Review

Recent Progress in Application of Molybdenum-Based Catalysts for Epoxidation of Alkenes

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Abstract: Epoxides are important industrial intermediates applied in a variety of industrial processes. During the production of epoxides, catalysts have played an irreplaceable and unique role. In this review, the historic progress of molybdenum-based catalysts in alkene epoxidation are covered and an outlook on future challenge discussed. Efficient catalysts are demonstrated including soluble molybdenum complexes, polyoxometalates catalysts, molybdenum-containing metal organic frameworks, silica supported molybdenum-based catalysts, polymer supported molybdenum-based catalysts, magnetic molybdenum-based catalysts, hierarchical molybdenum-based catalysts, graphene-based molybdenum containing catalysts, photocatalyzed epoxidation catalysts, and some other systems. The effects of different solvents and oxidants are discussed and the mechanisms of epoxidation are summarized. The challenges and perspectives to further enhance the catalytic performances in alkenes epoxidation are presented.

Keywords: molybdenum-based catalysts; epoxidation; alkene; mechanism

1. Introduction

Epoxides are essential raw materials in the production of fine chemicals, such as surfactants, epoxy resins, paints as well as vital intermediates in organic synthesis [1–4]. Epoxidation of alkenes has been an important main route to produce epoxides and has attracted a lot of researchers' attention. Generally, the chlorine-using non-catalytic process, co-epoxidation and catalytic processes using organic peroxides and peracids are traditional and common technologies in industrial processes [5,6]. However, these processes are not economic and capital intensive. Furthermore, environmental disadvantages occur as well. For instance, a massive output of chloride-laden sewage will be caused during the chlorine-using non-catalytic process, and a large deal of acid waste will also be produced by usage of peracids, as well as the difficulty of separation of homogeneous catalysts [7–9]. As to the co-epoxidation processes, the products from coupling might be equivalently commercially desired [10].

Metal catalyzed alkenes to epoxides with milder oxidants including O_2, H_2O_2 and alkyl hydroperoxides have gained a lot of interest and resulted in the improvement of highly efficient catalysts [11–13]. For metal-catalyzed epoxidations with alkyl hydroperoxides, metal-based catalysts with superior catalytic activity possess Lewis acidity and low oxidation potentials in their highest oxidation states, the order of active activity is Mo > W > Ti, V [14]. Moreover, molybdenum is abundant and non-noble. In these respects, many researchers have focused their attentions on molybdenum-based catalysts for epoxidation of alkenes in both industrial and laboratory [15].

The scope of this review is to display the historic progress of molybdenum-based catalysts and highlight the most advanced epoxidation catalysts at recent.

2. Homogeneous Molybdenum Complexes

Since the 1960s, scientists have found that soluble complexes of molybdenum were one of the most effective catalysts for epoxidation of alkenes. Molybdenum complexes as homogeneous epoxidation catalysts, including $Mo(CO)_6$, $MoO_2(acac)_2$, MoO_2-phthalocyanine, $MoO_2(octane-1,2-diol)_2$, MoO_2(*trans*-cyclohexane-1,2-diol)$_2$, etc., have been widely studied as epoxidation catalysts [16,17].

Since 1968, Mimoun and Sharpless's groups [18] have reported the peroxo species of molybdenum regenerated in situ during alkenes epoxidation, which were suggested as the key intermediates in this whole oxidation process. In 1973, Sharpless and Michaelson [19] discovered $Mo(CO)_6$, an efficient epoxidation catalyst, which exhibited remarkable reactivity in epoxidation of olefinic alcohols using *t*-BuOOH as oxidant and PhH as solvent. In 1974, Fusi et al. [20] reported molybdenum acetylacetonates ($MoO_2(acac)_2$) to directly catalyze epoxidation of alkenes resulting in high selectivity. Trifirò et al. [21] carried out the kinetic and spectroscopic studies with the presence of $MoO_2(oxine)_2$ in the epoxidation process of cyclohexene employing *tert*-butyl-hydroperoxide as oxidant.

Subsequently, molybdenum complexes with multifarious types of ligands have been studied and certified as efficient homogeneous catalysts in the epoxidation of alkenes [22,23]. It is widely considered that active metal containing Schiff base ligands are promising materials in catalytic epoxidation reactions [24]. Moreover, it is convenient to adjust the fabrication procedures of metal containing Schiff base complexes. *Cis*-[MoO_2L_2] which derived from the introduction of molybdenum complexes into Schiff base ligands, has been proved to be a promising catalyst to form epoxides with high reactivity. Judmaier et al. [25] employed Schiff base ligands (HL^X, X = 1–5) with molybdenum(VI) dioxo complexes ($MoO_2(\eta^2$-tBu$_2$pz)$_2$) to produce *cis*-[$MoO_2(L^X)_2$] with an intramolecular donor for efficiently selective alkenes epoxidation with 80% epoxide yield and 98% selectivity. Bagherzadeh et al. [26] fabricated oligomer molybdenum complexes [$MoO_2(L)]_n$ via the reaction of $MoO_2(acac)_2$ and an ONO-type Schiff-base ligand (L = 4-bromo-2-((2-hydroxy-5-methylphenylimino)methyl)phenol) and applied it as a catalyst in alkene epoxidation with high activity and selectivity as well as excellent turnover numbers. Antunes et al. [27] designed and prepared the complex (Htrz)$_2$[$Mo_3O_6(O_2)_4$(trz)$_2$]·H_2O, which isolated from the reaction of MoO_3 and H_2O_2 with the usage of 1,2,4-triazole(trz) and was employed in a model epoxidation reaction with *cis*-cyclooctene. In order to improve the reactivity of catalysts, Reich's group [28] attached fluorinated moieties to molybdenum tricarbonyl complexes by enhancing Lewis activity through a more electron deficient Mo atom. Arylated molybdenum tricarbonyl complexes were modified through varying the number and position of CF_3 group(s) on a benzyl moiety connected to a $CpMo(CO)_3$ entity. The as-obtained compounds exhibited better epoxidation activity benefiting from the modification of CF_3 groups. The results of epoxidation reactions by using different homogeneous molybdenum-based catalysts are summarized in Table 1.

Table 1. Results of epoxidation reactions by using homogeneous molybdenum-based catalysts.

Entry	Catalyst	Olefin	Oxidant	Solvent	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)	Ref.
1	*Cis*-[MoO$_2$(L^X)$_2$]-1	Cyclooctene	TBHP	Chloroform	50	1	100	99 (24 h)	[25]
2	*Cis*-[MoO$_2$(L^X)$_2$]-2	Cyclooctene	TBHP	Chloroform	50	1	100	99 (24 h)	[25]
3	*Cis*-[MoO$_2$(L^X)$_2$]-3	Cyclooctene	TBHP	Chloroform	50	1	22	99 (24 h)	[25]
4	*Cis*-[MoO$_2$(L^X)$_2$]-4	Cyclooctene	TBHP	Chloroform	50	1	30	99 (24 h)	[25]
5	*Cis*-[MoO$_2$(L^X)$_2$]-5	Cyclooctene	TBHP	Chloroform	50	1.5	100	99 (24 h)	[25]
6	[MoO$_2$L]$_n$	Cyclooctene	TBHP	1,2-dichloroethane	80	2	93	100	[26]
7	(Htrz)$_2$[Mo$_3$O$_6$(O$_2$)$_4$(trz)$_2$]·H$_2$O	*Cis*-cyclooctene	TBHP	α,α,α-trifluorotoluene	70	6	94	-	[27]
8	[MoO$_3$(trz)$_{0.5}$]	*Cis*-cyclooctene	TBHP	α,α,α-trifluorotoluene	70	6	83	-	[27]
9	[CpMo(CO)$_3$Bz-*m*-CF$_3$]	*Cis*-cyclooctene	TBHP	Benzene	55	24	100	99	[28]
10	[CpMo(CO)$_3$Bz-*m*-(-CF$_3$)$_2$]	*Cis*-cyclooctene	TBHP	Benzene	55	24	100	99	[28]

3. Heterogeneous Molybdenum-Based Catalysts

Although the catalytic activity of homogeneous catalysts is generally high, their non-recycling property has limited their application. Great efforts have been made to design and prepare heterogeneous catalysts for the case of overcoming the drawbacks of homogeneous catalysts, which offer the advantages of easy separation and are environmentally friendly [29]. Moreover, the superior properties of support materials (e.g., chemical and thermal stabilities, large specific surface area, hierarchical structures etc.) will exalt the catalytic activity as well [30]. Many stable materials have been used as supports, such as polymers [31], metal organic frameworks (MOFs) [32], carbon materials [33], porous silica materials [34] etc. Introducing active sites with diverse protocols on proper supports is a common and valid strategy of preparing heterogeneous catalysts. Impregnation [35], co-precipitation [36] and chemical bonding [37] are conventional and facile methods to achieve this goal.

3.1. Polyoxometalates (POMs) Catalysts

Polyoxometalates (POMs), anionic transition metal oxygen clusters with an extensive diversity of properties, have been widely used in catalysis, biology, electromagnetic functional materials, medicine etc. [38]. Interest has been paid in homogeneous and heterogeneous systems by making full use of the catalytic activity of polyoxometalates (POMs) in distinct oxidation processes. These superior applications may result from their unique properties, such as acid/base characterization, fast and reversible multi-electron redox transformations even under mild conditions, electron-transfer properties, thermal and oxidative strength, flexibility by the incorporation of appropriate metal ions or counterions to endow a superior catalytic performance [39,40].

Polyoxometalate nanoclusters can be used as an efficient catalyst in epoxidation directly. For instance, Rezaeifard's group [41] successfully used $\{Mo_{72}Cr_{30}\}$ Keplerate polyoxometalate nanoclusters as phase-transfer catalysts in safe and green ethanol with H_2O_2 as eco-friendly oxidant. The polyoxometalate acted as a homogeneous catalyst; however, it can be easily separated and reused like a heterogeneous catalyst. The dispersion of catalysts during the epoxidation process was shown in Figure 1a.

However, most of the efficient POMs catalysts for epoxidation are obtained after modification. Ghorbanloo's group [42] attached thiazole-hydrazone ligands with molybdenum(VI) complexes. As shown in Figure 1b, as-prepared $MoO_2L(EtOH)$ (Catalyst 2) and $[MoO_2(HL)(H_2O)]_2[Mo_6O_{19}]\cdot2MeCN$ (Catalyst 1) were obtained through the interaction between $[MoO_2(acac)_2]$ and (E)-2-((2-(benzo[d]thiazol-2-yl) hydrazono)methyl)-6-methoxyphenol (H_2L) by using ethanol and acetonitrile, respectively. These compounds were efficient catalysts for epoxidation reactions. Gao et al. [43] inserted molybdenum oxides clusters into the layer of two copper complexes, the resulted samples denoted as $[Cu(bipy)]_4[Mo_{15}O_{47}]\cdot2H_2O$ (bipy = 4,4′-bipyridine) and $[Cu^I(bix)][(Cu^Ibix)\ (\delta\text{-}Mo^{VI}_8O_{26})_{0.5}]$ (bix = 1,4-bis(imidazol-1-ylmethyl)benzene). The structures were shown in Figure 1c,d. The as-prepared catalysts revealed excellent reactivity for olefins epoxidation and could be recycled easily without obvious decrease. Due to the intense coordination bonds between copper complex and molybdenum oxide clusters, these catalysts had good stability during epoxidation. Taghiyar et al. [44] investigated three Keggin-type POMs encapsulated in molybdenum-iron-type Keplerate and studied their catalytic efficiency in alkenes epoxidation as a heterogeneous catalyst (Figure 1e). These catalysts showed higher reactivity than parent ones and could be easily recycled through filtration and used without significant loss over at least eight runs.

To overcome the shortcomings of homogeneous POMs-catalytic systems and enhance stability and reusability, POMs-based heterogeneous catalysts have been obtained by different "immobilization" or "solidification" processes with suitable modifications [45]. A variety of materials have been considered as proper supports for immobilizing POMs, e.g., zeolites, magnetic nanoparticles, metal-organic frameworks (MOFs), porous carbons, polymers, porous silica, transition metal oxides, etc. [46,47]. Boudjema et al. [40] supported 11-molybdovanado-phosphoric acid with the Keggin structure

$H_4[PVMo_{11}O_{40}]\cdot 13H_2O$ (PVMo) on acid-activated montmorillonite clay to optimize cyclohexene epoxidation with hydrogen peroxide. Jameel et al. [48] have used chloropropyltriethoxysilane functionalized SBA-15 as a support for immobilization of $Na_9PMo_{11}O_{39}(PMo_{11})$ and gold nanoparticles and studied the molecular oxygen reactivity and stability under facial reaction conditions.

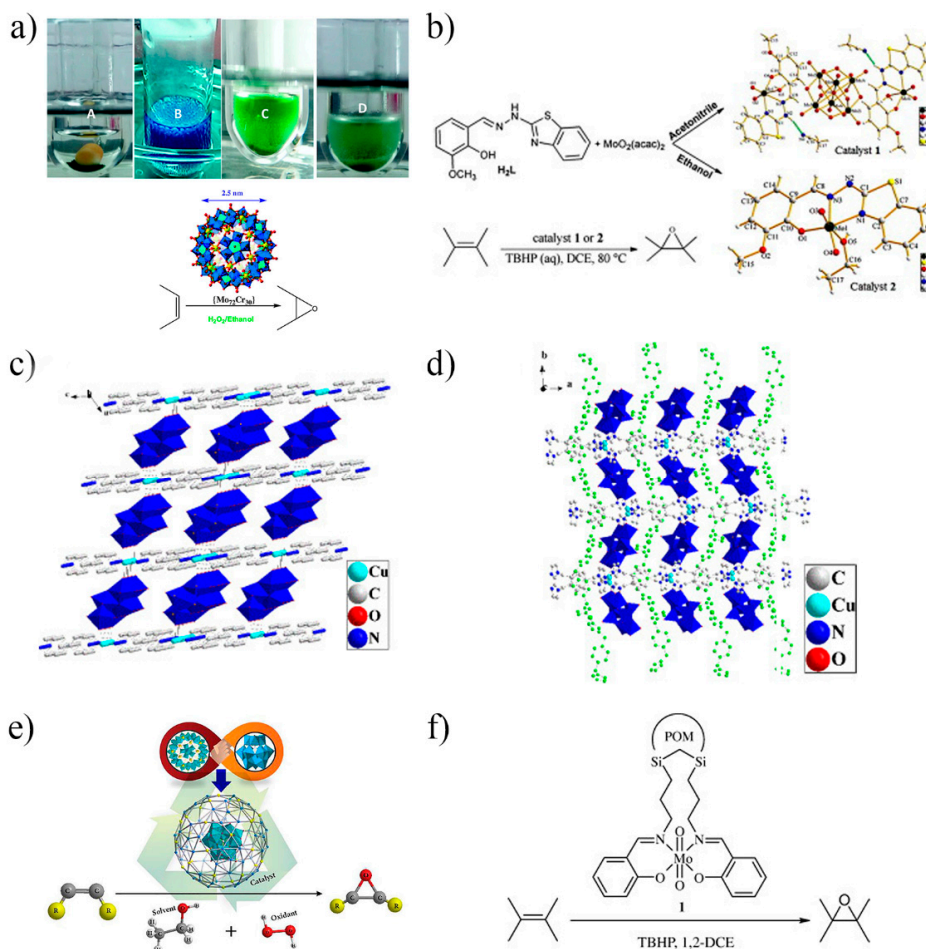**Figure 1.** (**a**) Photographs of epoxidation process using $\{Mo_{72}Cr_{30}\}$ as catalyst. Reproduced with permission from reference [41]. Elsevier (2017). (**b**) Schematic representation of synthesis procedure of $[MoO_2(HL)(H_2O)]_2[Mo_6O_{19}]\cdot 2MeCN$ (**1**) and $MoO_2L(EtOH)$ (**2**) and their epoxidation process. Reproduced with permission from reference [42]. Elsevier (2016). (**c**) View of the infinite-track Cu(bipy) chain-modified $[Mo_{15}O_{47}]_n^{4n-}$ in $[Cu(bipy)]_4[Mo_{15}O_{47}]\cdot 2H_2O$ (bipy = 4,4′-bipyridine); (**d**) The 3D polythreaded supramolecular structure along the given directions in $[Cu^I(bix)][(Cu^Ibix)(\delta\text{-}Mo^{VI}_8O_{26})_{0.5}]$ (bix = 1,4-bis(imidazole-1-ylmethyl)benzene) (green represents penetrated $[Cu^I2(bix2)]_n^+$ chains). Reproduced with permission from reference [43]. Elsevier (2015). (**e**) Epoxidation of alkenes by catalysts of Keggins encapsulated in molybdenum-iron-type Keplerate. Reproduced with permission from reference [44]. Elsevier (2018). (**f**) Epoxidation process of alkenes with $[Mo(O)_2(salen)\text{-}POM]$. Reproduced with permission from reference [49]. Elsevier (2010).

Stable polyoxometalates (POMs) can also be used as a support to immobilize molybdenum complexes. For instance, Moghadam et al. [49] used Keggin-type polyoxometalate $(K_8[SiW_{11}O_{39}])$ as a support and linked molybdenum (salen) [salen = N,N′-bis(salicylidene)ethylnediamine] complex through covalent attachment (Figure 1f). These as-prepared catalysts can catalyze epoxidation of different kinds of olefins even including non-activated terminal olefins. Moreover, two active sites will provide epoxidation reactivity if molybdenum complexes were supported on a molybdenum-base POMs. The results of epoxidation reactions by using polyoxometalates (POMs) catalysts are summarized in Table 2.

Table 2. Results of epoxidation reactions by using polyoxometalates (POMs) catalysts.

Entry	Catalyst	Olefin	Oxidant	Solvent	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)	Ref.
1	20% PVMo/Hmont	Cyclooctene	60 wt% H_2O_2	Acetonitrile	70	9	91	96	[40]
2	{$Mo_{72}Cr_{30}$}	Cyclooctene	30 wt% H_2O_2	Ethanol	70	0.75	97	>99	[41]
3	[$MoO_2(HL)(H_2O)]_2[Mo_6O_{19}]\cdot$2MeCN	Cyclooctene	TBHP	1,2-dichloroethane	80	5	100	100	[42]
4	[Cu(bipy)]$_4$[$Mo_{15}O_{47}]\cdot$2H_2O	Cyclooctene	TBHP	Chloroform	35	8	96	≈100	[43]
5	[Cu^I(bix)][(Cu^Ibix)(δ-$Mo^{VI}_8O_{26})_{0.5}$]	Cyclooctene	TBHP	Chloroform	35	10	92	≈100	[43]
6	(H_2bix)[(Hbix)$_2$(γ-Mo_8O_{26})]2$\cdot H_2O$	Cyclooctene	TBHP	Chloroform	35	10	39	≈100	[43]
7	{$Mo_{72}Fe_{30}$}	Cyclooctene	30 wt% H_2O_2	Ethanol	75	3.25	73	97	[44]
8	$PMo_{12} \subset Mo_{72}Fe_{30}$	Cyclooctene	30 wt% H_2O_2	Ethanol	75	3.25	82	98	[44]
9	$SiMo_{12} \subset Mo_{72}Fe_{30}$	Cyclooctene	30 wt% H_2O_2	Ethanol	75	3.25	91	99	[44]
10	$BW_{12} \subset Mo_{72}Fe_{30}$	Cyclooctene	30 wt% H_2O_2	Ethanol	75	3.25	93	99	[44]
11	1% Au/PMo_{11}/CPTES-SBA-15	Cyclohexene	O_2 (0.4 MPa)	-	50	24	48.1	35.9	[48]
12	[Mo(O)$_2$(salen)-POM]	Cyclooctene	TBHP	1,2-dichloroethane	75	6	100	100	[49]

3.2. Molybdenum-Containing Metal Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) are popular functional materials, which are organic-inorganic hybrid nanoporous crystals composed by metal nodes and connected organic linkers [50]. These materials have various superior properties such as microporosity, large specific surface area and flexible structural tailory [51,52]. These properties endow wide applications consisting of catalysis, gas storage, sensors and drug delivery [53,54]. Remarkably, MOFs are able to insert a lot of functional groups into the structures via a direct one-step synthesis [55,56]. Whereas, under solvothermal conditions, chemical or thermal instability occur among a number of modified ligands under solvothermal conditions and the desired chemical functionality will not be accomplished. Thus, post-synthetic strategy was carried out to endow MOFs with specific functions. After chemical modification, organic linkers and unsaturated metal centres will exist following the removal of solvent [57]. Abednatanzi et al. [58] modified $Cu_3(BTC)_2$ with molybdenum species using a two-step post-synthetic method. In this strategy, covalent connection of aminopyridine groups was first accompanied and subsequently reacted with bis(acetylacetonato) dioxomolybdenum(VI) (Figure 2a). The as-obtained molybdenum containing MOFs exhibited multi-functions, which could transfer both alkenes and allylic alcohols to epoxides as a heterogeneous catalyst (Figure 2b). Furthermore, the catalyst revealed size-selective properties which indicated the existence of reaction in pores. Noh et al. [59] utilized condensed-phase deposition method to immobilize molybdenum (VI) oxide on NU-1000 (metal-organic frameworks). The microporous and mesoporous properties (pore sizes of 10 and 31 Å, respectively) of NU-1000 provided excellent transformation of reactants/products and convenient access to target active sites (Figure 2c). Density functional theory calculations were utilized to further verify the stability of Mo-SIM, which revealed that the dissociation of the molybdenum (VI) species from the node of NU-1000 was endergonic (Figure 2d). Ni et al. [60] synthesized two kinds of Mo containing metal-organic frameworks via a post-synthetic method (Mo@COMOC-4) and a ship-in-bottle strategy (PMA@MIL-101), respectively. Mo@COMOC-4 was observed to be a promising catalyst for propylene epoxidation with cumene hydroperoxide (CHP). By a post-synthetic strategy, MoO_2Cl_2 complex was successfully immobilized onto the bipyridine sites of the framework (COMOC-4 = $Ga(OH)(OOC-C_{12}N_2H_6-COO)$). A strong affinity existed between MoO_2Cl_2 complex and bipyridine sites, which led to good regeneration property. PMA@MIL-101(Cr) was constructed through a ship-in-bottle method to trap a Keggin-type polyoxometalate ($H_3PMo_{12}O_{40}$). However, the strong acidity derived from heteropoly acids led to decomposition of CHP during the epoxidation reaction. In conclusion, suitable ligands should be chosen to construct molybdenum containing MOFs as epoxidation catalysts.
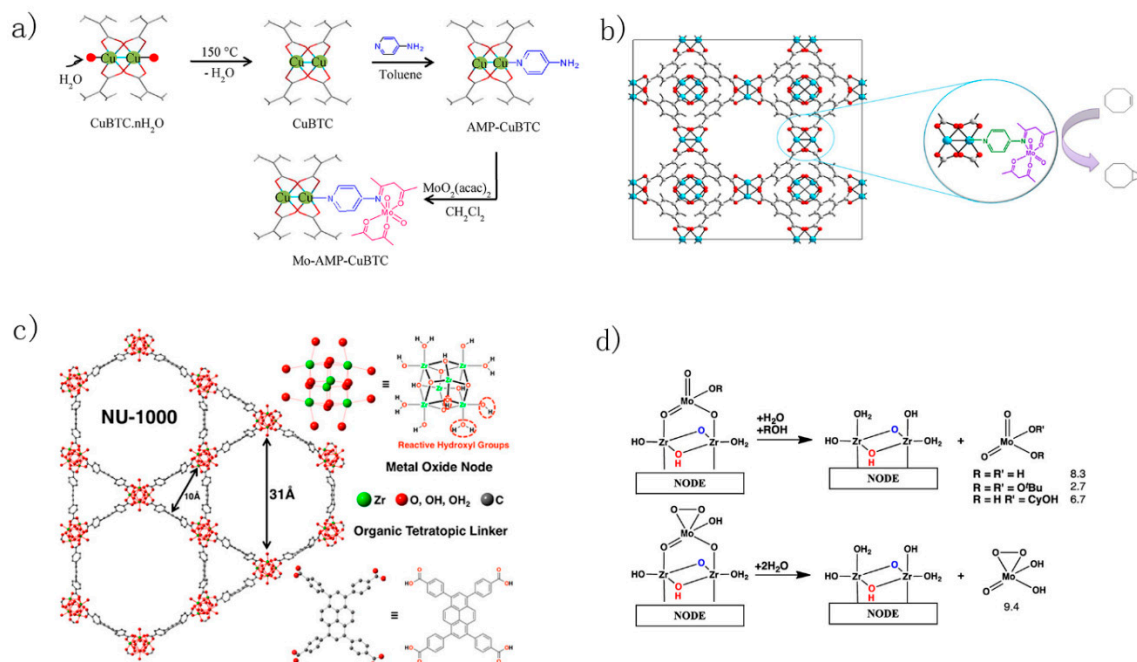
Figure 2. (**a**) The schematic process for modification of CuBTC with molybdenum complexes; (**b**) Structure and epoxidation process of molybdenum containing CuBTC catalysts. Reproduced with permission from reference [58]. Elsevier (2015). (**c**) Schematic illustration of nonmetalated NU-1000 with triple pore sizes and structures of metal oxide node and organic linker; (**d**) Thermodynamics of the leaching process of Mo-SIM. ΔG_{tol} in kcal/mol. Reproduced with permission from reference [59]. ACS Publications (2016).

3.3. Silica Supported Molybdenum-Based Catalysts

Inorganic porous silica materials are stable materials in epoxidation without swelling or dissolving in organic solvents. These silica materials also have excellent properties such as large and defined pore sizes and specific surface area, fantastic mechanical and thermal stabilities as well as easy functionalization [61]. Molecular sieve materials, e.g., TS-1, MCM-41, MCM-48 and SBA-15, are common and popular inorganic mesoporous silica materials. The existence of substantial silanol (Si-OH) groups facilitate these silica materials for organic functionalization [62]. At the same time, the resulting silica-supported catalysts generally consist of large specific surface area, uniform pore size distribution, large pore volume and flexible dimensionality of pore channels and structure [63]. These properties promote the reactivity of catalysts. Molybdenum has been incorporated into supports (e.g., molecule sieves, silicates, etc.) by various strategies such as wet or dry impregnation [64], thermal spreading [65], post-synthetic surface grafting protocol and direct synthesis methodology [66].

Soluble molybdenum complexes usually grafted on silica supports by post-synthetic surface grafting protocols through an organometallic precursor to react with the surface silanol groups to produce Mo-O-Si bond. In 2007, Luts et al. [67] covalently attached the Mo (IV)-Salen complexes to silica supports and investigated their epoxidation performances. After comparison, the operation of immobilization endowed both the advantages of homogeneous (enantioselectivity, high catalytic activity) and heterogeneous (easy separation and recovery, reusing) catalysts. This method overcame the problems with separation and recycling, greatly improving their properties and commercial value. Morales-delaRosa et al. [15] used bis-oxomolybdenum(VI) acetylacetonate as molybdenum precursor and incorporated the molybdenum into a silica gel support. By changing different kinds of solvents and the amount of molybdenum precursors in the synthetic process, different samples were obtained. When proper solvents (THF series) were chosen, the incorporation of molybdenum in silica occurred through a reaction between the molybdenum precursor and the surface hydroxyl groups on silica. Zhang et al. [68] successfully immobilized two molybdenum(VI) tridentate Schiff base complexes

on modified SBA-15 by a covalent grafting method. Interestingly, silylation treatment was used to improve the hydrophobicity of the silica surface via replacing residual Si-OH groups by Si-OTMS and the catalytic activity was proved to be improved. Higher hydrophobicity of the catalysts was considered to increase the compatibility between the catalysts and the reactants. Baskaran et al. [69] constructed a facile protocol to graft molybdenum carbonyl onto diaminosilane-modified SBA-15. Generally, the introduction of molybdenum oxo-species on SBA-DA-Mo led to promising reactivity for alkene epoxidation. Moreover, the active sites were tested to be stable on the surface and showed good recyclability.

The accessibility of the active metallic species is easy to achieve when the molybdenum complexes are grafted on supports by chemical bonding. However, the risk of leaching of active species still exists. Besides molybdenum complexes, molybdenum oxides are also efficient candidates for epoxidation. Choudhary and coworkers [70] used MoO_3 as epoxidation catalysts and obtained high catalytic reactivity for selective epoxidation of styrene with TBHP as oxidant. Fernandes et al. [71] successfully fabricated α-MoO_3 nanoparticles with an average size smaller than 100 nm, which were obtained from thermal oxidative annealing of MoO_2 nano-crystalline particles. Carreiro et al. [72] made efforts to carry out a facial alkenes epoxidation system using MoO_3 as catalysts and TBHP as oxidant, with the addition of pyridine and pyrazole to accelerate the reaction. The highest conversion was gained with styrene (92%) and the highest selectivity with β-methylstyrene ($\geq$99%), respectively. Incorporation of molybdenum oxides on supports will greatly improve the stability of catalysts as well as promote the conversion and yield of epoxidation from specific characteristics of supports. Scientists have made efforts to discover a different synthetic strategy to obtain highly dispersed metal species as well as create simple accessibility to molybdenum sites. Melero et al. [73] presented a direct synthetic procedure for the fabrication of molybdenum-containing SBA-15 materials under high acidic conditions using ammonium molybdate tetrahydrate ((NH_4)$_6Mo_7O_{24}\cdot4H_2O$) as metallic source and tetraethylorthosilicate (TEOS) as silicon precursors. The as-prepared materials showed good catalytic activity, stability and reusability in olefins epoxidation with alkyl hydroperoxides as oxidants. In 2002, Briot et al. [74] proposed a novel method of incorporating molybdenum oxo species with high dispersion into SBA-15 with the presence of H_2O_2. In this procedure, low-condensed neutral or anionic oxoperoxometalate species were supposed to generate under the condition of pH 1–2 with excess H_2O_2. The excess of H_2O_2 was expected to prevent the formation of oligomeric species such as the Keggin units ([$SiM_{12}O_{40}$]$^{4-}$, M = Mo, W), which would decrease the high dispersion of metal species in supports. This method has been successfully used in preparing efficient epoxidation catalysts. Bakala et al. [75] applied this method to insert MoO_x within MCM-41, SBA-15 and other silica materials. The catalysts were obtained by the reaction between Mo (VI) peroxo species and silica supports or precipitated silica in an acidic and peroxidic medium (peroxo route). In conclusion, MoO_x has been successfully inserted into mesoporous materials and resulted in excellent epoxidation reactivity. By using peroxo routes, molybdenum oxide species could be successfully inserted and/or supported in specific support. Moreover, the porosity of silica-based materials also contributes to restrict the size of molybdenum species and to achieve MoO_x species in high dispersion. We [76] used this route to incorporate molybdenum species in silica nanoparticles and obtained molybdenum incorporated silica nanoparticles. These catalysts have been used in epoxidation of alkenes and obtained efficient reactivity. Miao and coworkers [77] used the sol-gel method to prepare MoO_3/SiO_2 catalysts with different surface molybdenum species, which included polymolybdate, α-MoO_3, β-MoO_3, monomeric molybdenum species and silicomolybdic acid. Certain amount of (NH_4)$_6Mo_7O_{24}\cdot4H_2O$ was added during the sol-gel process of TEOS. The preparation conditions and MoO_3 loading have been verified to affect the distributions and subsistence states. The catalysts displayed catalytic activities for propylene epoxidation with cumene hydroperoxide. Chandra et al. [78] used SiO_2, TiO_2 and ZrO_2 nanospheres to immobilize ultrasmall MoO_3 nanoparticles in a one-pot reverse micelle method. After recycling for five runs, the catalytic activity and selectivity was maintained with minor loss. Ramanathan et al. [79] reported evaporation induced self-assembly method to prepare

molybdenum-incorporated mesoporous silicates. During the procedure, P123 triblock copolymer and $MoCl_5$ were employed as structure-directing agent and molybdenum source, respectively. The as-prepared catalysts displayed tunable acidity and promising catalytic activity for the metathesis of 2-butene and ethylene to production of propene. Smeets et al. [80] designed and prepared a SiO_2-TiO_2 mesoporous epoxidation catalyst via non-hydrolytic sol-gel strategy. This catalyst was employed in cyclohexene epoxidation with the presence of H_2O_2 in acetonitrile, which showed equivalent performance comparing with a TS-1 catalyst. One-pot synthesis silanization with methyltrichlorosilane and post-synthesis silanization with methyltrimethoxysilane were investigated. The latter method could greatly improve the catalytic performances, which resulted from a hydrophobic surface with a high active site content. The surface hydrophobization producing from methyl groups was proved to contribute the catalytic reactivity as referred in Zhang's work [68]. The aforementioned silica supported molybdenum-based catalysts are summarized in Table 3.

Table 3. Results of epoxidation reactions by using various silica supported molybdenum-based catalysts.

Entry	Catalyst	Olefin	Oxidant	Solvent	Temperature (°C)	Time (h)	TOF (h^{-1})	Conversion (%)	Selectivity (%)	Ref.
1	Peptide immobil. Mo-Salen	Cyclooctene	TBHP	Toluene	75	3	24.5	≈100	≈100	[67]
2	Mo-FSAP-CH$_3$-Cl-SBA-15	Cyclohexene	TBHP	1,2-Dichloroethane	80	4	-	68	95	[68]
3	SBA-DA-Mo	Cyclooctene	TBHP	Mesitylene	70	4	-	93	86	[69]
4	MoO$_3$	Styrene	TBHP	-	82-83	3	10.7	42	76.2	[70]
5	MoO$_3$ and 0.17 Pyrazole	Styrene	TBHP	Toluene	100	1	-	44	91	[72]
6	Mo-SBA-15	1-octene	TBHP	Decane	80	6	97.2	58.5	99.9	[73]
7	Mo-MCM-41(68)	Cyclooctene	TBHP	Acetonitrile	40	3	-	66	>99	[75]
8	Mo-SBA-15(122)	Cyclooctene	TBHP	Acetonitrile	40	3	-	85	93	[75]
9	Mo-SiO$_2$-bead(160)	Cyclooctene	TBHP	Acetonitrile	40	3	-	51	50	[75]
10	Mo-MSN-50	Cyclooctene	H$_2$O$_2$	Acetonitrile	70	4	-	79	>95	[76]
11	MoO$_3$/SiO$_2$	Propylene	CHP	*tert*-butyl alcohol	80 (2.6 MPa)	4	-	99	85.3	[77]
12	MoO$_3$/SiO$_2$	Cyclooctene	TBHP	1,2-dichloroethane	80	2	72.3	90	100	[78]
13	MoO$_3$/TiO$_2$	Cyclooctene	TBHP	1,2-dichloroethane	80	2	24.8	37	100	[78]
14	MoO$_3$/ZrO$_2$	Cyclooctene	TBHP	1,2-dichloroethane	80	2	25.9	39.6	100	[78]
15	NHSG	Cyclooctene	30 wt% H$_2$O$_2$	Acetonitrile/H$_2$O	60	2	-	13	16	[80]
16	NHSG@0.3Me	Cyclooctene	30 wt% H$_2$O$_2$	Acetonitrile/H$_2$O	60	2	-	13.7	37	[80]

3.4. Polymer Supported Molybdenum-Based Catalysts

Besides POMs and silica materials, the design of polymer-supported catalysts has gained a lot of attention since the 1970s. Molybdenum complexes have been widely immobilized on polymers including various resins, cross-linked poly(ethylene oxide), polyvinylalcohol, poly(vinylpyridine) etc. Nowadays, a great number of chelating functional molybdenum-based copolymers have been prepared and applied as alkenes epoxidation catalysts [24]. Fan et al. [81] used cross-linked porous copolymer to immobilize $MoO_2(acac)_2$ through covalent bonds under facile conditions. The resulting materials were proved efficient epoxidation catalysts for a variety of alkenes with *tert*-butyl hydroperoxide (TBHP). Furthermore, these materials could be easily reused at least five runs with no obvious loss in catalytic activity.

3.5. Magnetic Molybdenum-Based Catalysts

The utilization of different supports is a convenient method for obtaining distinct heterogenous catalysts. However, there is an activity loss during the separation process of filtration and centrifugation. To solve these problems, some scientists has immobilized catalysts on magnetic nanoparticles, which can simplify the recycling process. Zhang et al. [82] fabricated magnetic γ-Fe_2O_3@C@MoO_3 core-shell structures and investigated their catalytic performance in heterogeneous epoxidation reaction (Figure 3a,b). From the results of epoxidation, good conversion (100%) and selectivity (>99%) were observed under gentle conditions with low catalyst dosage. Moreover, the catalyst could be conveniently recycled through an external magnet with no obvious decrease in activity and selectivity after nine runs (Figure 3c). Zare et al. [83] used magnetic nanoparticles as supports and applied two methods to anchor a molybdenum (VI) complex (MoO_2(sal-phz)(CH_3OH)) on their surface (Figure 3d). The first protocol was directly modified the magnetic nanoparticles' surface with 3-chloropropyltrimethoxysilane (1A). In the second protocol, tetraethoxysilane was used to construct a silica coating on the surface of magnetic nanoparticles, then functionalized with 3-chloropropyltrimethoxysilane (2B). Afterwards, composites 2A and 3B were obtained by the interaction between complex 1 and 1A/2B through covalent attachment, respectively. Compared with composite 3B, nanocomposite 2A revealed better reactivity and stability during the liquid phase epoxidation reactions. The better catalytic activity and selectivity might be attributed to the higher hydrophobicity of 2A. First, the good hydrophobicity would improve the adsorption of reactants. Second, the higher hydrophobicity was assumed to reduce the abilities of adsorbing final products and oxidants. Hence, the final products would easily desorb from the surface.
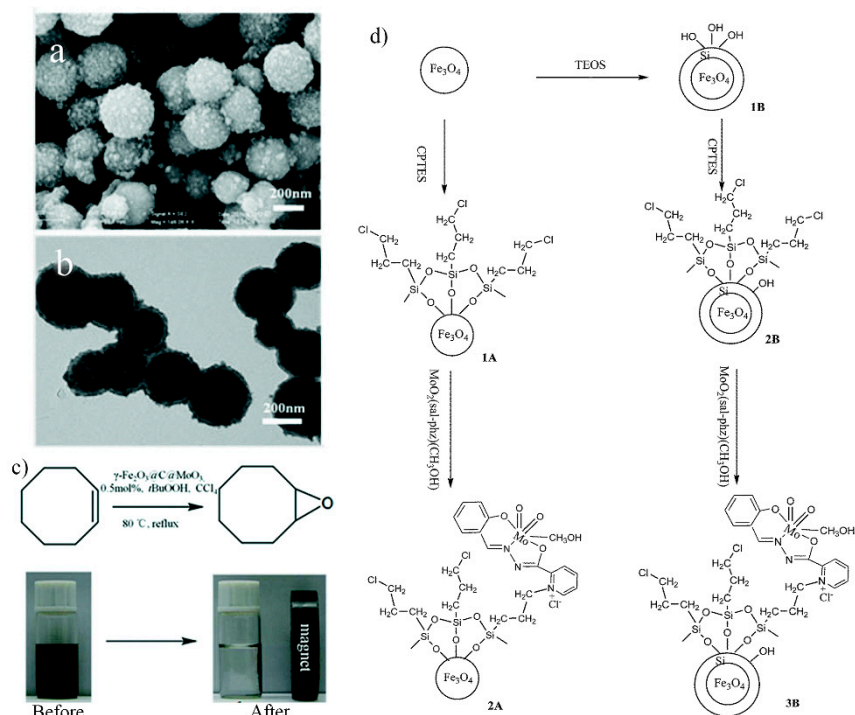
Figure 3. Scanning electron microscope (SEM) (**a**) and transmission electron microscope (TEM) (**b**) images of the as-prepared γ-Fe$_2$O$_3$@C@MoO$_3$ core/shell nanoparticles (NPs); (**c**) Photographs of reaction mixtures before and after magnetic separation. Reproduced with permission from reference [82]. Royal Society of Chemistry (2014). (**d**) Two synthetic pathways of preparing molybdenum Schiff base complexes modified Fe$_3$O$_4$. Reproduced with permission from reference [83]. Royal Society of Chemistry (2016).

3.6. Hierarchical Molybdenum-Based Catalysts

Hierarchically porous materials have attracted tremendous attentions resulting from their diversity and superior performance, and possess multiple porosities and structures. In general, the hierarchical pore sizes are organized by bimodalities (micro-meso, meso-macro, and micro-macro) or even trimodalities (micro-meso-macro, meso-meso-macro) [84]. Attribute to these special structures, hierarchically porous materials possess superior properties including high surface area, low density, easy transformation, flexible chemical compositions and hierarchical porosity and structure. These characterizations are favourable for numerous applications and have been widely applied in energy storage and conversion, catalysis, photocatalysis, adsorption, separation, gas sensing, and biomedicine etc. [85]. Amongst them, nanomaterials with hollow structure have attracted much attention, and possess tunable morphology and structure. Hollow silica materials as easily available, abundant and cheap materials have unique properties, e.g., large specific surface areas, large capacity, low toxicity, superior thermal and mechanical stability, low density and high biocompatibility. These properties endow tremendous applications in drug delivery, various catalysis, electronic devices, bioimaging, energy-storage etc. Our group [86] proposed a modified immersion method to obtain highly dispersed molybdenum (VI) that incorporated hollow mesoporous silica catalyst. Benefiting from the modified immersion method and the special hierarchical structure, the active sites were introduced into shell and the active metal species could be isolated effectively (Figure 4a). In this way, highly dispersed molybdenum species were obtained. Meanwhile, the hollow interior and the shorter pore channels also contributed to the easy transfer of reactants and products in and out of the supports with less transformation blockage. Thanks to the properties of catalysts, such materials displayed high TON values. Kuwahara and his workers [87] presented a one-pot strategy of preparing yolk-shell MoO$_x$-SiO$_2$ nanostructured composites organized by MoO$_x$ NPs cores and porous hollow

silica spheres (Figure 4b,c), which were constructed by a self-assembly approach. Herein, poly(acrylic acid) was used as an organic template and dodecyltrimethoxysilane acted as a pore-directing agent (Figure 4d). The as-prepared yolk-shell MoO$_x$-SiO$_2$ composites showed promising catalytic stability in the liquid-phase alkenes epoxidation with TBHP as oxidants. The high reusability was assumed to result from the permeable silica shell, which made it a prominent heterogeneous catalyst.
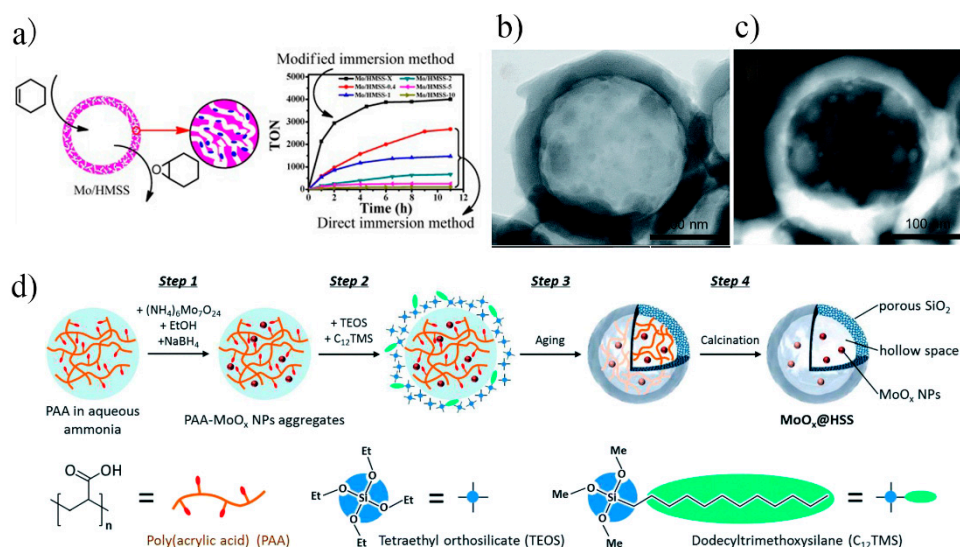

Figure 4. (**a**) Epoxidation process (left) and turnover number (TON) (right). Reproduced with permission from reference [86]. Elsevier (2017). (**b**) Scanning transmission electron microscope (STEM) image of MoO$_x$@HSS-2; (**c**) high-angle annular dark-field imaging STEM (HAADF-STEM) image of MoO$_x$@HSS-2; (**d**) Schematic illustration of the preparation process of MoO$_x$@HSS. Reproduced with permission from reference [87]. Royal Society of Chemistry (2017).

3.7. Graphene-Based Molybdenum-Containing Catalysts

Graphene oxide (GO) has been widely studied as an efficient support for heterogeneous catalytic reactions, which have oxygen-containing functional groups, superior mechanical strength as well as considerable specific surface area. Masteri-Farahani et al. [88] used carboxylic acid ligands to functionalize the surfaces of GO and rGO and then coordinated with bis(acetylacetonato)dioxomolybdenum (VI) (Figure 5a). The resulting catalysts acted as desired molybdenum-based catalysts in epoxidation reactions. High turnover frequencies (TOFs) and good selectivity (100%) were observed from both of the catalysts in the epoxidation process (Figure 5b,c). Furthermore, the catalyst using reduced graphene oxide as support exhibited better catalytic activity benefiting from the stronger hydrophobic nature, which could make easy access of the olefin to the catalytic active sites. Our group [89] demonstrated a novel mesoporous MoO$_2$ composite supported on graphene oxide (m-MoO$_2$/GO) and certified as a more efficient epoxidation catalyst than pure mesoporous MoO$_2$ (m-MoO$_2$). During the epoxidation reaction, the conversion and selectivity for cyclooctene were both above 99% after reacting for 6 h. The mesoporous structure in m-MoO$_2$/GO deriving from SiO$_2$ nanospheres resulted in better catalytic performance for long chain olefins or large ring size: the conversion of methyl oleate can be as high as 82%. Such a robust catalyst was easily reused with no obvious loss of catalytic activity after recycling for 5 runs.
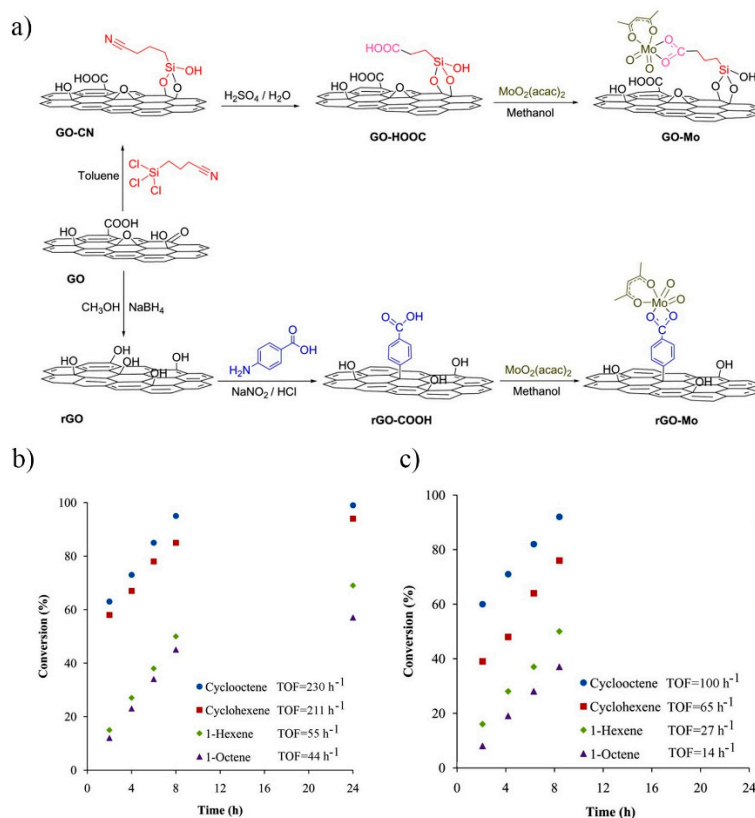
Figure 5. (**a**) Synthetic strategy of GO-Mo and rGO-Mo catalysts; (**b**) alkenes epoxidation procedure with rGO-Mo; (**c**) alkenes epoxidation procedure with GO-Mo. Reproduced with permission from reference [88]. Elsevier (2018).

3.8. Photocatalyzed Epoxidation Catalysts

Due to the severe global energy problems and the consumption of fossil fuels, more attention has been paid to environmental and clean energy. As a renewable and inexhaustible energy, solar energy, has attracted a lot of scientists' interest. This energy has been applied in overall water splitting and degradation of organics. Nowadays, this energy has started to be utilized in organic reactions, such as epoxidation. Martínez et al. [90] anchored dichloro-dioxo-[4,4-dicarboxylato-2,2-bipyridine]-Mo(VI) complexes on different mesoporous TiO_2 materials (Figure 6a). These catalysts were presented as efficient and durable catalysts for photo-epoxidation of alkenes under ultraviolet-visible (UV-vis) light and using molecular oxygen as oxidant (Figure 6b). The catalytic activity was considered to be relevant to the –OH density on the surface of titania which facilitated the high dispersion of Mo(VI) complex and promoted the catalytic properties. Higher content and even dispersion of the grafted $Mo^{(VI)}Cl_2O_2Bipy$ complex could be obtained from the mesoporous TiO_2 produced under supercritical CO_2 conditions. This kind of mesoporous TiO_2 support was proved to own the most suitable structures and was considered the most efficient support for the formation of epoxides compared with other TiO_2 discussed in this work. Remarkably, these catalysts showed good stability even after a long-term photo-oxidation process. Our group [91] supported Schiff (Mo) base complex on graphene oxide sheets and subsequently combined with graphitic carbon nitride (g-C_3N_4) to endow its photoactivity (Figure 6c). The photocatalytic activity of epoxidation was investigated under simulated sunlight (AM 1.5) with different olefin substrates. GO and the metal active sites were confirmed to efficiently accelerate electron transformation, which led to superior catalytic performance (Figure 6d).
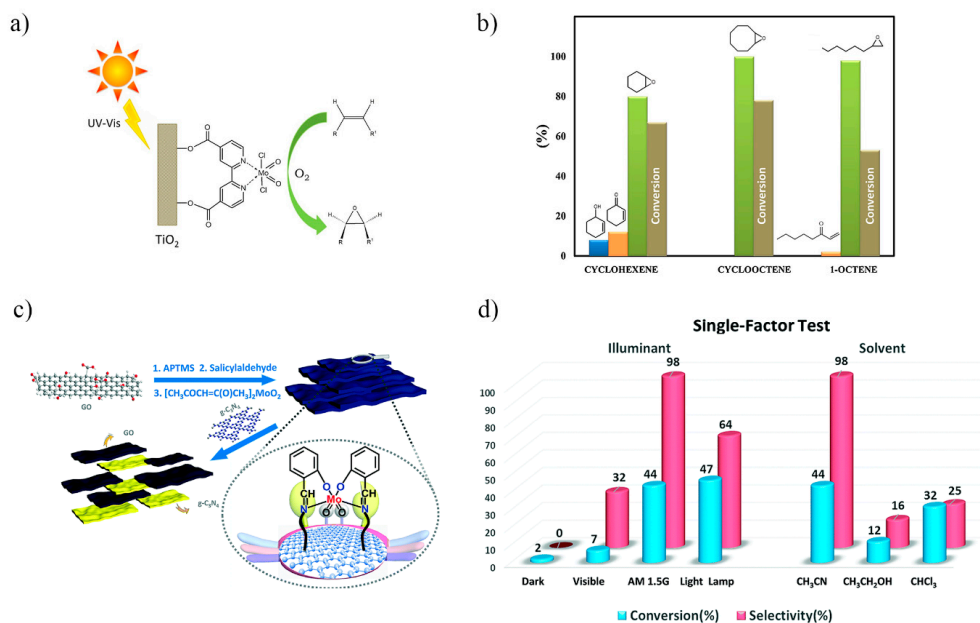
Figure 6. (**a**) Proposed photo-epoxidation catalyzed by dichloro dioxo-(4,4′-dicarboxylato-2,2′-bipyridine) molybdenum (VI) grafted on mesoporous TiO_2; (**b**) selectivity and conversion values for the photo-oxidation of different alkenes catalyzed by $Mo^{(VI)}Cl_2O_2Bipy/TiO_2(SC-150)$ after reacting for 35 h. Reproduced with permission from reference [90]. Elsevier (2016). (**c**) Synthetic route to prepare Mo-GO/g-C_3N_4 composite; (**d**) photocatalytic performance of Mo-GO/g-C_3N_4 during cyclooctene epoxidation assessed using different illuminants [a] and solvents [b]. [a] Reaction conditions: cyclooctene (10 mmol), CH_3CN (10 mL, solvent), chlorobenzene (5 mmol), catalyst (10 mg) and O_2. The mixture was continuously stirred under different illuminants for 6 h. [b] Reaction conditions: cyclooctene (10 mmol), solvent (10 mL), chlorobenzene (5 mmol), catalyst (10 mg) and O_2. The mixture was continuously stirred under a Xe lamp (300 W) with an AM 1.5 G filter for 6 h. Reproduced with permission from reference [91]. Royal Society of Chemistry (2018).

3.9. Others

Besides the aforementioned supports, many other materials are also used as supports to design epoxidation catalysts. Clay minerals, which present various superior properties including high surface area, large reservation, and cheap price etc., have been widely used in many scientific applications. These materials are composed of octahedral and tetrahedral silica units containing pores and –OH groups which are outstanding candidates to immobilize active complexes. Golmohamadpour et al. [30] prepared a sepiolite-type molybdenum catalyst by using 3-(tri-methoxysilyl)propylamine functionalized surface of sepiolite clay mineral to immobilize $MoO_2(acac)_2$. This catalyst was later applied in the epoxidation of *cis*-cyclooctene with high catalytic activity even in a large-scale process. Thus, this material was considered as a convincing candidate for epoxidation in both research and industrial applications. Mirzaee et al. [92] used boehmite (γ-AlOOH) nanoparticles to immobilize acetylacetonate complexes of vanadium and molybdenum and applied in *cis*-cyclooctene and other alkenes. 3-(trimethoxysilyl) propylchloride and 3-(trimethoxysilyl) propylamine were used to covalently functionalize boehmite nanoparticles, and the functionalized nanoparticles were utilized to immobilize bis-acetylacetonato-di-oxo molybdenum complexes subsequently. Metal oxides can also be used as efficient supports. Mirzaee et al. [93] utilized 3-(trimethoxysilyl)-propylamine and salicyl aldehyde to covalently functionalize hydrous zirconia nanoparticles and grafted bis-acetylacetonato-di-oxo-molybdenum (VI) and some molybdenum containing Keggin-type heteropolyacids on hydrous zirconia nanoparticles. The catalysts were successfully employed in epoxidation of *cis*-cyclooctene and other linear/non-linear alkenes. The results of epoxidation by using different types of heterogeneous molybdenum-based catalysts are summarized in Table 4.

Table 4. Results of epoxidation by using different types of heterogeneous molybdenum-based catalysts.

Entry	Catalyst	Olefin	Oxidant	Solvent	Temperature (°C)	Time (h)	TOF (h^{-1})	Conversion (%)	Selectivity (%)	Ref.
1	Mo-AMP-CuBTC	Cyclooctene	TBHP	Chloroform	60	2	521	99	>99	[58]
2	Mo-SIM	Cyclohexene	TBHP	Toluene	60	7	420	93	99	[59]
3	DVB-AA-Mo	Cyclooctene	TBHP	Chloroform	70	4	-	95	100	[81]
4	γ-Fe$_2$O$_3$@C@MoO$_3$	Cyclooctene	TBHP	Tetrachlormethane	80	6	-	97.3	99.9	[82]
5	MoO$_2$(sal-phz)(CH$_3$OH)/ Chloropropyltriethoxysilane coated Fe$_3$O$_4$	Cyclooctene	TBHP	1,2-dichloroethane	84	1	426	98	99	[83]
6	Mo/HMSS-X	Cyclohexene	TBHP	1,2-dichloroethane	80	4	893	87	99	[86]
7	MoO$_x$@HSS-2	Cyclooctene	TBHP	1,2-dichloroethane	80	8	-	80	99	[87]
8	GO-Mo	Cyclooctene	TBHP	Chloroform	Reflux	8	100	92	>99	[88]
9	rGO-Mo	Cyclooctene	TBHP	Chloroform	Reflux	8	230	95	>99	[88]
10	m-MoO$_2$/GO	Cyclooctene	TBHP	Chloroform	60	6	410	>99	>99	[89]
11	Mo$^{(VI)}$Cl$_2$O$_2$Bipy/TiO$_2$ SC-150	Cyclohexene	O$_2$ (UV-vis)	Acetonitrile	19	56	-	65.9	83	[90]
12	Mo-GO/g-C$_3$N$_4$	Cyclooctene	O$_2$ (AM 1.5G)	Acetonitrile	Ambient temperature	6	164	44	98	[91]
13	Sep-Am-MoO$_2$	Cyclooctene	TBHP	1,2-dichloroethane	84	1.25	74.16	98	100	[30]
14	Mo-Im-BNPs	Cyclooctene	TBHP	Tetrachlormethane	Reflux	1	126	97	97	[92]
15	Mo-A-BNPs	Cyclooctene	TBHP	Tetrachlormethane	Reflux	3.5	89	97	97	[92]
16	PMo-AFZNP	Cyclooctene	TBHP	1,2-dichloroethane	Reflux	2	49	98	100	[93]
17	SiMo-AFZNP	Cyclooctene	TBHP	1,2-dichloroethane	Reflux	3	35	98	100	[93]
18	Mo-AFZNP	Cyclooctene	TBHP	1,2-dichloroethane	Reflux	4.5	12	90	100	[93]
19	Mo-IFZNP	Cyclooctene	TBHP	1,2-dichloroethane	Reflux	1	119	91	100	[93]

4. Reaction Conditions and Mechanisms

4.1. Oxidizing Agents

The choice of oxidants is one of the most significant factors in improving the efficiency of the epoxidation reaction. In the industrial production of fine chemicals, organic peracids such as peracetic acid and *m*-chlorobenzoic acid are usually used as oxidants. However, the employment of organic peracids will produce massive acid waste. It is essential to develop new epoxidation methods by using safer and green oxidants with little waste. Nowadays, there has been a trend to develop catalysts with high atom economy and selectivity as well as broad substrate scope. O_2 is considered the ideal oxidant with the potential atom economy of 100% and its ubiquity. Some works even used air as an oxidant [34]. Unfortunately, molecular oxygen is unreactive toward olefins at recent. Furthermore, the reaction which requires high temperatures has an intrinsic possibility to totally oxidize alkenes to CO_2. Remarkably, hydrogen peroxide becomes an environmental and economic choice and has received a lot of attention. The advantages of H_2O_2 are that it contains high oxygen content, and has a cheap price and commercial availability [94]. Actually, hydrogen peroxide owns high atom economy (48%) and the only byproduct is just water [95]. However, a general and highly enantioselective epoxidation of unfunctionalized olefins with hydrogen peroxide has not been developed [96]. Another major oxidant group are alkyl peroxides [97], such as *tert*-butyl-hydroperoxide (TBHP) or cumene hydroperoxide (CHP). This kind of oxidants has good compatibility with alkenes, which provide high activity. However, either they form stoichiometric byproducts, which are commercialized or costly recycled. Thus, the choice of oxidant should continue to be considered in the future. Green and environmental oxidants (air, O_2, H_2O_2) should be used more and more, which drives us to develop relevant epoxidation technologies.

4.2. Solvents

During the epoxidation reaction, the reaction medium is also a significant factor. Organic solvents have been widely used as a common reaction medium in industrial production. The use of solvents facilitates to homogenize the liquid phase, which prevents the difficulty of mass-transfer to promote the access and interaction between reactants and catalysts. In fact, the role of solvents is complex. Many factors endow epoxidation activity, such as the aprotic/protic properties and polarity of solvents, the solubility of reactants and products in solvents, the diffusion and counter diffusion effects [98,99]. Furthermore, the interaction between the solvent and the oxidant or the intermediate species will dramatically affect the pathways of epoxidation. There is a competition between solvents and oxidants for coordinating to the active sites. Coordinating solvents (alcohols, ethers, etc.) will form complexes with the catalyst and hinder the formation of the catalyst-hydroperoxide complex [100]. Thus, the rate and selectivity of epoxidation will be low. In conclusion, many factors should be considered to choose an optimal solvent.

Due to toxicological and environmental pollution problems, volatile solvents are limited to applications in pharmaceutical and chemical industries. Recently, solvent-free epoxidation has attracted numerous attentions [101,102]. As is known to all, water is highly cheap, safe, sustainable and environmentally benign. However, few reports have efficiently used water as a successful reaction medium resulting from low solubility of substrates and the rashly decomposition of active species in water. Currently, these shortcomings have been resolved by synthesis of catalysts with specific properties [103]. Rezaeifard at al. [104] studied a Keplerate {Mo$_{132}$} nanoball, $[(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ and applied it in the aerobic epoxidation of olefins "on water" at ambient temperature and pressure in the absence of reducing agent or radical initiators (Figure 7a). This catalyst showed high yield and selectivity as well as stability (Figure 7b). The discrete single-molecular clusters were considered to contribute the high activity, which was generated in aqueous solution benefiting from the good dispersity of {Mo$_{132}$}-type cluster. In order to further confirm the reactivity, {Mo$_{132}$} was replaced by simple salts of Mo(VI), such as MoO_3, $Na_2MoO_4 \cdot 4H_2O$ and

$(NH_4)_6MO_7O_{24} \cdot 4H_2O$, and no oxidation product was found even after 24 h reaction (Figure 7c). Owing to the flexibility of steric or electronic characterizations of Schiff bases through the adjustments of corresponding aldehyde and amine contents, Schiff bases with different functions have been obtained. Cindrić et al. [105] constructed molybdenum (VI) complexes coordinating with ONO or ONS ligands and utilized in epoxidation of alkenes without organic solvents (Figure 7d). Furthermore, the synthesis process was green as well, presenting first time liquid-assisted mechanosynthesis. Distorted octahedral Mo(VI) coordination by ONO donor atoms from a dianionic tridentate Schiff-base ligand was observed via crystal structure analysis of mononuclear complexes. In virtue of the *trans* effect of the oxido oxygen atom, Mo-O(MeOH) was the longest bond distance within the Mo coordination sphere and was considered to be the important factor to contribute maximum reactivity. Zare et al. [106] anchored a molybdenum (VI)-oxodiperoxo complex which contained an oxazine ligand $(MoO(O_2)_2(phox))$ onto chloro-functionalized SBA-15 by covalent attachment. The covalent bonding was generated between the chloropropyl group from the internal surface of the pores and the nitrogen atom from oxazine ligand (Figure 7e). $[MoO(O_2)_2(phox)]$/SBA-15 was applied in alkenes epoxidation as a heterogeneous catalyst, which showed good catalytic activity in accordance with homogeneous catalyst $[MoO(O_2)_2(phox)]$ without the use of solvents. Moreover, the catalysts displayed good stability that its recyclability was maintained the same even after nine cycles.
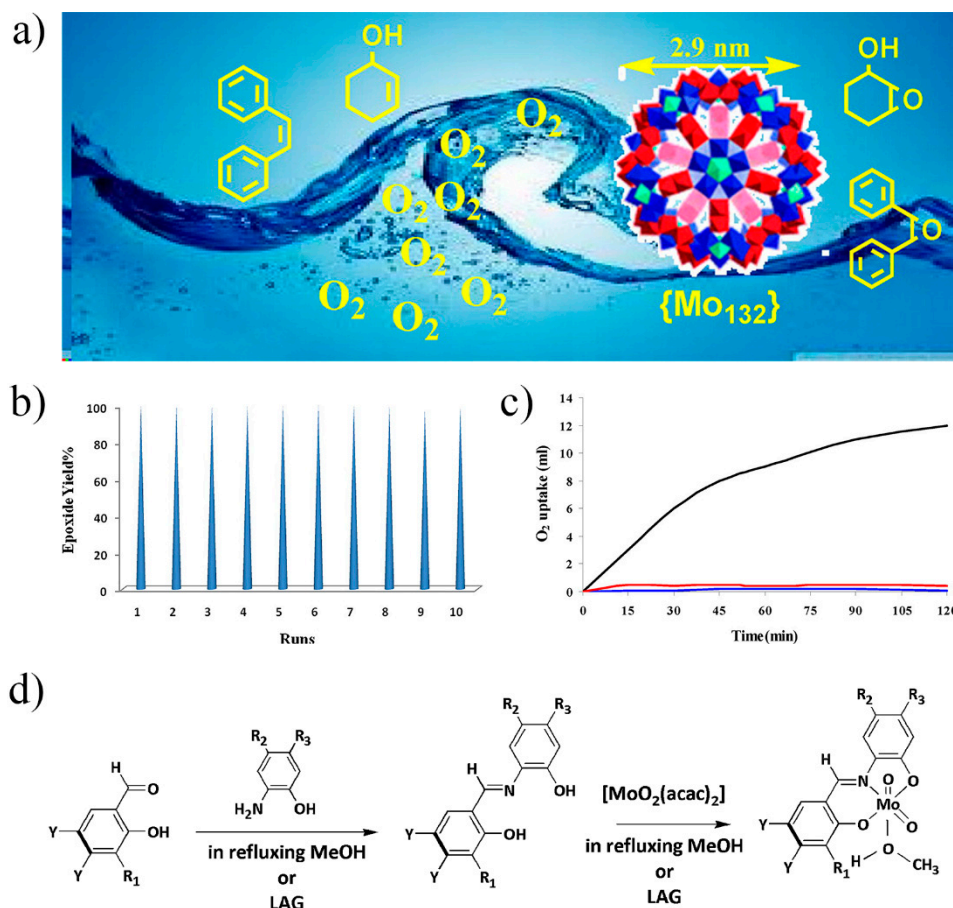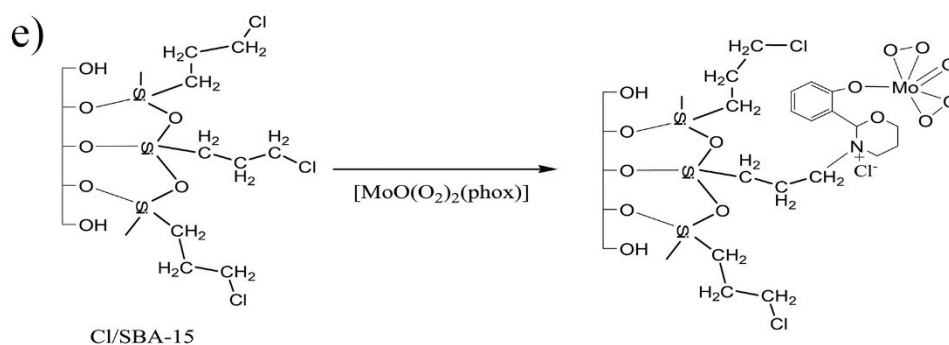

Figure 7. *Cont.*

Figure 7. (**a**) Epoxidation of alkenes in water with {Mo$_{132}$} nanoball; (**b**) time course of oxygen uptake by cyclooctene in the presence of {Mo$_{132}$} (black line), (NH$_4$)$_6$Mo$_7$O$_{24}$·6H$_2$O (blue line), and NaMoO$_4$·2H$_2$O (red line) in water; (**c**) recycling of the catalytic system for aerobic epoxidation of cyclooctene in water. Reproduced with permission from reference [104]. ACS Publications (2013). (**d**) Two synthetic strategies of molybdenum (VI) complexes and ligands in epoxidation catalysts. Reproduced with permission from reference [105]. The Royal Society of Chemistry (2017). (**e**) Immobilization of the [MoO(O$_2$)$_2$(phox)] complex on Cl/SBA-15 mesoporous silica. Reproduced with permission from reference [106]. Elsevier (2017).

4.3. Mechanism

In the 1970s, two general mechanisms of Mo-based catalyzed epoxidation of olefins were proposed by Mimoun (Figure 8a) and Sharpless's groups (Figure 8b). Mimoun [107] put forward a multi-step mechanism, where alkene was inserted into the metal-peroxo bond and then it was coordinated with the metal center. A five-membered metallacycle was assumed to act as an intermediate. Sharpless [17,18] proposed a mechanism which did not include a direct interaction between the metal and the olefin. This suggestion considered that direct interaction between the alkene and one of the peroxide oxygen atoms occurred and a spiro-like transition state was formed. Most of the mechanism studies have been based on these two theories. Thiel et al. [108] presented a DFT study which involved TBHP as an oxidant for molybdenum precursors and gained results highly in accord with Sharpless' proposal. Nevertheless, the practical epoxidation reactions seemed to be more complex than originally considered [109]. Lewis acidity of metal centers has been considered in the mechanism. A general mechanism which is widely recognized is depicted in Figure 8c [93]. The first stage included the transfer of the oxidant (TBHP, in this case), and the hydroxy proton was coordinated with a terminal oxygen atom from molybdenum sites. This result led to the interaction between the *tert*-butylperoxide anion and the Lewis acidic metal sites. Afterwards, the metal oxygen bond from the coordinated peroxide electrophile anion was inserted by the alkenes which acted as nucleophile. The above mechanism is widely accepted and can easily illustrate the reason for more efficient catalytic activity of the electron-rich alkenes (cyclic alkenes with higher electron density and nucleophilicity) compared with the electron-poor ones (terminal alkenes) [88]. Then the epoxides were produced, and at the same time the *tert*-butylperoxide anion transferred to the *tert*-butoxide anion. Finally, the peroxides were released and the epoxidation progress was driven by a reborn *tert*-butylperoxide to take the place of tertbutoxide anion. Kinetic study of the epoxidation reaction is also discussed, and some researchers have certified the reaction rates of epoxidation to be a first-order reaction depending on the reactants concentrations [110].
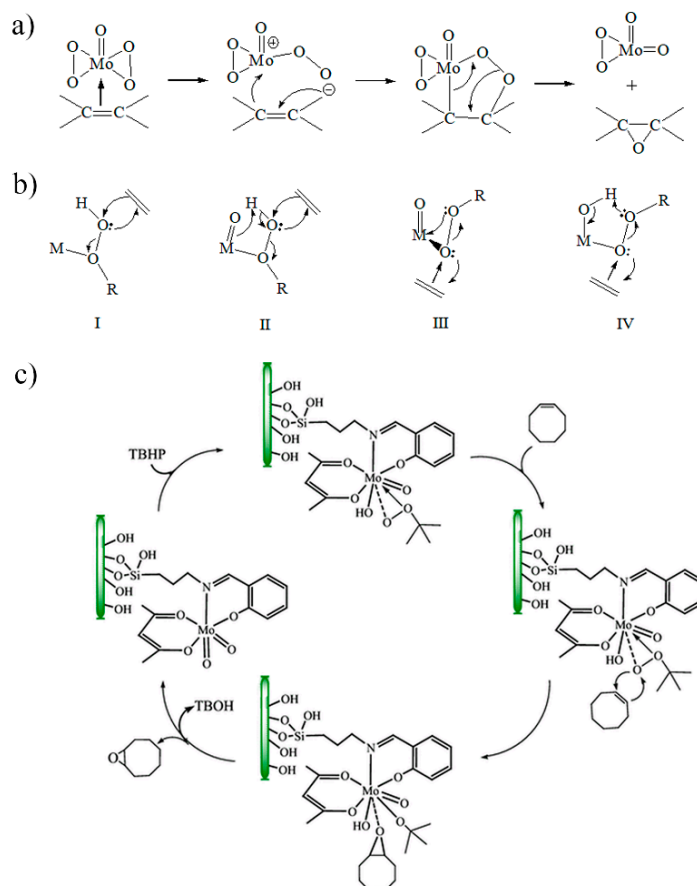
Figure 8. (**a**) Mechanism for epoxidation of alkenes proposed by Mimoun et al. Reproduced with permission from reference [107]. Pergamon (1970); (**b**) Epoxidation mechanisms involving coordinated alkyl hydroperoxide. Reproduced with permission from reference [17]. ACS Publications (1977); (**c**) Proposed mechanism for alkenes epoxidation with TBHP using molybdenum-based catalysts. Reproduced with permission from reference [93]. Springer (2018).

5. Summary

In this review we have discussed the development in molybdenum-based catalyzed epoxidation of alkenes. In conclusion, tremendous progress has been achieved, and most epoxidation reactions of alkene substrates have acquired excellent stereoselectivity and yield. A diversity of strategies has been used for preparing efficient catalysts. According to sustainable and environmentally friendly principles, photo-catalyzed epoxidation and solvent-free epoxidation have attracted scientists, and some progress has been achieved in these fields. However, there are still large challenges in obtaining high selectivity and yield for photo-catalyzed and solvent-free epoxidation reactions. On the other side, to improve the selectivity and yields for terminal and long-chain alkenes still needs to be solved. In order to fulfill the ultimate aim by which they can be used in industrial production, much work, such as enhancing the turn-over frequencies, still needs to be done in the future.

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