress of arsenomolybdates for degradation of organic dyes. Arsenomolybdates possess

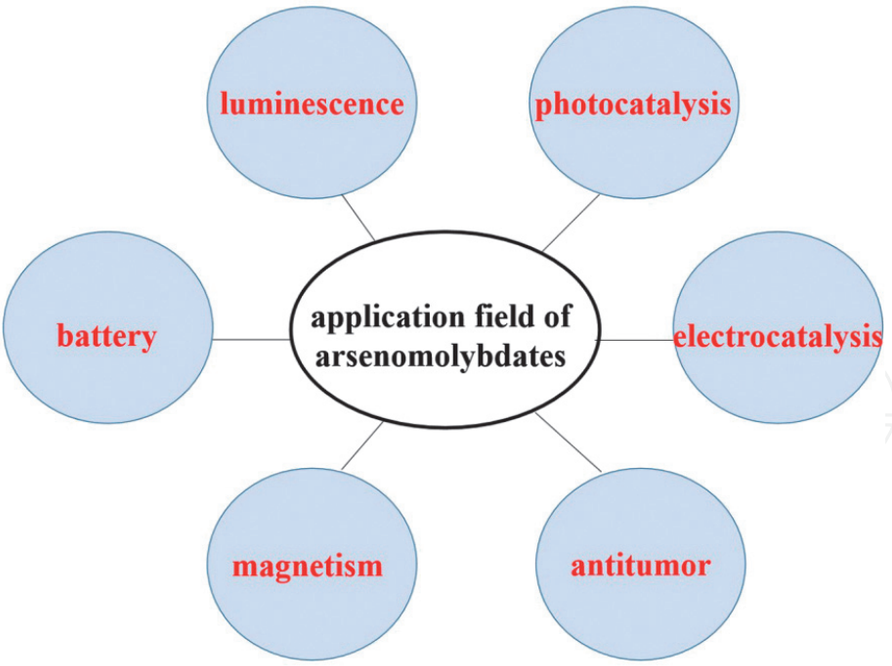

Figure 1.
The potential application field of arsenomolybdates.

high-efficient proton delivery, fast multi-electron transfer, strong solid acidity and excellent reversible redox activity [27], which may result to prominent photocatalytic activities. In particular, the integration of metal-organic frameworks (MOFs) into arsenomolybdates for photocatalysis has attracted widespread attention over the past decade, since MOFs combine porous structural and ultrahigh internal surface areas.

Based on these results, we provide a summary of recent works in the synthesis, structure, the photocatalytic activity, reaction kinetics and mechanism mechanisms of arsenomolybdates, which aim at finding the direction followed with the opportunities and challenges for the arsenomolybdates photocatalysis to accelerate the step to realize its practical application in degradation of organic dyes.

2. Syntheses and structure of arsenomolybdates

2.1 Syntheses of arsenomolybdates

Arsenomolybdates crystals reported were almost synthesized via self-assembly processes using hydrothermal method (**Figure 2**). Many factors in the synthetic process should be considered, such as reaction time and temperature, concentration of staring materials, compactness, pH values, and so on. The some experiments indicate that the temperatures are in the range of 110–180°C for srsenomolybdates synthesized, when the pH value of the mixture is adjusted to approximately 3–6.8, $[H_xAs_2Mo_6O_{26}]^{(6-x)-}$ (abbreviated $\{As_2Mo_6\}$), $[(MO_6)(As_3O_3)_2Mo_6O_{18}]^{4-}$ (abbreviated $\{As_6Mo_6\}$) and $[As^{III}As^{V}Mo_9O_{34}]^{6-}$ (abbreviated $\{As_2Mo_9\}$) types were easy to formed, when the pH value is within the range of 2.5–5.5 and 2–4, $[AsMo_{12}O_{40}]^{3-}$ (abbreviated $\{AsMo_{12}\}$) and $[As_2Mo_{18}O_{62}]^{6-}$ (abbreviated $\{As_2Mo_{18}\}$) types were successfully synthesized. At the same time, the choice of transition metal, organic ligand, and molybdenic source have also affect for

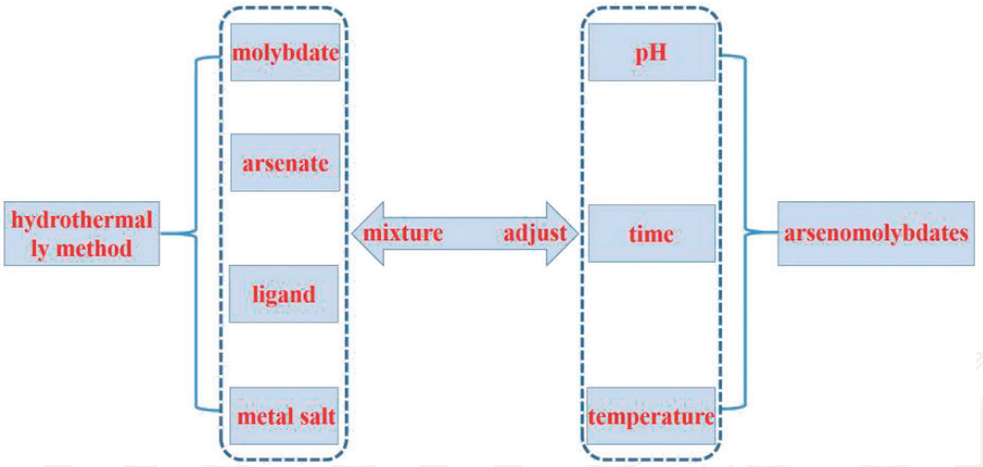

Figure 2.
The synthesis chart of arsenomolybdates crystal.

arsenomolybdates crystals. Therefore, further exploration of synthetic conditions is necessary, which can provide more experimental data for arsenomolybdates.

2.2 Structure of classical arsenomolybdates

Up to now, various structures of arsenomolybdates were reported and discussed in detail. The following types are classical arsenomolybdates clusters: (i) $\{As_2Mo_6\}$ type, Pope's group reported the first $\{As_2Mo_6\}$ cluster [28], in which the Mo_6O_6 ring is constructed from six MoO_6 octahedra connected via an edge-sharing mode, the opposing faces have two capped AsO_4 tetrahedra. Then Zubieta's group and Ma's group reported $[Mo_xO_yRAsO_3]^{n-}$ ($RAsO_3$ = organoarsenic acid) and $[Mo_6O_{18}(O_3AsPh)_2]^{4-}$(Ph = $PhAsO_3H_2$) clusters [29, 30]. (ii) $\{As_6Mo_6\}$ type, which is derived from the A-type Anderson anion $[(MO_6)Mo_6O_{18}]^{10-}$, the central $\{MO_6\}$ octahedron is coordinated with six $\{MoO_6\}$ octahedra hexagonally arranged by sharing their edges in a plane. The cyclic As_3O_6 trimers are capped on opposite faces of Anderson-type anion plane. Each As_3O_6 group consists of three AsO_3 pyramids linked in a triangular arrangement by sharing corners and bonded to the central MO_6 octahedron and two MoO6 octahedra via μ_3-oxo groups. Wang and co-workers reported the compound $(C_5H_5NH)_2(H_3O)_2[(CuO_6)Mo_6O_{18}(As_3O_3)_2]$ [31], Zhao groups synthesized the compound $[Cu(arg)_2]_2[(CuO_6)Mo_6O_{18}(As_3O_3)_2]\cdot 4H_2O$ [32]. (iii) $\{AsMo_{12}\}$ type, has a AsO_4 tetrahedron at the center and 12 surrounding MoO_6 octahedra, such as $[NBu_4]_6[Fe(C_5H_5)_2][HAsMo_{12}O_{40}]_2$ [33]. $\{As_2Mo_9\}$) type, is derived from the trivacant Keggin moiety, which is capped by a triangular pyramidal $\{AsO_3\}$ group, e.g., $[Cu(en)_2H_2O]_2\{[Cu(en)_2][Cu(en)_2As^{III}As^{V}Mo_9O_{34}]\}$ $2\cdot 4H_2O$ and $[Cu(en)_2\ (H_2O)]_4[Cu(en)_2(H_2O)_2]\{[Cu(phen)(en)]$ $[As^{III}As^{V}Mo^{VI}{}_9O_{34}]_2\}$ [34, 35]. (iv) $\{As_2Mo_{18}\}$ type, as a classical Wells–Dawson cluster, can be described as two $[AsMo_9O_{34}]^{9-}$ units derived from an Keggin anion by the removal of a set of three corner-sharing MoO_6 octahedra, e.g., $[Himi]_6[As_2Mo_{18}O_{62}]\cdot 11H_2O$ [36].

In comparison with the classical arsenomolybdates, many nonclassical arsenomolybdates have also been prepared in the past of years, such as $Ag_{12.4}Na_{1.6}Mo_{18}As_4O_{71}$ [37], $(NH_4)_{11}[AgAs_2Mo_{15}O_{54}]_3\cdot 6H_2O\cdot 2CH_3CN$ [38], $[As^{III}{}_2Fe^{III}{}_5MMo_{22}O_{85}\ (H_2O)]^{n-}$ (M = Fe^{3+}, n = 14; M = Ni^{2+} and Mn^{2+}, n = 15) [39], $\{Cu(2,2'\text{-bpy})\}_2\{H_2As_2Mo_2O_{14}\}$ [40], $[\{Cu(imi)_2\}_3As_3Mo_3O_{15}]\cdot H_2O$ [41], and so on. The novel arsenomolybdate structure is gaining more and more attention.

3. Photocatalytic activity of arsenomolybdates

3.1 Photodegradation process

In recent years, POMs have attracted a lot of attention as photocatalysts for the decomposition of wastewater [42]. Organic dyes, such as methylene blue (MB), rhodamine B (RhB), azon phloxine (AP), and so on, is a typical organic pollutant in waste water. In this work, the photocatalytic activities of arsenomolybdates are investigated via the photodecomposition of organic dyes under UV light irradiation (**Figure 3**). The photocatalytic reactions were conducted using a common process [27]: arsenomolybdates and organic dyes solution were mixed and dispersed by ultrasonic. The suspension was stirred until reached the surface-adsorption equilibrium. Then, a high pressure Hg lamp was used as light source to irradiate the mixture, which was till stirred for keeping the mixture in suspension. At regular intervals, the sample was withdrawn from the vessel and arsenomolybdates was removed by several centrifugations, and the clear liquid was analyzed by using UV–Vis spectrophotometer.

3.2 Photocatalytic degradation of MB

The common arsenomolybdates photocatalysis are shown in **Figure 4**. The photocatalytic activities of arsenomolybdates are review via the photodecomposition of MB under UV light irradiation (**Figure 5**). Su groups reported six compounds with $[H_xAs_2Mo_6O_{26}]^{(6-x)-}$ clusters and copper-organic complexes. Six $\{As_2Mo_6\}$ compounds were irradiated for 135 min under, the photocatalytic decomposition rates are 94.5%, 93.0%, 92.1%, 92.2%, 93.6%, and 96.5%, respectively [43]. Then the $\{Co(btb)(H_2O)_2\}_2\{H_2As_2Mo_6O_{26}\}\cdot 2H_2O$ exhibited better photocatalytic activity in the degradation of MB at the same process, the photocatalytic decomposition rate is 94.27% [44]. Su groups synthesized two $\{As_2Mo_6\}$ compounds with $[H_xAs_2Mo_6O_{26}]^{(6-x)-}$ clusters and free organic ligands, photocatalytic activities of they are detected, the conversion rate of MB is 91.8% and 92.2% when adding two $\{As_2Mo_6\}$ compounds as the catalyst 160 min later, respectively [45].

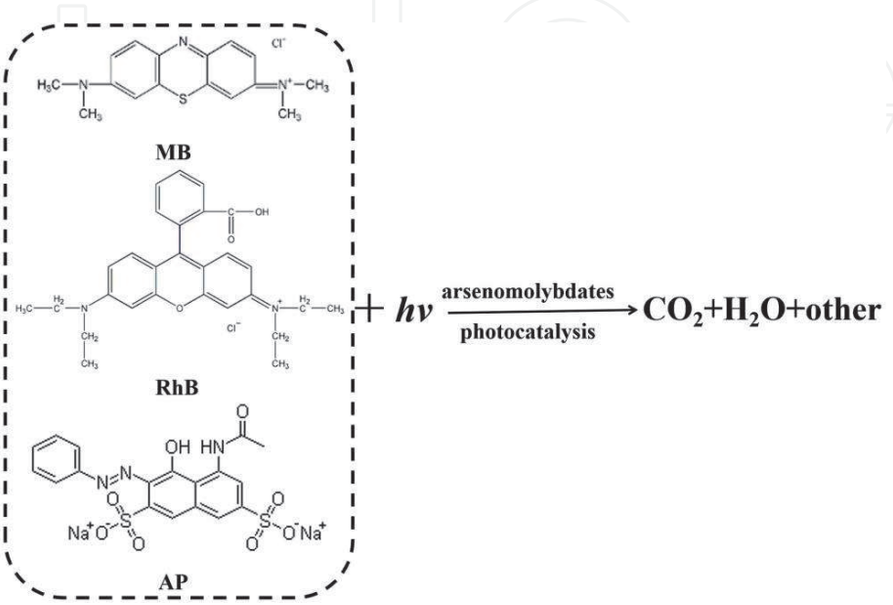

Figure 3.
The structure of dyes and photodecomposed product.

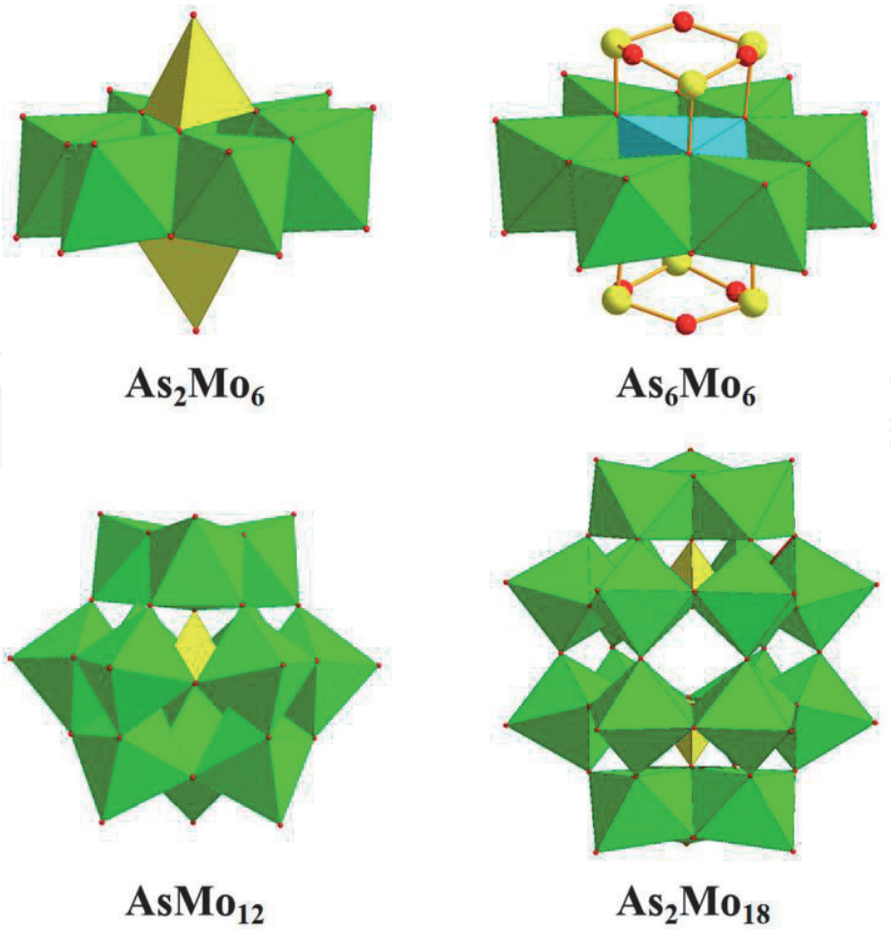

Figure 4.
The common arsenomolybdates photocatalysis polyoxoanion.

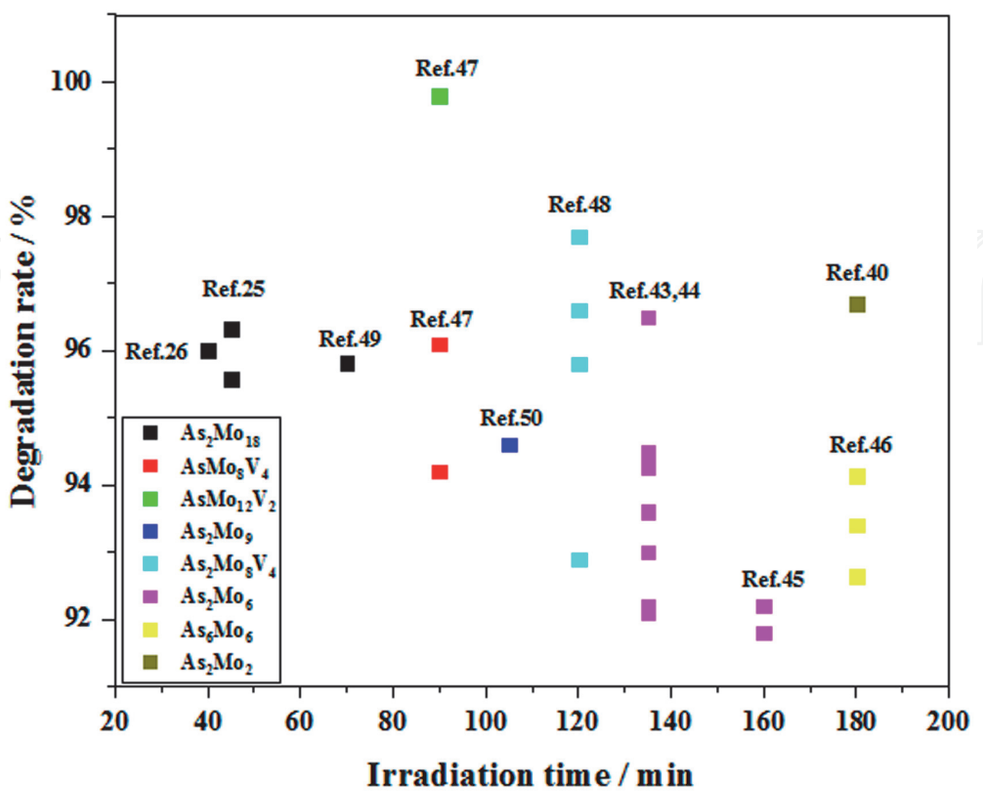

Figure 5.
The arsenomolybdates photocatalytic decomposition rates of MB under UV irradiation.

The above data show that the photocatalytic activity of the compound composed of $[H_xAs_2Mo_6O_{26}]^{(6-x)-}$ clusters and metal-organic complexes is higher than supramolecular assemblies based on isomers $[H_xAs_2Mo_6O_{26}]^{(6-x)-}$ clusters in the degradation of MB under UV irradiation, which maybe that the polyoxoanions can connect with transition metals in diverse modes, which enhanced the contact area between catalysts and substrates availing charge-transfer.

The three $\{As_6Mo_6\}$ compounds, $((phen)(H_2O)_4]_2$ $[(CoO_6)(As_3O_3)_2Mo_6O_{18}]\cdot 2H_2O$,$\{[Co(phen)_2(H_2O)]_2[(CoO_6)(As_3O_3)_2Mo_6O_{18}]\}\cdot 4H_2O$ and $\{[Zn(biim)_2(H_2O)]_2[(ZnO_6)(As_3O_3)_2Mo_6O_{18}]\}\cdot 4H_2O$), as catalysts under UV light irradiation after 180 min [46], the photocatalytic decomposition rates of MB are about 92.64, 93.40, and 94.13%.

Yu groups prepared three Keggin arsenomolybdates, the photocatalytic decomposition rates of MB are 94.2% for $(Hbimb)(H_2bimb)[AsMo_8{}^{VI}V^V{}_4Co_2O_{40}]$, 96.1% for $(Hbimb)_2(H_2bimb)_{0.5}$ $[AsMo_8{}^{VI}V^V{}_4Cu_2O_{40}]\cdot 1.5H_2O$, 99.8% for $[Cu^I(imi)_2]$ $[\{Cu^I(imi)_2\}_4\{AsMo_6{}^V Mo_6{}^{VI}O_{40}(V^{IV}{}_2O_2)\}]$ after 90 min irradiation, respectively [47].

Four biarsenate(III) capped Keggin arsenomolybdates with tetravanadium(IV) substituted were prepared, which exhibit excellent degradation activity for MB under UV light. The absorption peaks of MB reduced obviously after 120 min in the presence of four Keggin arsenomolybdates, the degradation rates for MB are 92.9%, 95.8%, 96.6%, and 97.7%, respectively [48].

The photocatalytic decomposition rate of MB is about 96% for $[\{Cu(btp)_2\}_3\{As_2Mo_{18}O_{62}\}]$ after 40 min [26], and the photocatalytic decomposition rates were 96.32% and 95.57% for $[Cu(pyr)_2]_6[As_2Mo_{18}O_{62}]$ and $[Ag(pyr)_2]_6[As_2Mo_{18}O_{62}]$ after irradiation for 45 min [25]. Yu reported that $(H_2bimyb)_3(As_2Mo_{18}O_{62})$ exhibits high-efficient degradation ability for MB under UV light. After UV light irradiation of $(H_2bimyb)_3(As_2Mo_{18}O_{62})$ for 70 min, the photocatalytic decomposition rate is 95.82% [49].

It is reported that the conversion rate of MB is 94.6% when adding compound $[Cu(imi)_2]_5Na[(AsO_4)Mo_9O_{27}(AsO_3)]\cdot 5H_2O$ as the photocatalyst after 105 min [50]. $\{Cu(2,2'\text{-bpy})\}_2\{H_2As_2Mo_2O_{14}\}$ as photocatalyst was investigated via the photodecomposition of MB under UV light irradiation and the same conditions. The photocatalytic decomposition rate of MB that is 96.7% after 180 min [40].

3.3 Photocatalytic degradation of RhB

The photocatalytic activities of arsenomolybdates as photocatalysts are review via the photodecomposition of RhB under UV light irradiation. The photocatalytic decomposition rates of RhB are about 96.34 and 95.7% for $\{Co(btb)(H_2O)_2\}_2\{H_2As_2Mo_6O_{26}\}\cdot 2H_2O$ and $[\{Cu(abi)\{H_4As^{III}As^VMo_9O_{34}\}](abi)_4[Cu(abi)_2]\cdot H_2O$ as photocatalysts under UV light irradiation after 135 and 140 min, respectively [27, 44]. $[\{Cu(btp)_2\}_3\{As_2Mo_{18}O_{62}\}]$ as photocatalyst was investigated decomposition rate of RhB after 40 min is about 96% [26]. The photocatalytic decomposition rates of RhB are 94.42 and 95.07% for $[M(pyr)_2]_6[As_2Mo_{18}O_{62}]$ (M = Cu,Ag) under UV light irradiation after 45 min [25].

The photocatalytic decomposition rates of RhB are 95.9% for $(Hbimb)(H_2bimb)[AsMo_8{}^{VI}V^V{}_4Co_2O_{40}]$, 94.3% for $(Hbimb)_2(H_2bimb)_{0.5}[AsMo_8{}^{VI}V^V{}_4Cu_2O_{40}]\cdot 1.5H_2O$, 95.8% for $[Cu^I(imi)_2][\{Cu^I(imi)_2\}_4\{AsMo_6{}^VMo_6{}^{VI}O_{40}(V^{IV}{}_2O_2)\}]$ after 108 min irradiation, respectively [47].

3.4 Photocatalytic degradation of AP

AP, as one of the azo dyes, is relatively difficult to degrade, and so it was used as target molecules to evaluate the photocatalytic activity of arsenomolybdates under

UV irradiation. The photocatalytic activity of $\{pyr\}\{Hbib\}_2\{As^{III}{}_2(OH)_2As^{V}{}_2Mo_{18}O_{62}\}$ was evaluated for the degradation of AP under UV irradiation [51], the degradation rate is 91.02% after UV light irradiation 90 min. In addition, the photocatalytic activity of noncapped 0D analog $(H_2bimyb)_3(As_2Mo_{18}O_{62})$ was also studied under the same condition. Compared with $\{pyr\}\{Hbib\}_2$ $\{As^{III}{}_2(OH)_2As^{V}{}_2Mo_{18}O_{62}\}$, only 32.76% of AP was degraded by $(H_2bimyb)_3(As_2Mo_{18}O_{62})$ after 90 min [49], which indicates that the photocatalytic degradation effect of the bi-arsenic capped Dawson compound on AP is much better than that of noncapped analog. The 3D Dawson organic-inorganic hybrid arsenomolybdate, $\{Ag(diz)_2\}_3[\{Ag(diz)_2\}_3(As_2Mo_{18}O_{62})]\cdot H_2O$ exhibits merit photocatalytic properties for degradation of refractory dyes AP under UV light [52], the photocatalytic decomposition rate is 93.24% after 80 min.

The photocatalytic activities of $(imi)_2[\{Cu^{I}(imi)_2\}_2\{Na(imi)_2\}$ $\{As^{III}As_2{}^{V}Mo_{18}O_{62}\}]\cdot 2H_2O$ and $\{Cu^{I}{}_{0.5}(trz)\}_6[\{Cu^{I}{}_{0.5}(trz)\}_6(As_2Mo_{18}O_{62})]$ were evaluated for degradation of AP under UV irradiation. The photocatalytic decomposition rates are 89.06 and 96.38% after 80 min [53]. The photocatalytic decomposition rates are 92.49% of AP for $[Cu(pyr)_2]_6[As_2Mo_{18}O_{62}]$ and 92.25% of AP for $[Ag(pyr)_2]_6[As_2Mo_{18}O_{62}]$ after irradiation 135 min [25].

On the basis of the aforementioned points, $\{As_2Mo_{18}\}$ type arsenomolybdates with 3D networks possess the highest photocatalytic activities for photodecomposition of MB, RhB and AP under UV light irradiation. The following factors are maybe considered: First, quantity of Mo and O atoms in unit cell is a factor, which can increases the amount of charge-transfer from HOMO of O to LUMO of Mo, generating more electron-hole pairs. Second, the enhanced photocatalytic activity may have arisen from the 3D architecture, more extended 3D frameworks favor the migration of excited holes/electrons to the surfaces of $\{As_2Mo_{18}\}$ type to initiate the photocatalytic degradation reaction with organic dyes.

3.5 Reaction mechanisms of photocatalytic performance

Experimental and theoretical studies of arsenomolybdates photocatalysis have revealed that it typically proceeds based on the following mechanism [41, 42, 48, 52]: Irradiated of arsenomolybdates by UV light with energy equal to or greater than the E_g value of itself, which induces intramolecular charge-transfer from the HOMO of O to the LUMO of Mo, leading to the formation of photoexcited states, subsequently photogenerated electron–hole pairs were generated. The O_2 captures electron to form $^{\bullet}O_2^-$ and the hole reacts with H_2O or OH^- ions to form $^{\bullet}OH$. The $^{\bullet}O_2^-$ and $^{\bullet}OH$ radical decompose organic dyes' molecules into the final product, the detail of photocatalytic reaction is shown in Eqs. (1)–(4).

$$arsenomolybdate + hv \Rightarrow arsenomolybdate * \left(e^- + h^+\right) \quad (1)$$

$$e^- + O_2 \Rightarrow {}^{\bullet}O_2^- \quad (2)$$

$$h^+ + H_2O \Rightarrow H^+ + {}^{\bullet}OH \quad (3)$$

$$dye + {}^{\bullet}O_2^- + {}^{\bullet}OH \Rightarrow H_2O + CO_2 + other \quad (4)$$

3.6 Stability

Some research data show that the samples were washed and dried after the arsenomolybdates as photocatalysis several cycles, and the infrared or X-ray diffraction test were carried out, the infrared spectra or X-ray diffraction data of arsenomolybdates demonstrate that there are almost unchanged before and after

photocatalytic reaction [44–48], which indicate that arsenomolybdates photocatalysis have excellent structural stability.

4. Conclusions

In this chapter, the arsenomolybdates are presented, and the attention is mainly focus on photocatalytic degradation of organic dyes. Various strategies are summarized and discussed based on the knowledge of synthesis, structure and photocatalytic properties for arsenomolybdates, which reflects the major directions of recent research in this field. There are vast research opportunities as new arsenomolybdates architectures are discovered in future; the great effort to promote the development of arsenomolybdates is needed to reduce the gap with commercial applications.

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Conflict of interest

The authors declare no competing financial interest.

Abbreviations

arg	L-arginine
en	ethylenediamine
imi	imidazole
2,2′-bipy	2,2′-bipyridine
btb	1,4-bis(1,2,4-triazol-1-y1)butane)
phen	1,10′-phenanthroline
biim	biimidazole
bimb	1,4-Bis(imidazol-l-yl)butane
btp	1,3-bis(1,2,4-triazol-1-yl)propane
pyr	pyrazole
bib	1, 4-bis(1-imidazoly)benzene
bimyb	1,4-Bis(imidazol-l-ylmethyl) benze
abi	2-aminobenzimidazole
bib	1,4-bis(1-imidazolyl)benzene
diz	1,2-diazole
trz	1,2,3-triazole

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