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Review

Polyoxometalate-based heterogeneous catalysts for liquid phase selective oxidations: Comparison of different strategies

O.A. Kholdeeva *, N.V. Maksimchuk, G.M. Maksimov

Boreskov Institute of Catalysis, Lavrentieva 5, Novosibirsk, Russia

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ABSTRACT

Recent achievements in the preparation of polyoxometalate-based heterogeneous catalysts using different immobilization techniques, such as embedding into a silica matrix by sol–gel method, irreversible adsorption on active carbon, electrostatic attachment to NH_2-modified mesoporous silica, and incorporation within nanocages of the metal-organic framework MIL-101 are surveyed. The catalyst characterization is reported, and their catalytic performances in liquid phase selective oxidations are compared, with special attention being paid to the questions of catalyst stability to leaching, nature of catalysis and catalytic properties after recycling. The scope and limitations of the POM-based heterogeneous catalysts are discussed.

Contents

1. Introduction

The design of active, selective, easily recyclable and true heterogeneous catalysts is a challenging goal of liquid phase oxidation catalysis. Early transition-metal oxide anionic clusters (polyoxometalates or POMs for short) have received increasing attention as oxidation catalysts due to unique ensemble of properties, including inorganic nature, metal oxide-like structure, thermodynamic stability to oxidation, thermal and hydrolytic stability, tunable acidities, redox potentials, solubilities, etc. [1–5]. The apparent structural analogy of POMs and metal oxide surfaces allows considering POMs as discrete, soluble fragments of extended metal oxide lattices which can be comprehensively investigated at the atomic level. Transition-metal-monosubstituted POMs (M-POMs) comprise an active center M isolated in the tungsten oxide matrix and strongly bound through M–O–W bridges, which prevents it from hydrolysis and oligomerization and allows considering M-POMs as perspective building blocks for

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* Corresponding author.
E-mail address: khold@catalysis.nsk.su (O.A. Kholdeeva).

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designing single site heterogeneous catalysts [6,7]. The development of strategies for converting soluble POMs to solid materials containing spatially well-separated and firmly attached to surface POM molecules is of primary importance, and many research groups are involved in this activity [1–5,8–13]. Such materials are expected to combine advantages of molecular complexes and reusable solids; furthermore, new activities and selectivities may arise due to confinement effects.

In this short review paper, we survey our recent achievements in the preparation of POM-based heterogeneous catalysts using different immobilization techniques, such as embedding POM into a silica matrix using sol–gel method [14], irreversible adsorption on active carbon, electrostatic attachment to NH_2-modified mesoporous silica [11,15], and incorporation within nanocages of the coordination polymer MIL-101 [16]. We report on the physicochemical characterization of the catalysts and compare the results of their application in the liquid phase selective oxidations of alkenes with the green oxidants—O_2 and H_2O_2. Special attention is paid to analyze the confinement effects and frequently success-limiting issues of catalyst activity and selectivity after recycling, stability to leaching and nature of catalysis. The scope and limitations of the POM-based heterogeneous catalysts are discussed

2. Experimental

2.1. Reactants

Hydrogen peroxide was used as 30 wt.% solution in water; its concentration was determined iodometrically prior to use. α-Pinene containing 98% of α-pinene and 2% of β-pinene was obtained by vacuum rectification of gum turpentine. Isobutyraldehyde (IBA, Aldrich) was distilled prior to use. All other reactants were obtained commercially and used without further purification.

2.2. Catalysts preparation

Co-substituted polyoxometalates (Co-POM), $Na_5PW_{11}Co(H_2O)O_{39}$ and $[Bu_4N]_4H[PW_{11}Co(H_2O)O_{39}]$, were synthesized following the procedures reported in [11]. Ti-substituted polyoxometalates (Ti-POM), $H_5PW_{11}TiO_{40}$ and $NaH_4PW_{11}TiO_{40}$, were prepared as described in [17,18], respectively; $H_5PW_{11}ZrO_{40}$ (Zr-POM) was prepared analogously to $H_5PW_{11}TiO_{40}$ [19]. Heteropolyacid $H_3PW_{12}O_{40}{\cdot}6H_2O$ (PW_{12}) was a commercial product and was purified by extraction with diethyl ether. The purity of the POMs synthesized was confirmed by FT-IR and ^{31}P NMR spectroscopic techniques.

Carbon supports, mesoporous Sibunit [20] (S 670 m^2/g) and microporous L2701 (S 1240 m^2/g), were obtained commercially. Mesostructured silicates SBA-15 [21] and MCF [22] were prepared according to the published protocols. NH_2-functionalized supports were prepared as described in [11,15]. MIL-101 was synthesized by a hydrothermal reaction of terephthalic acid with $Cr(NO_3)_3{\cdot}9H_2O$, HF and H_2O following the procedure reported by Ferey et al. [23].

POM/SiO_2 composite materials were prepared by the sol–gel method using tetramethoxysilane as the silica precursor and 10 wt.% $H_5PW_{11}TiO_{40}$ or $Na_5PW_{11}CoO_{39}$ via a two step procedure described earlier [11,14]. Electrostatic attachment to NH_2-modified silica was carried out at room temperature using acid tetrabutylammonium (TBA) salts of POMs dissolved in MeCN [11,15]. Adsorption of POMs on carbons was carried out from 10 wt.% aqueous solutions at 25 °C for 3 days. The resulting materials were separated by centrifugation, washed with a large amount of hot water and dried at 150 °C. POM/MIL-101 hybrid materials were prepared by adsorption of POMs from MeCN ($NaH_4PW_{11}TiO_{40}$ and $[Bu_4N]_4HPW_{11}CoO_{39}$) or H_2O ($H_3PW_{12}O_{40}$) at 25 °C for 3 h. The completion of the adsorption process was checked by UV–vis as described earlier [16].

2.3. Catalyst characterization

Textural characteristics of the catalysts and of the supports were determined from nitrogen adsorption isotherms. The structure of the SBA-15 and MIL-101 materials was confirmed by XRD. All solid catalysts were characterized by elemental analysis, FT-IR and DR-UV spectroscopic techniques.

2.4. Instrumentation

GC analyses were performed using a gas chromatograph "Tsvet-500" equipped with a flame ionization detector and a quartz capillary column (30 m × 0.25 mm) Agilent DB-5MS. GC–MS analyses were carried out using a gas chromatograph Agilent 6890 (quartz capillary column 30 m × 0.25 mm/HP-5 ms) equipped with a quadrupole mass-selective detector Agilent MSD 5973. Nitrogen adsorption at 77 K was studied using an ASAP-2020 instrument. XRD measurements were performed on a high-precision X-ray diffractometer Philips APD1700 using cupric radiation ($CuK_{\alpha 1;2}$ 1.54060 Å; 1.54439 Å). FT-IR spectra were recorded using pellets containing 2 mg of a sample and 500 mg of KBr on a BOMEM-MB-102 spectrometer in the 250–4000 cm^{-1} range. DRS-UV measurements were performed on a Shimadzu UV-VIS 2501PC spectrophotometer. UV–vis spectra in solution were recorded using an Agilent 8453 spectrophotometer (cell thickness l = 10 mm). ^{31}P NMR spectra of POMs in H_2O or MeCN were recorded on Bruker Avance-400 spectrometer at operating frequency of 161.98 MHz, with a 5-kHz sweep width, 10-μs pulse width, and 30-s pulse delay. Spectra were referenced to 85% H_3PO_4 as external standard.

2.5. Catalytic oxidations

Catalytic experiments were carried out in thermostated glass vessels at 25–50 °C under vigorous stirring (500 rpm). Either O_2 (Co-POM) or H_2O_2 (Ti-POM, Zr-POM and PW_{12}) were used as oxidants. Before reuse, the catalyst was filtered off, washed with acetonitrile and methanol, dried in air at room temperature overnight or evacuated at 130 °C for 2 h (α-pinene/IBA co-oxidation). The reaction products were identified by GC–MS and quantified by GC using an internal standard.

3. Results and discussion

3.1. Embedding POM into silica by sol–gel method

A promising approach to heterogenize POM is occluding it into an inert matrix during the matrix synthesis. Izumi was the first who suggested inserting a catalytically active POM into silica by means of sol–gel method [24]. Mrowiec-Bialon et al. developed this method further [25]. Composite materials containing 4 and 9 wt.% of $Na_5PW_{11}Co(H_2O)O_{39}$ and $H_5PW_{11}TiO_{40}$, respectively, have been prepared following similar procedures [11,14]. The N_2 adsorption measurements showed that the Co-POM/SiO_2 composite was microporous while Ti-POM/SiO_2 was nonporous. A restriction of moving POM within solid matrix is crucial to prevent POM leaching into solution. DR-UV–vis (Fig. 1) and IR [11,14] spectra of the composite materials and bulk POMs revealed the same principle bands, which confirmed the retention of the POM structure after immobilization.

The catalytic properties of Ti-POM/SiO_2 and Co-POM/SiO_2 were assessed in the selective oxidation of several organic substrates,

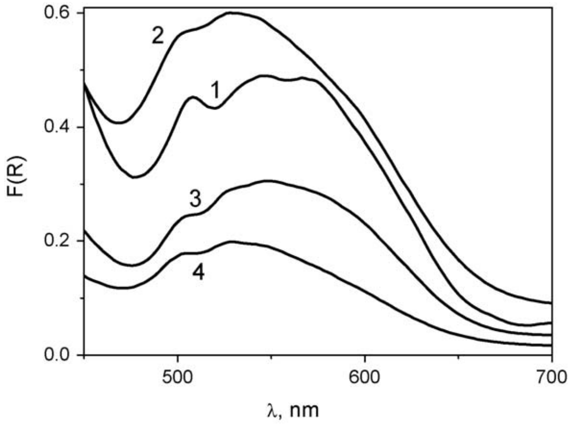

Fig. 1. DR-UV–vis spectra of bulk Co-POM (1), Co-POM/SiO_2 (2), Co-POM/NH_2–MCF (3) and Co-POM/NH_2–SiO_2 (4).

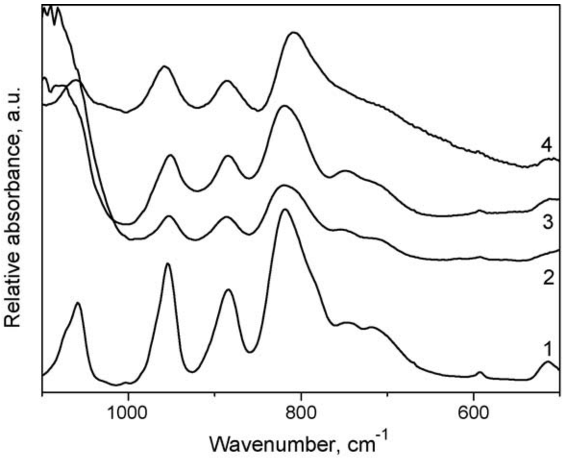

Fig. 2. FT-IR spectra of bulk Co-POM (1) and Co-POM supported on NH_2–X (X = SBA-15 (2) and MSF (3)) and carbon L2701 (4). The spectra of the supports are subtracted.

including the natural terpene hydrocarbon, α-pinene [5,14,15]. H_2O_2 and O_2 were used as oxidants for the Ti- and Co-containing catalysts, respectively. Both reactions were found to produce allylic oxidation products, verbenol and verbenone, useful intermediates in the production of many fine chemicals.

The selectivity to verbenol/verbenone depends strongly on the alkene conversion and attains 78–85% at 17–20% conversion [14,15]. At a higher conversion, the selectivity has a tendency to decrease due to overoxidation processes. The catalytic activity of the silica-embedded POMs expressed in TOF values was superior to the activity of the corresponding homogeneous Co-POM. Both Ti- and Co-containing composite materials were used repeatedly without loss of the activity and selectivity. No leaching of the active species occurred according to the elemental analysis data, and hot catalyst filtration tests proved true heterogeneous nature of catalysis [14,15].

3.2. Electrostatic attachment to NH_2-modified mesoporous silica

Electrostatic attachment to a support modified with ligands bearing cationic groups has been widely used for POM binding *via* anion exchange or ion paring [10,13,26–28]. Silica surface can be easily functionalized by ligands containing quaternary ammonium cations or amine groups. Using an acid, NH_2–silica can be transformed to a cationic form, and then the counter anion is exchanged with a polyoxoanion. Yet, a one-step procedure for POM binding has been elaborated using a protonated form of POM—an acid salt or heteropolyacid [11,15]:

$X\text{–}NH_2 + \text{H-POM} = X\text{–}NH_3^{+}\text{POM}^{-}$

To support Co-POM, different kinds of mesoporous silica, including amorphous SiO_2 and mesostructured SBA-15 and MCF materials, were used. The Co-POM loading depended on the surface concentration of NH_2 groups and varied in the range of 15–32 wt.%.

The DRS-UV–vis and FT-IR studies were performed to assess whether the Co-POM structure is retained in the supported samples or not. The IR spectra of the supported Co-POM samples are very similar after subtraction of the peaks due to X–NH_2 (Fig. 2). The spectra clearly exhibit the principal stretching modes of the Keggin Co-POM unit (956, 888, 818, 752, 720 cm^{-1}) consistent with maintenance of the POM structure after the supporting procedure. In turn, the DR-UV–vis spectra of the supported Co-POM (Fig. 1) are quite similar and resemble the spectrum of $Na_5PW_{11}Co(H_2O)O_{39}$ in water [11 and references therein]. Some shifts of the d–d bands position can be due to partial removal and/or replacement of water for MeCN in the coordination sphere of Co(II) [11]. Importantly, these spectra differ from those published for Co-POMs datively linked to NH_2–silica [8]. Indeed, no peaks or shoulders were observed in the range of 628–640 nm, indicating no formation of dative bonds between NH_2 groups and cobalt and thus pointing to the electrostatic character of binding between Co-POM and the support. Another argument in favor of the coulombic nature of the interaction between Co-POM and NH_3^+-groups of the silica supports is the fact that the POM can be removed from the solid matrix by extraction with a 1 M solution of $TBAClO_4$ in MeCN [15].

Two model reactions have been chosen to study catalytic behavior of the supported Co-POM–α-pinene oxidation with O_2 leading to the formation of the allylic oxidation products and α-pinene co-oxidation with IBA producing epoxide and isobutyric acid.

Importantly, the activity of the supported Co-POM catalysts was comparable to the activity of homogeneous Co-POM. The nature of the support had a very little effect on the selectivity of α-pinene allylic oxidation. On the contrary, the selectivity of the epoxide formation could be improved significantly by increasing NH_2/POM ratio (Fig. 3), most likely, due to neutralization of the carboxylic acid product by amine groups present on the surface. As a result, the yield of α-pinene epoxide attained 94% over the Co-POM/NH_2–MCF catalyst.

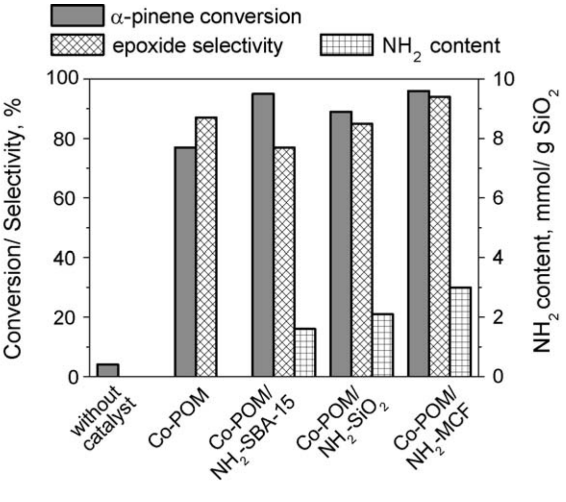

Fig. 3. α-Pinene and IBA co-oxidation over Co-POM/NH_2–silica catalysts. Reaction conditions: α-pinene, 0.1 mmol; O_2, 1 atm; IBA, 0.4 mmol; catalyst, 6×10^{-4} mmol Co; MeCN, 1 mL; 25 °C, 1 h.

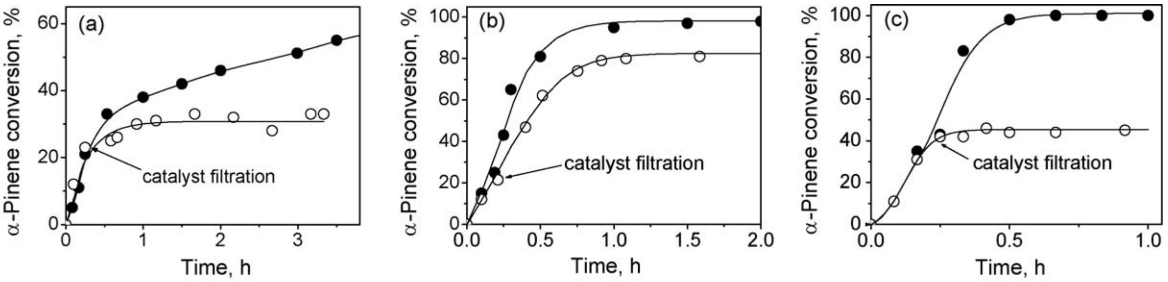

Fig. 4. Catalyst filtration experiments for (a) α-pinene oxidation with O_2 over 15% Co-POM/NH_2–SBA-15 (α-pinene, 0.1 mmol; O_2, 1 atm; catalyst, 6×10^{-4} mmol Co; MeCN, 1 mL; 25 °C) and for α-pinene/IBA co-oxidation over (b) 15% Co-POM/NH_2–SBA-15 and (c) 6.5% Co-POM/Sibunit (α-pinene, 0.1 mmol; IBA, 0.4 mmol; O_2, 1 atm; catalyst, $(5–6) \times 10^{-4}$ mmol Co; MeCN, 1 mL; 25 °C). (●)—Without filtration, (○)—with filtration.

The Sheldon's test [29] revealed that catalysis of α-pinene oxidation by molecular oxygen over the electrostatically immobilized Co-POM has true heterogeneous nature (Fig. 4a). The catalysts can be recycled several times without suffering a loss in the activity and selectivity. In contrast, the filtration test unambiguously showed that homogeneous catalysis contributes significantly into the α-pinene/IBA co-oxidation process due to Co-POM leaching into solution (Fig. 4b). Meanwhile, the catalytic activity can be kept constant during several catalytic cycles if catalyst regeneration via evacuation is performed to remove adsorbed isobutyric acid [15].

3.3. Irreversible adsorption on active carbon

Entrapping POMs inside pores of active carbon was also first pointed out by Izumi and Urabe [30]. In the present work, we accomplished immobilization of several redox active POMs on two commercial active carbons, microporous L2701 and mesoporous Sibunit. The interaction between POM and carbon appeared to be so strong that even after washing with hot ethanol or acetic acid the POM loading remained unchanged.

Retention of POM structure after adsorption on carbon was confirmed by FT-IR spectroscopy (an example is given in Fig. 2). Depending on the nature of POM and carbon, irreversible entrapment of 7–17 wt.% of POM occurred. The maximum Co-POM loading was twice higher for L2701 compared to Sibunit, but the catalytic performance of the Sibunit-supported catalyst was superior. Thus, in α-pinene/IBA co-oxidation, nearly 100% epoxide selectivity at 100% substrate conversion and 75% selectivity at only 12% conversion were attained after 1 h over 6.5% Co-POM/Sibunit and 12% Co-POM/L2701, respectively.

The Sibunit-supported Ti- and Zr-POM catalysts were fairly active in H_2O_2-based oxidations. The oxidation of α-pinene over 16% Zr-POM/C produced verbenol and verbenone with the selectivity of 43% at 40% substrate conversion after 4 h at 30 °C, while 13% Ti-POM/C gave 59% verbenol/-one selectivity at 32% conversion at the same conditions. Zr-POM/C catalyst was used repeatedly without loss of the activity and selectivity (Fig. 5a). It is worth of noting that catalysis over POM/C has true heterogeneous nature (Fig. 5b), even if highly polar products, such as carboxylic acids, form in the reaction (Fig. 4c). This strongly supports an irreversible character of POM sorption on the active carbon. However, the nature of POM binding to carbon is not understood at the moment. Catalyst treatment with 1 M $TBAClO_4$ did not allow recovering POM into MeCN solution, which might indicate that not only electrostatic interactions are responsible for keeping POM on the carbon support.

3.4. Incorporation within nanocages of the metal-organic framework MIL-101

In the past decade, metal-organic frameworks (MOFs) have attracted considerable attention due to a unique combination of properties, such as high surface area, open crystalline structures, tunable pore size and functionality, etc. [23,31–34]. All these allow considering MOFs as perspective catalytic materials and supports for immobilization of homogeneous catalysts [23,33,35–39]. In 2005, Ferey et al. reported the synthesis of the mesoporous chromium terephthalate coordination polymer MIL-101 which possesses a rigid zeotype crystal structure, extremely large surface area (up to 3900 m^2/g) and quasi-spherical cages of two modes (free internal diameters are close to 29 and 34 Å, while the cages

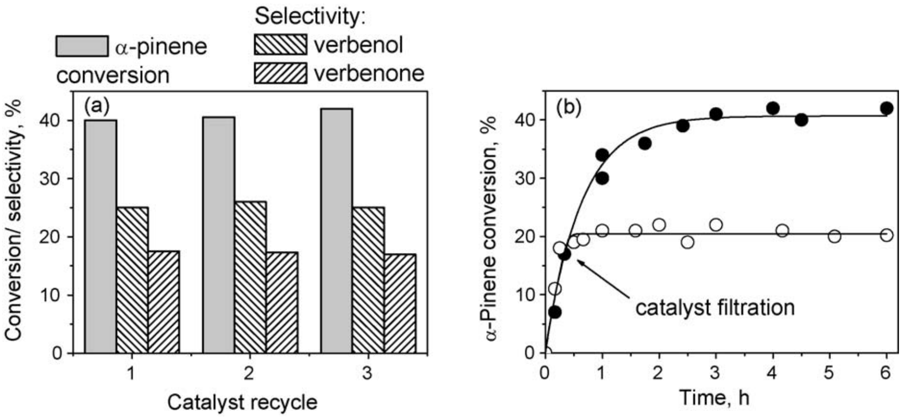

Fig. 5. (a) Recycling and (b) hot catalyst filtration experiments for α-pinene oxidation with H_2O_2 over 16% Zr-POM/Sibunit. Reaction conditions: α-pinene, 0.1 mmol; H_2O_2, 0.12 mmol; catalyst, 8×10^{-4} mmol Zr; MeCN, 1 mL; 30 °C, 4 h. (●)—Without filtration, (○)—with filtration.

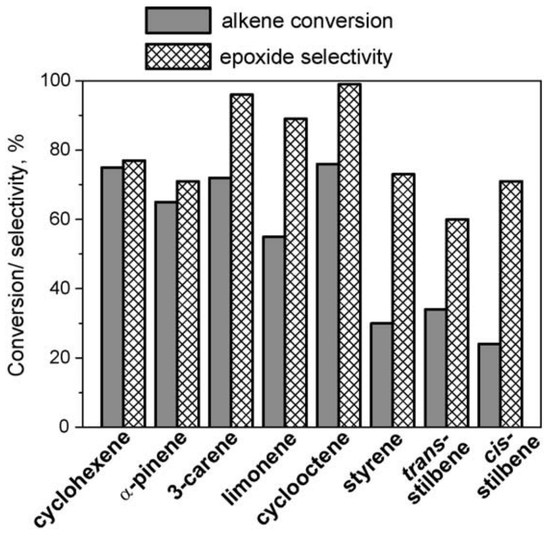

Fig. 6. Alkene epoxidation with H_2O_2 over 5% PW_{12}/MIL-101. Reaction conditions: alkene, 0.1 mmol; H_2O_2, 0.2 mmol; catalyst, 6×10^{-3} mmol W; MeCN, 1 mL; 50 °C; 3 h.

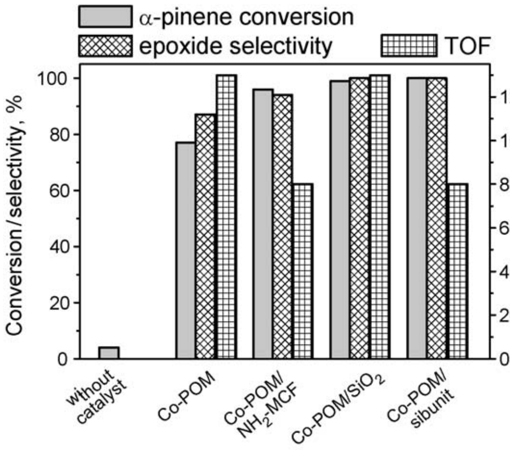

Fig. 8. α-Pinene and IBA co-oxidation over Co-POM supported catalysts. Reaction conditions: α-pinene, 0.1 mmol; O_2, 1 atm, IBA, 0.4 mmol; catalyst, 6×10^{-4} mmol Co; MeCN, 1 mL; 25 °C, 1 h.

are accessible through windows of *ca*. 12 and 16 Å) [23]. Importantly, this MOF is resistant to air, water, common solvents and thermal treatment (up to 320 °C) [23,33]. Ferey et al. estimated that *ca*. five Keggin polyanions can be incorporated within a large cage of MIL-101 [23]. However, we have recently shown that only one Keggin POM per nanocage (this corresponds to 7–10 wt.% of POM loading) is adsorbed irreversibly from MeCN or H_2O solutions [16]. Significantly, POM can be re-extracted from MIL-101 into MeCN by using a 1 M solution of $TBAClO_4$, thus pointing out an electrostatic character of POM binding to the MOF.

Ti- and Co-POMs incorporated within MIL-101 demonstrated fairly good catalytic activities and selectivities in α-pinene allylic oxidation with H_2O_2 and O_2, respectively [16]. A range of epoxides was obtained using H_2O_2 and commercial PW_{12} supported on MIL-101 (Fig. 6). In contrast to the homogeneous systems, the use of a higher H_2O_2/alkene molar ratio allowed increasing simultaneously both the alkene conversion and epoxide selectivity, which is quite unusual. Typically, an excess of alkene is employed to achieve a high selectivity of epoxidation because the selectivity tends to decrease with conversion due to consecutive epoxide ring opening and overoxidation processes [40]. We may suppose that the unusual behavior of PW_{12}/MIL-101, most likely, results from hydrophobicity of the organic linker and specific sorption properties of MIL-101 [41].

It has been established that all the MIL-supported POMs behave as true heterogeneous catalysts, do not suffer from POM leaching, can be recycled and used repeatedly without suffering a loss of the catalytic properties under mild reaction conditions. After immobilization and also after catalytic oxidations (50 °C, 1 atm O_2 or 0.2 M H_2O_2), the structure of both POM and MIL-101 remained unchanged as was verified by FT-IR technique [16]. Yet, the ^{31}P NMR MAS study showed that confinement of PW_{12} within MIL-101 allowed increasing resistance of the polyoxotungstate towards solvolytic destruction in the presence of an excess of H_2O_2 [42].

3.5. Comparison of different approaches

Finally, we would like to perform a comparison of different approaches for POM immobilization as applied to some specific oxidation reactions.

Fig. 7a shows the performances of different supported Ti-POM catalysts in the allylic oxidation of α-pinene with H_2O_2, while Fig. 7b represents the results acquired using supported Co-POM and dioxygen. One can see that the highest activity in both Ti-POM/H_2O_2 and Co-POM/O_2-based systems was observed for the composite POM/SiO_2 catalysts prepared by sol–gel techniques. It was suggested by Izumi [24] that POM is entrapped in the silica

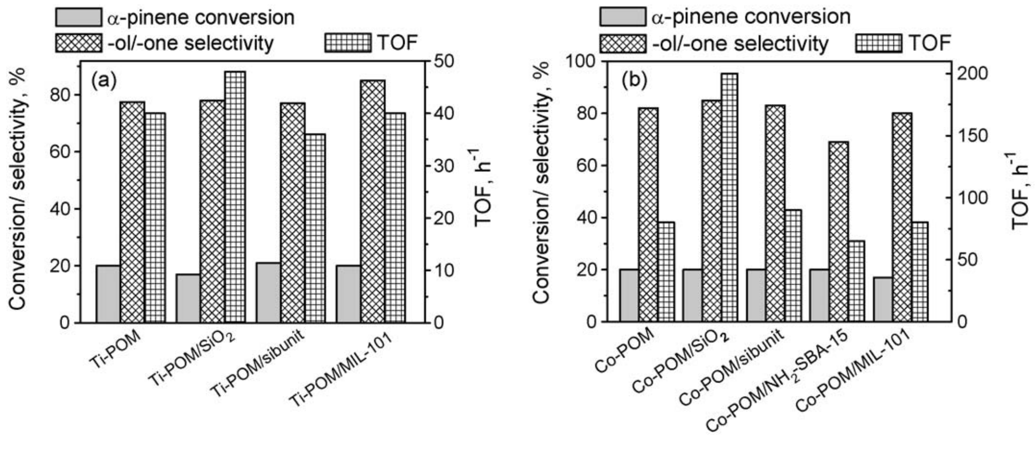

Fig. 7. α-Pinene oxidation to verbenol/verbenone over supported POM catalysts: (a) with H_2O_2 (Ti-POM, 30 °C) and (b) with O_2 (Co-POM, 50 °C). Reaction conditions: α-pinene, 0.1 mmol; O_2, 1 atm (or H_2O_2, 0.12 mmol); catalyst, 14 mg ((4–6) × 10^{-4} mmol Ti or Co); MeCN, 1 mL.

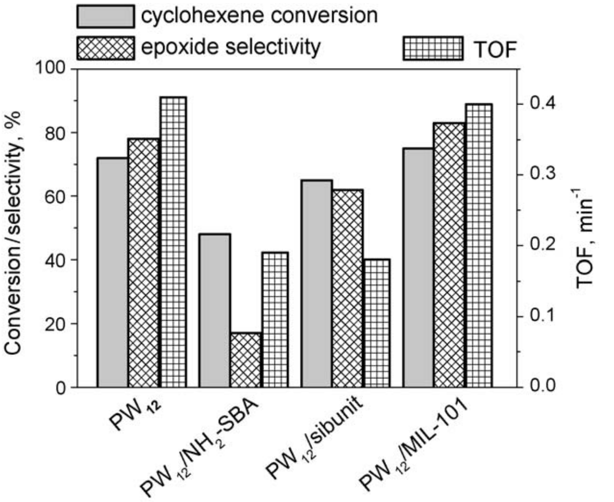

Fig. 9. Cyclohexene epoxidation with H_2O_2 over supported PW_{12} catalysts. Reaction conditions: cyclohexene, 0.1 mmol; H_2O_2, 0.2 mmol; catalyst, 6×10^{-3} mmol W; MeCN, 1 mL; 50 °C, 3 h.

network as a highly concentrated solution, which may account for the increased catalytic activity. The best selectivity (84%) to verbenol/verbenone was achieved using Ti-POM incorporated within MIL-101 (Fig. 7a).

The comparison of Co-POM catalysts in α-pinene/IBA co-oxidation is given in Fig. 8. One can see that almost quantitative yields of epoxide were attained using silica-embedded and carbon-entrapped Co-POM. Both the epoxide selectivity and the alkene conversion were superior to those acquired using homogeneous Co-POM catalyst. Despite the activity (TOF) of carbon-entrapped Co-POM was lower than that of the silica-embedded Co-POM, the former was the only catalyst among the supported Co-POMs, for which true heterogeneous catalysis has been revealed by the catalyst filtration test (Fig. 4c). Hence, POMs supported on activated carbon demonstrate advantages in terms of stability in the reactions which produce highly polar products, such as carboxylic acids.

Fig. 9 shows an evaluation of PW_{12} catalysts prepared by different immobilization techniques in cyclohexene oxidation with aqueous H_2O_2. One can see that PW_{12} supported on MIL-101 was the best catalyst in terms of both activity and epoxide selectivity. Furthermore, using PW_{12}/MIL-101 a higher alkene conversion and epoxide yield could be achieved compared to the corresponding homogeneous PW_{12} (Fig. 9). We suppose that zeotype structure of MIL-101 and hydrophobic nature of the linker may enhance the reaction selectivity by suppressing hydrolysis, overoxidation and polymerization processes. Yet, the acidity of heteropolyacids is reduced upon incorporation within MIL-101 nanocages via anion exchange. This may also lead to enhancing selectivity of the reactions which are accompanying by acid-catalyzed rearrangements of substrate and/or target product.

4. Conclusion

The elaborated POM-based heterogeneous catalysts demonstrate fairly good catalytic and recycling performance in selective alkene oxidations with H_2O_2 and O_2, behave as true heterogeneous catalysts and do not suffer from POM leaching if carboxylic acids are not the reaction products. The use of carbon as support allows preparation of POM/C catalysts stable towards POM leaching by carboxylic acids. By controlling the type of transition metal ions in the structure of POM as well as the nature and porous structure of the support, it is possible to accomplish highly selective catalytic oxidations. Some immobilization techniques offer benefits in terms of catalytic activity, selectivity and stability of POMs.

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