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Review

Synthesis, Characterization and Applications in Catalysis of Polyoxometalate/Zeolite Composites

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Abstract: An overview of the synthesis, characterization and catalytic applications of polyoxometalates/zeolites composites is given. The solids obtained by direct synthesis of the polyoxometalate in the presence of the zeolite are first described with their applications in catalysis. Those obtained by a direct mixing of the two components are then reviewed. In all cases, special care is taken in the localization of the polyoxometalate, inside the zeolite crystal, in mesopores or at the external surface of the crystals, as deduced from the characterization methods.

Keywords: polyoxometalates; zeolites; encapsulation; impregnation; synthesis; catalysis

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1. Introduction

In chemistry, a polyoxometalate is a polyatomic anion that consists of three or more transition metal atoms linked together by oxygen atoms. The metal atoms are usually from groups 5 (vanadium, niobium, tantalum) or 6 (molybdenum, tungsten) in their higher oxidation states [1]. The polyoxometalates can be divided into isopolyoxometalates (with only one transition metal) and heteropolyoxometalates (with one transition metal and a main group oxyanion such as phosphate, silicate, *etc.*). These polyoxometalates have interesting properties in a lot of domains [2–9]. Those usually used in catalysis, the subject of this review, have in most cases the so-called "Keggin" structure [10]. There are a lot of reasons for this choice, namely they are: (i) easy to prepare; (ii) more thermally stable than the other; (iii) acidic or redox systems depending on their atoms and (iv) some of them are commercially available. Heteropolyacids of the Keggin type consist of a central ion surrounded symmetrically by 12 MO_6 octahedra, which form four groups of three edge-shared octahedra (Figure 1). The central atom is usually phosphorus or silicon, while tungsten or molybdenum form MO_6 groups. The anion of a polyoxometalate with the Keggin structure is close to a sphere in shape, with a diameter of about 1 nm. These heteropolyoxometalates with the Keggin structure possess acidic and redox properties, which can be easily tailored by changing the composition of the Keggin units [4,5]. Their formula is $[XM_{12}O_{40}]^{n-}$ with X = P, Si, . . . and M = W, Mo. From this point onward, it will be abbreviated as XM_{12}. When the polyacid or an acidic form is referred to, it will be abbreviated as HXM_{12}.

Zeolites, the second component of the composites studied here, are crystalline microporous aluminosilicates, which are commonly used as adsorbents and catalysts due to their unique properties. By changing either their nature or the identity of the cations present in their structure (each aluminium atom in the framework will create a negative charge compensated by a cation, some or all of which can be exchanged with a different cation), it is possible to achieve fine separations such as oxygen/nitrogen. When the cation is a proton, the zeolite displays very acidic properties which are used industrially, for example in petroleum chemistry. Zeolites occur naturally but are also produced industrially on a large scale. A lot of zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known [11].

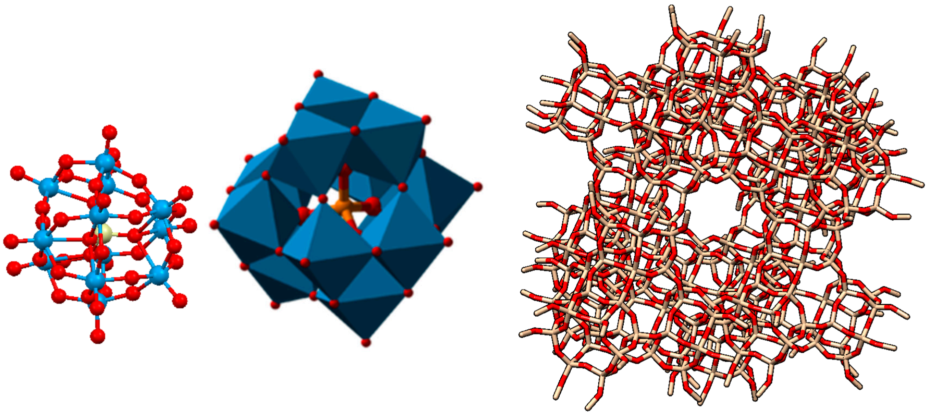

(**a**) (**b**)

Figure 1. Schematic drawings of (**a**) Keggin heteropolyoxometalate (red: oxygen, blue: tungsten, orange: X atom) and (**b**) supercage of Y zeolite (red: oxygen, yellow: silicon or aluminium). The drawings are not at the same scale.

One of these zeolites, faujasite, is very interesting in view of its application to form composites with polyoxometalates as its framework forms large cages (called "supercages") with a 1.12 nm diameter (Figure 1). These supercages are interconnected by windows of 0.735 nm in diameter. Therefore, this zeolite should be an ideal material for the encapsulation of Keggin polyoxometalates, which should then be sterically trapped in the supercages without any possibility to leave (Figure 2).

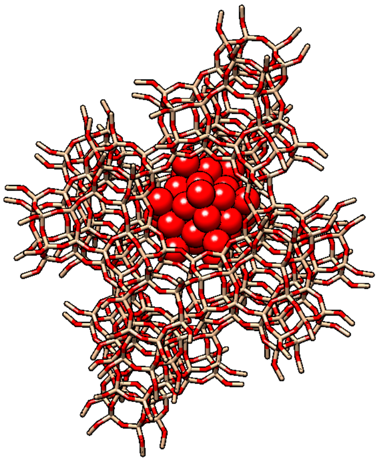


Figure 2. Keggin polyoxometalate in the supercage of Y zeolite (red: oxygen, yellow: silicon or aluminium).

The main interest of such materials should be that they can combine the advantages of the zeolite (for example, its adsorption capacities) and those of the polyoxometalate (for example, its acidic properties), without polyoxometalates' main disadvantage, which is a high solubility in polar solvents that prevents its use in heterogeneous catalysis in their presence. As the polyoxometalate cannot pass through the windows of the supercages, it is not possible to obtain encapsulated materials by adding the polyanion to the zeolite, and allowing it to diffuse in the framework. The only possibility is to synthesize it directly inside the zeolite crystal. Unfortunately, the synthesis of Keggin compounds can only be made in very acidic media (pH < 1) and the commercial Y zeolite (with a Si/Al ratio near 2.5) is not very stable in these conditions. It is then necessary to dealuminate it, for example by a hydrothermal treatment, before use, although some papers have reported syntheses in these conditions (see below). The emphasis of these papers is the catalytic performance, rather than the physical characterization, of the composite materials thereby obtained.

The materials prepared by this way can be divided into two groups, depending on the transition metal used, molybdenum or tungsten. We will then describe two recent papers where the zeolite is synthesized around the polyoxometalate. The next part will be devoted to the systems prepared by combining the Keggin polyoxometalate with the zeolite and, finally, we will describe the systems based on other polyoxometalates.

2. Synthesis of Molybdic Keggin Species or Their Salts in/on Zeolites

The 12-phosphomolybdate Keggin species ($[PMo_{12}O_{40}]^{3-}$, referred to as PMo_{12} from this point forward) can be easily synthesized from MoO_3 and H_3PO_4:

$$12\,MoO_3 + H_3PO_4 \rightarrow H_3PMo_{12}O_{40} \quad (1)$$

This reaction has been applied to the preparation of materials where the polyoxometalate was expected to be located in the supercages of Y zeolite simply by performing the synthesis in the presence of the zeolite.

2.1. The Pioneering Works of Mukai et al. [12–15]

Mukai *et al.* [12–15] synthesized $H_3PMo_{12}O_{40}$ from MoO_3 and phosphoric acid in the presence of dealuminated Y-zeolite (US-Y), previously exchanged with NH_4Cl and calcined, in order to obtain it in its H-form. They studied the resulting solid in the esterification of acetic acid with ethanol. They pointed out that it was necessary to use a dealuminated zeolite as the usual Y zeolite, with its high aluminium content (Si/Al = *ca.* 2.5), is not stable in the acidic medium needed for the synthesis of the polyoxometalate. As the intent was to prepare an acid catalyst with protons on the polyoxometalate, the use of its H form was also needed to avoid formation of salts of $[PMo_{12}O_{40}]^{3-}$. An indirect proof of the presence of Keggin units in the supercages obtained from the adsorption of isobutene, which was lower than that achieved with the unmodified zeolite. The isotherms were analyzed by the Dubinin–Astakhov equation to obtain the micropore volumes. It was deduced from these values that about one third of the supercages were filled by $[PMo_{12}O_{40}]^{3-}$ molecules. As the polyoxometalate can be synthesized not only in the supercages but also on the external surface of the crystallites, the samples were immersed in hot water (at 80 °C) [13]. After one hour of agitation, the samples were removed from hot water and the amount of dissolved molybdenum was determined by inductively coupled plasma analysis. This washing sequence was repeated five times. The amount of polyanion on the support varied from 0.16 g per g of support after the first wash to 0.09 g after the fourth and fifth ones (Figure 3).

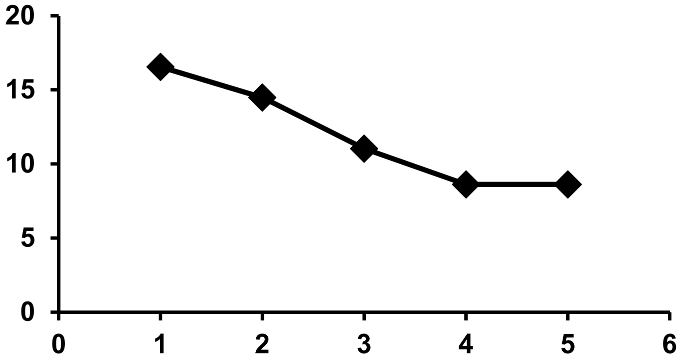


Figure 3. Amount of PMo_{12} remaining on the sample (in wt %, Y-axis) as a function of the number of washing steps (X-axis). Adapted from [13].

Clearly, after four washing steps, no further molybdenum can be extracted from the solid in agreement with the formation of the Keggin anion in the supercages of the zeolite. This point is very important for liquid phase catalysis as heteropolyacids are known to be highly soluble in polar solvents, such as water or alcohols. This solid is then a good potential heterogeneous and recyclable catalyst for reactions in polar solvents. The solid was used in the model reaction of esterification of acetic acid with ethanol. The performance was lower than that of the pure heteropolyacid, but better than that of $H_3PMo_{12}O_{40}$ supported on the same zeolite.

An increased resistance towards leaching was obtained by replacing, after the synthesis, some protons by cesium cations through a reaction with cesium carbonate [14]. Indeed, cesium salts of polyoxometalates are generally insoluble and so it can be expected that a higher stability could be achieved by this treatment. In order to retain some Bronstead acidity that is necessary for catalytic activity, only partial replacement of protons by cesium cations was conducted, leading to $Cs_xH_{3-x}PMo_{12}O_{40}$ formulations with $x = 1$, 2 and 2.5. The resulting solids were also tested in the esterification of acetic acid with ethanol and showed only a small decrease of the catalytic activity but without leaching (Table 1).

Table 1. Conversion after 180 min in the esterification of acetic acid with ethanol catalyzed by various PMo_{12} catalysts synthesized in Y zeolite [a]. Adapted from [14].

Catalyst	Conversion (%)
no catalyst	4.9
$H_3PMo_{12}O_{40}$	9.0
$CsH_2PMo_{12}O_{40}$	8.3
$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	7

[a] Reaction conditions: 60 °C, 0.5 mol acetic acid and ethanol, PMo_{12} concentration 1.2 mol· m^{-3}.

Mukai *et al.* also determined the key factors for the encapsulation of the heteropolyoxometalates in the supercages of Y-zeolite [12]. Encapsulation occurs only when the Si/Al ratio is between 10 and 50. When the amount of aluminium atoms is too high, the zeolite is decomposed during the synthesis of the polyacid. When it is too low, no encapsulation occurs, even if the polyoxometalate is synthesized in the reaction mixture. The presence of cations in the supercage is then needed to ensure the encapsulation. One explanation could be that highly siliceous zeolites are hydrophobic. As the polyoxometalate is hydrophilic, it cannot interact with the framework in these conditions. Another key parameter was the identity of the cation in the zeolite. No encapsulation occurred when it was Na^+, K^+, Ca^{2+} or Ba^{2+}. The best results were obtained with Cs^+, while $NH_4{}^+$ led only to a partial encapsulation. However, when the synthesis was made in the presence of these two cations, some insoluble salts were also obtained at the surface of the zeolite crystals. Finally, a study of the effect of the degree of ion exchange on encapsulation found that encapsulation occurred for cesium even with low exchange, whereas for ammonium it was necessary to have a high degree of exchange to achieve encapsulation.

In another paper [15], they showed that only a conventional synthesis starting from MoO_3 and H_3PO_4 led to encapsulation of the polyoxometalate. Addition of *t*-butyl alcohol had a beneficial effect on the encapsulation, which could occur even at low synthesis temperatures.

2.2. Other Reports of Syntheses of Encapsulated PMo_{12} in Y Zeolite

The synthesis was further improved by Tran *et al.* who prepared encapsulated PMo_{12} and $SiMo_{12}$ ($[SiMo_{12}O_{40}]^{4-}$) in US-Y in its H form by a two steps method [16]. They had observed that the method of Mukai did not give reproducible loadings. Their assumption was that this was due to the low solubility of MoO_3 in water. Therefore, they applied a hydrothermal technique to introduce the molybdenum oxide in the supercages and then to synthesize the polyoxometalate by introduction of phosphoric acid (for the obtention of encapsulated $HPMo_{12}$) or nitric acid (for $HSiMo_{12}$). The resulting materials could have high polyoxometalate loadings ranging from 1.2 to 11.1 wt % in a relatively predictable fashion. The solids were characterized by infrared spectroscopy, X-ray Diffraction (XRD) and Extended X-ray Absorption Fine Structure (EXAFS) to reveal the local structure around Mo. Tran *et al.* observed the formation of $SiMo_{12}$ even in the case of the synthesis in presence of phosphoric acid and attributed it to the fact that the slurry was refluxed during the preparation. However, they claimed that additional investigations were necessary to determine the formation conditions of both $SiMo_{12}$ and PMo_{12} on supports in the presence of phosphoric acid. The solids were then used for the partial oxidation of methane to formaldehyde at high temperatures (600 °C). Due to the presence of water vapor in the feedstock, the polyoxometalates were stabilized at this temperature and good HCHO yields were achieved. However, high CO amounts were observed, due to the decomposition of the aldehyde inside the supercages.

Wang *et al.* reported a synthesis of PMo_{12} encapsulated in dealuminated Y zeolite derived from that of Mukai but where the zeolite, in its ammonium form, and various amounts of MoO_3 were first mixed, ground uniformly to a fine powder and calcined at 500 °C for 4 h [17]. This treatment led to a spontaneous dispersion of MoO_3 onto the Y zeolite surface to form an amorphous layer. The desired amount of H_3PO_4 was then added and the sample heated at 95 °C for 3 h. The slurry was finally filtered and washed three times with hot water in order to remove the polyoxometalate located on the zeolite surface. The resulting solids were characterized by infrared spectroscopy, XRD and nitrogen adsorption. As the zeolite was in its ammonium form, one can expect that the synthesized PMo_{12} was in the form of its ammonium salt, which is insoluble and so the washing step could not remove it from the external surface of the zeolite. Unfortunately, no indication was given of the PMo_{12} amount before and after the washing. The solid was then used as catalyst for the oxidative desulfurization of dibenzothiophene by H_2O_2 in acetonitrile. The best results were obtained with the sample containing 10 wt % PMo_{12} (83.2% desulfurization efficiency) and the catalyst could be recycled at least three times without loss of activity. However, this system was less active than PMo_{12} in solution and it must be pointed out that in these conditions the active species is not the Keggin species but the peroxo complex $PO_4[MoO(\mu\text{-}O_2)(O_2)]_2^{3-}$, which is formed by contacting it with H_2O_2.

Wei *et al.* proposed a method derived from the studies of Mukai for the encapsulation of phosphomolybdic acid in a non-dealuminated Y zeolite (Si/Al = 2.6) [18]. The protons of the zeolite were first replaced by cesium cations by reaction with the desired amount of cesium carbonate followed by calcination. The polyoxometalate was then synthesized "*in situ*" by addition of sodium molybdate and phosphoric acid, with the pH adjusted to 2 or 3 by addition of HCl. The solid was separated by centrifugation and washed with hot water. It was characterized by X-ray diffraction, infrared spectroscopy and ^{31}P Magic Angle Solid-state Nuclear Magnetic Resonance (MAS NMR) spectroscopy. Unfortunately, the ^{31}P MAS NMR spectrum showed the presence of an additional broad signal proving the existence of other species. It is therefore difficult to draw conclusions about whether the polyoxometalate is entirely encapsulated within the zeolite or not, especially as the cesium salt of PMo_{12} is insoluble and could be located on the external surface. In addition, X-ray data showed that, at high loadings, the crystallinity of the zeolite was lost, as expected from the works of Mukai *et al.* who observed the destruction of the framework in the presence of the highly acidic PMo_{12}. This solid was used for the esterification of acetic acid with *n*-butanol and did not show any deactivation after five runs.

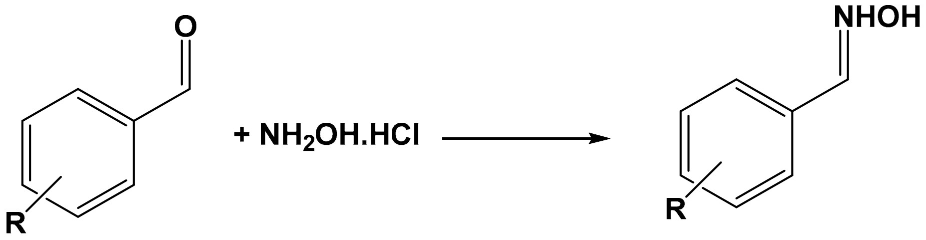
2.3. Synthesis of PMo_{12} on ZSM-5

Chen *et al.* reported the synthesis of $H_3PMo_{12}O_{40}$ encaged in nanocrystalline H-ZSM-5 and its use in combination with Ni for the hydroconversion of *n*-octane [19]. The zeolite crystals sizes were *ca.* 18 nm with formation of particles of 70–100 nm. The solids were characterized by a lot of physicochemical methods including solid-state NMR and Electron Spin Resonance (ESR). It was concluded (as expected when looking at the crystallographic data of the zeolite) that PMo_{12} could not fit the pore channels of H-ZSM-5 but was located in the secondary pore system formed by the nanocrystals. This solid was compared to a system obtained by classical impregnation in the hydroconversion of *n*-octane. The performances of the encapsulated material were slightly better than those of that prepared by classical impregnation.

2.4. Applications in Catalysis

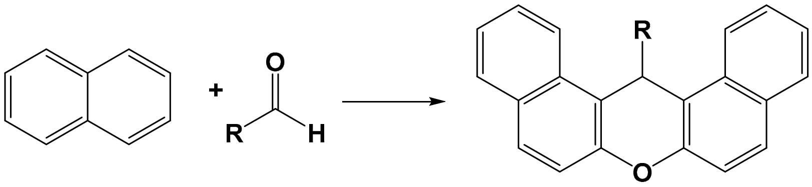
Moghadam *et al.* used the method proposed by Mukai *et al.* for the synthesis of $HPMo_{12}$ encapsulated in US-Y (Si/Al = 3.8) and its use for the oximation of aldehydes [20]. After synthesis and washing with hot water, the remaining protons of the zeolite were exchanged for Na^+ by suspending the solid in a solution of sodium chloride for 4 h. The catalyst, which contained 5.0 wt % Mo, was characterized by infrared spectroscopy (which showed the characteristic bands of the polyoxometalate but slightly shifted), X-ray powder diffraction and BET surface area analysis. An electrochemical characterization of this material was also reported [21]. The electrochemical studies revealed that the encapsulated PMo_{12} showed electrochemical responses much slower than those of impregnated ones, arising from the restraints in the zeolite pores towards diffusion or charge-balancing electrolytes.

This material was used for the oximation of various aldehydes with $NH_2OH\cdot HCl$ (Scheme 1) [20]. The reaction was performed under mechanical stirring, ultrasonic irradiation or without any solvent. High yields were achieved in all cases with short reaction times, the best results being obtained under solvent free conditions. For example, for 2-chlorobenzaldehyde a 100% yield was achieved in 10 min. However, in all cases, some molybdenum was leached, in agreement with the results of Mukai *et al.* (see Figure 3). The amount of leached Mo decreased with the number of recycles (as also observed by Mukai) and after three runs it was null, while the yield had only slightly decreased. However, this late result must be taken with care because the yield values were near 100% and this could mask an activity decrease.



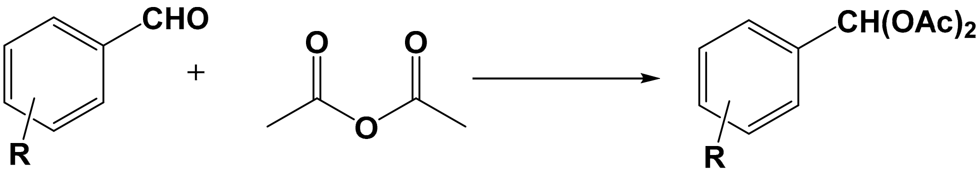
Scheme 1. Oximation of substituted benzaldehydes with $NH_2OH\cdot HCl$.

The same group used also this catalyst for the synthesis of 14-substituted-14-*H*-dibenzo [*a*,*j*] xanthenes [22] (Scheme 2). Both thermal and microwave irradiation conditions were studied. High yields (more than 90%) were obtained by use of microwave irradiation after short reaction times (a few minutes). As above, leaching was observed during the first runs, but ceased later, without a noticeable modification of the catalytic activity.



Scheme 2. Synthesis of 14-substituted-14-*H*-dibenzo [*a*,*j*] xanthenes.

The same material was also used for the synthesis and deprotection of 1,1-diacetates under solvent-free conditions [23] (Scheme 3). As above, a non-negligible amount of molybdenum leached during the first runs, leading to a decrease of the catalytic activity that was initially very good (yields higher than 90%).



Scheme 3. Protection-deprotection of 1,1-diacetates.

Ferreira *et al.* synthesized $HPMo_{12}$ encapsulated in dealuminated NaY zeolite (Si/Al = 30) and used the thereby obtained catalysts for the esterification of glycerol with acetic acid [24]. The synthesis was performed as described by Mukai and the samples were thoroughly washed with hot water. Four different catalysts were prepared with amounts of PMo_{12} varying from 0.006 to 0.054 g per g of zeolite. The solids were characterized by nitrogen adsorption, infrared spectroscopy and XRD. The catalytic activity reached a maximum for a PMo_{12} loading of 0.019 g/g of zeolite (conversion = 68%) with a high selectivity towards mono- (37%) and di-esters (59%). A study of recycling was also made and no decrease of activity was observed after four consecutive runs (the catalyst was separated by centrifugation, washed with water and dried at 120 °C before reuse).

Vital *et al.* studied the hydration of α-pinene catalyzed by $HPMo_{12}$ encapsulated in US-Y [25]. The solid was prepared by the method described by Mukai *et al.* and was characterized by infrared spectroscopy and nitrogen adsorption. The main reaction product of α-pinene hydration was α-terpineol, along with minor amounts of other monoterpenes. The selectivity was higher than for PMo_{12} supported on silica, whatever the conversion, and could reach 75% at 100% conversion. The catalyst could be reused at least four times but it showed a decrease of activity from 1.5×10^{-3} to 0.75×10^{-3} $mol \cdot h^{-1} \cdot g_{cat}{}^{-1}$.

This catalyst was later dispersed in polydimethylsiloxane (PDMS), leading to an $HPMo_{12}$-US-Y/PDMS membrane, resulting in an increase of the catalytic activity [26]. The activity increased in the subsequent uses of the same membrane, probably due to the interaction between retained α-terpineol and the polymer matrix.

3. Synthesis of Tungstic Keggin Species or their Salts in/on Zeolites

Quite simultaneously with Mukai *et al.*, Sulikowski *et al.* reported the encapsulation of 12-tungstophosphoric acid (HPW_{12}) in the supercage of Y faujasite [27]. As above, the zeolite was first dealuminated (by treatment with $SiCl_4$ or EDTA) prior synthesis of the polyoxometalate. Unfortunately, no indication was given about the method used for the encapsulation of 12-tungstophosphoric acid (the reference is "Patent Application" and there is no patent in the literature). The resulting solid was characterized by infrared spectroscopy and solid-state ^{31}P MAS NMR and used in the isomerization and disproportionation of *m*-xylene. The encapsulation was claimed on the basis of the ^{31}P MAS NMR spectrum which gave a broad peak (linewidth *ca.* 15 ppm, while the sample prepared by classical impregnation led to a very sharp signal). This broadening was interpreted as due to the interaction between the zeolite and the polyoxometalate. The encapsulated material showed a drastic increase of activity (from 8% to more than 31% at 300 °C) and selectivity (from 5% to 50%) towards disproportionation into toluene and trimethylbenzenes compared to the starting faujasite.

Jin *et al.* reported the synthesis and encapsulation of HPW_{12} in the supercages of ultra-stable Y zeolite under microwave irradiation [28]. The reaction occurred in a few minutes (3–9 min). The solids were then washed 20 times with hot water to remove HPW_{12} located on the external surface of the crystallites. The resulting material was characterized by various methods such as ^{31}P MAS NMR spectroscopy, High-Resolution Transmission Electron Microscopy (HR-TEM), nitrogen adsorption, Inductively Coupled Plasma (ICP) analysis and XRD. The ^{31}P MAS NMR spectrum was quite similar to that reported by Sulikowski (broad signal at −15 ppm with a 20 ppm linewidth). XRD data showed that increasing the microwave irradiation time resulted in a partial destruction of the zeolitic framework. HR-TEM micrographs showed clearly the encapsulation of the polyoxometalate into the zeolite. Temperature-Programmed Desorption of NH_3 (NH_3-TPD) showed that HPW_{12}-US-Y exhibited a stronger acidity than that of pure US-Y, and adsorbed pyridine infrared spectroscopy disclosed that the concentration of Brönsted acid sites increased. This hybrid solid acid exhibited an activity higher than those of the zeolite and HPW_{12} in the synthesis of 4,4′-dimethyldiphenylmethane from toluene and formaldehyde and could be used as a solid acid catalyst in aqueous solutions.

Anandan *et al.* described the synthesis of HPW_{12} encapsulated in a titanium-exchanged Y zeolite and its photocatalytic properties [29,30]. The zeolite was first dealuminated in a steam atmosphere for 10 h. After obtention of the H-form of the zeolite, titanium was introduced by exchange with an aqueous solution of ammonium titanyl oxalate. HPW_{12} was finally synthesized by addition, to a suspension of the TiHY zeolite, of sodium tungstate and disodium phosphate and a stoichiometric amount of HCl. Finally, the zeolite was isolated and washed thoroughly with hot water. The system was mainly characterized by solid-state ^{31}P MAS NMR. Five relatively sharp peaks were observed between -11 and -14 ppm and attributed to HPW_{12} in various environments and in the supercages. When looking at the above results it seems more probable that these peaks, which are relatively sharp, correspond to decomposition products of HPW_{12} and/or HPW_{12} at the external surface of the crystals.

The infrared spectra showed some characteristic peaks of the $[PW_{12}O_{40}]^{3-}$ anion, but they were shifted by *ca.* 5–8 cm^{-1} compared to the values of pure HPW_{12}. This shift was much the same as that observed when HPW_{12} was interacting with TiO_2 in a colloidal solution [31]. The system was 20 times more active than the same system without titanium for the photodegradation of methyl orange [29] (see below a detailed explanation of the mechanism of this reaction). It was also studied in the generation of hydrogen and oxygen from aqueous solutions upon illumination through two photon reactions [30].

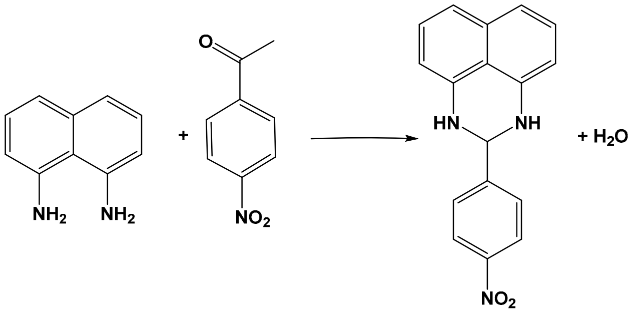
To our knowledge, the method used for the synthesis of encapsulated $HPMo_{12}$ (predispersion of the oxide) has not been applied to the synthesis of tungstic heteropolyacids inside the supercages of Y zeolite, even if it has been reported that WO_3 could be efficiently introduced into the channels for tungsten loadings below 11.4 wt % [32].

4. Synthesis of the Zeolite around the Polyoxometalate

Rather than synthesizing the polyoxometalate inside the supercages of the zeolite, another possibility would be to build the zeolite around it. However, as previously noted, Y zeolite must be selectively synthesized under conditions typically detrimental to the stability of the polyoxometalate, with the available pH range being particularly restrictive. To our knowledge, there are only two reports that utilize this strategy, with claims of polyoxometalate encapsulation poorly evidenced by physical characterization.

Zendehdel *et al.* reported the synthesis of PW_{12}/NaY and PW_{12}/NaY/MCM-41 composites by synthesis of the zeolite in the presence of the polyoxometalate [33]. HPW_{12} (10 g) was mixed with 16.13 g of sodium silicate and 6 mL of the initiator (with the composition 16 Na_2O:Al_2O_3:15 SiO_2:320 H_2O aged at 32 °C for 32 h). Then, 13.2 mL of sodium hydroxide (24 wt %) and 5.2 mL of deionized water were added and the mixture was placed in an autoclave at 100 °C for 24 h. The solid, called HPW_{12}/NaY, was recovered, washed and dried in air. It was characterized by XRD and infrared spectroscopy and then used for the synthesis of substituted perimidines. When looking at the preparation method, the polyoxometalate cannot be stable in the starting medium which is highly basic and it must decompose. However, the infrared spectrum of the composite displays three characteristic bands of the polyoxometalate at 980, 888 and 790 cm^{-1}. It is then necessary to suppose that the Keggin unit has been rebuilt during the hydrothermal treatment. Unfortunately, this was the only evidence for the presence of the polyoxometalate in the composite and additional experiments, including ^{31}P solid-state NMR, will be necessary before drawing conclusions about the presence of the polyoxometalate and its localization inside the supercages or elsewhere.

This solid was used as catalyst for the preparation of 2-(4-nitrophenyl)-2,3-dihydro-1*H*-perimidine by reaction of 1,8-naphthalenediamine with 4-nitrobenzaldehyde in ethanol at 80 °C (Scheme 4). Yields around 70% were obtained and the catalyst could be recycled three times (after filtration and washing with ethanol) without a significant loss of activity. This reaction is catalyzed by Brönsted acid sites, which must arise from the polyoxometalate as the zeolite is in its sodium form.



Scheme 4. Synthesis of substituted perimidine catalyzed by the encapsulated polyoxometalate.

Very recently, Sun reported a "build-bottle-around-ship" synthesis of $HPMo_{12}$ encapsulated in Y zeolite [34]. The preparation involves also the introduction of the polyoxometalate in a basic solution (pH = 10) of initiator containing silicon and aluminium (formed by dissolution of a natural clay in highly alkaline medium and hydrothermal synthesis) followed by a hydrothermal treatment at 130 °C for 48 h. The resulting solid was collected by filtration, treated with 0.01 M nitric acid at 60 °C for 10 h in order to remove the unencapsulated polyoxometalate and was finally washed with hot water. The main difference is that, in the present case, the polyoxometalate was not in its acid form but as its ammonium salt, $(NH_4)_3[PMo_{12}O_{40}]$. Two relatively high PMo loadings (15 and 6 wt %) were obtained by varying the amount of added polyoxometalate. The solids were characterized by X-ray fluorescence, X-ray diffraction, infrared spectroscopy, nitrogen adsorption–desorption and solid-state ^{27}Al and ^{31}P MAS NMR spectroscopy. As in the above case, the polyoxometalate should not be stable in the synthesis medium, but the ^{31}P MAS NMR spectra provide evidence of the presence of the Keggin unit in the resulting solid, with only a sharp peak at −3.5 ppm is observed. A reason for this result could be that the ammonium salt of 12-phosphomolybdate is insoluble and so its reaction with the very basic medium occurs only slowly. X-ray diffraction shows only the peaks of the Y zeolite while the nitrogen sorption capacities decrease when the HPMo loading increases. The presence of the Keggin units in the supercages was concluded from these results. Even if additional experiments are needed to conclusively prove the encapsulation of the polyoxometalate, the use of insoluble salts could provide a good approach to overcome the problem of the instability in basic media. Unfortunately, this solid was only used for adsorption/desorption of alkaline cations and no catalysis application was evaluated.

5. Keggin Polyoxometalates Supported on Zeolites

5.1. Preliminary Studies

Pamin *et al.* prepared 12-tungstophosphoric acid on Y zeolite by impregnation in water [35]. Before encapsulation, the zeolite was first dealuminated by treatment with $EDTAH_4$. The resulting Si/Al ratio of the material was 4.24. This treatment led to the formation of a secondary pore system with pores ranging from 12 to 50 Å and a mean value of 15 Å. The polyoxometalate loading varied between 1 and 10 wt %. The samples were characterized by various physicochemical methods including XRD, thermogravimetry, infrared spectroscopy and solid-state MAS NMR spectroscopy. The main conclusions were that two types of Keggin units were present on the surface: those strongly interacting with the hydroxyl groups of the support (probably via their protonation [36]), prevailing at low coverage, and those interacting weakly with the zeolite crystals and corresponding to bulk heteropolyacid, prevailing at high coverage. These solids were tested in the transformation of *m*-xylene by isomerization, disproportionation and dealkylation. Deposition of the 12-tungstophosphoric acid dramatically increased the selectivity for disproportionation. The results were comparable to those obtained by the same group with the encapsulated polyoxometalate [27].

These solids were also used for catalysis in liquid phase for the oxidation of various substrates by hydrogen peroxide [37]. Only activated molecules (containing, for example, hydroxyl groups) could be oxidized but unfortunately no studies were made on leaching and recycling.

Sulikowski also prepared samples by impregnation of the same dealuminated zeolite with HPW_{12} in diethyl ether [38]. The mixture was stirred in a closed vessel at room temperature for 1.5 h and then the solid was isolated by filtration and washed with diethyl ether. PW_{12} loadings ranging from 2 to 38 wt % were prepared by this protocol. Similar conclusions to Parmin *et al*. were drawn about the presence of two types of Keggin units, even if in the present case the bulk heteropolyacid was also present at low coverage. These solids were tested in the disproportionation of toluene and its transalkylation with 1,2,4-trimethylbenzene. All hybrid catalysts exhibited enhanced catalytic activity in both processes, but the Keggin units located in the mesopores were found to be the most active species.

Haber *et al.* [39] performed a detailed study on HPW_{12} supported on dealuminated zeolite as a function of the HPW_{12} loading (between 0.00016 and 46.8 wt %). The samples were prepared by impregnation in water as in the first paper [35]. These catalysts were fully characterized and studied in the vapor-phase dehydration of ethanol. It was concluded that the catalytic behavior was determined by few very active sites, composed of Keggin anions and lacunary Keggin anions located in the supercages opened at the surface, which has a honeycomb structure. This structure was formed during the zeolite surface pretreatment and dealumination, resulting in a disintegration of the zeolite crystals and a breaking of the supercages forming "bowls" which could perfectly fit the Keggin anions (Figure 4).

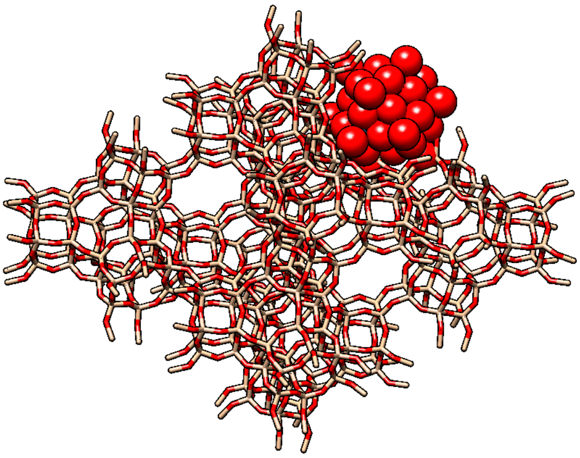


Figure 4. Location of Keggin polyoxometalate on the surface of Y zeolite (colors same as in Figures 1 and 2).

5.2. Applications in Refining (Hydroisomerization of Alkanes, Hydrodesulfurization)

There are some reports on the use of catalysts based on PW_{12} and platinum on zeolites in the hydroisomerization of alkanes. These catalysts are quite similar to those prepared on more classical supports such as silica. Their main interest is to combine three different functions: the acidity of the polyacid, that of the zeolite and the noble metal.

The hydroisomerization of *n*-heptane was studied on PW_{12}/DUS-Y (dealuminated ultra-stable Y zeolite) [40,41]. The catalysts were prepared by impregnation of the US-Y or DUS-Y zeolite with 12-tungstophosphoric acid, followed by wet impregnation with a platinum salt. Although Pt/zeolite catalysts were active for this reaction, an additional synergic effect was observed in the case of the DUS-Y sample in the presence of platinum and PW_{12}. Unfortunately, the selectivity decreased when the temperature was increased, irrespective of sample composition, and around 300 °C the formation of toluene was also observed. This promotion effect was not observed on US-Y or silica. It was assumed that the polyoxometalate was not located in the supercages of faujasite but in the mesopores of the solid, their mean pore diameter being 1.8 nm for US-Y and 2.3 nm for DUS-Y. In the case of US-Y, the low catalytic activity was explained by assuming that the protons of PW_{12} had been neutralized by extra framework aluminum, resulting in a poorly active system.

Wei *et al.* [42] studied the hydroisomerization of *n*-heptane on HPW_{12} supported on Hβ zeolite in presence of platinum. As this zeolite can only accommodate spheres of 0.67 nm in diameter and possesses channels *ca*. 0.6 nm in diameter [11], the polyoxometalate cannot fill them and is deposited on the external surface of the crystallites. The zeolite was used as received or dealuminated by a hydrothermal treatment followed by HCl washing. The samples were prepared by impregnation as in [41] with 0.4 wt % Pt and 5 to 15 wt % HPW_{12}. The catalytic experiments were made at 250 °C (0.5 g catalyst, weight hourly space velocity 2 h^{-1}, H_2 to *n*-C7 molar ratio 7.9, pretreatment under hydrogen at 300 °C). Only the XRD patterns were presented and did not show any peak for Pt or HPW_{12}. Unfortunately, no further characterization of the solids was made. The cracking products were only propane and butane. The catalytic results are given below (Table 2) where Hβ-*m*(*n*) is a Hβ zeolite treated hydrothermally at *m* °C during *n* h.

Table 2. Comparison of the activity and selectivity of various catalysts in the hydroisomerization of *n*-hexane [42] [a].

Catalyst	Conversion (%)	Selectivity for Isomerization (%)
Pt/Hβ	27.9	99.0
Pt-5% PW_{12}/Hβ	32.2	96.1
Pt-10% PW_{12}/Hβ	47.1	83.8
Pt-15% PW_{12}/Hβ	34.5	70.0
Pt/Hβ-650(5)	14.8	100
Pt-10% PW_{12}/Hβ-300(5)	21.1	95.0
Pt-10% PW_{12}/Hβ-550(5)	25.3	91.1
Pt-10% PW_{12}/Hβ-650(5)	39.6	88.5
Pt-10% PW_{12}/Hβ-700(5)	20.1	92.4
Pt-10% PW_{12}/Hβ-650(4)	19.3	96.0
Pt-10% PW_{12}/Hβ-650(6)	21.0	91.1
Pt-10% PW_{12}/Hβ-650(7)	20.3	93.8

[a] Reaction conditions: 0.5 g catalyst, weight hourly space velocity 2 h^{-1}, H_2 to *n*-C7 molar ratio 7.9, pretreatment under hydrogen at 300 °C. Numbers in brackets denote hours at the treatment temperature.

These results are relatively difficult to explain as they depend on many parameters, with some of them being not known. For example, the amount of acidic sites, the Pt dispersion or the porosity of the samples. Some features can still be deduced from the data, such as the ideal PW12 loading for Hβ is 10 wt %. As the polyoxometalate cannot fill the channels of the zeolite, this value is probably related to the optimal amount of isolated Keggin units. A puzzling feature of the data is the large deviation of the conversion observed for zeolite pretreated at 650 °C for 5 h, as compared to zeolite pretreated at 650 °C for 4 or 6 h. There is probably another unobserved variable responsible for the anomalous result for zeolite pretreated at 650 °C for 5 h, with all the other pretreatments yielding conversions comparable to zeolite without hydrothermal treatment. If one accepts this data point, the results show conversion close to 20%, with a selectivity between 90% and 95%, showing that a pretreatment at 300 °C is sufficient to roughly halve the conversion.

Later, the same group studied the effect of the incorporation of another metal, namely chromium or lanthanum, on the catalytic activity [43]. The catalysts were characterized by X-ray diffraction (absence of peaks arising from crystalline polyoxometalate), infrared spectroscopy (presence of the bands of the polyoxometalate), BET surface area analysis and H_2 adsorption (increase of Pt dispersion when the Cr amount increases). The addition of chromium leads to an increase of both the conversion and the selectivity to isomerization. A study was made as a function of both the Cr and PW_{12} loading and the reaction conditions (temperature and ratio alkane/catalyst). The conversion could reach 75.3% with 91.3% selectivity to isomerization. This effect was attributed to the improvement of the polyoxometalate, the higher dispersion of platinum and the creation of a "desorption-transfer promoting site", due to the introduction of chromium in the catalyst. Introduction of lanthanum instead of chromium also led to an improvement of the catalytic activity but the effect was less pronounced.

This study was also extended to the introduction of Cerium in the Pt-PW_{12}/DUS-Y system with quite the same conclusions, the presence of cerium increasing the dispersion of platinum [44]. As above, the solids were characterized by X-ray diffraction, infrared spectroscopy, BET surface area analysis and hydrogen chemisorption.

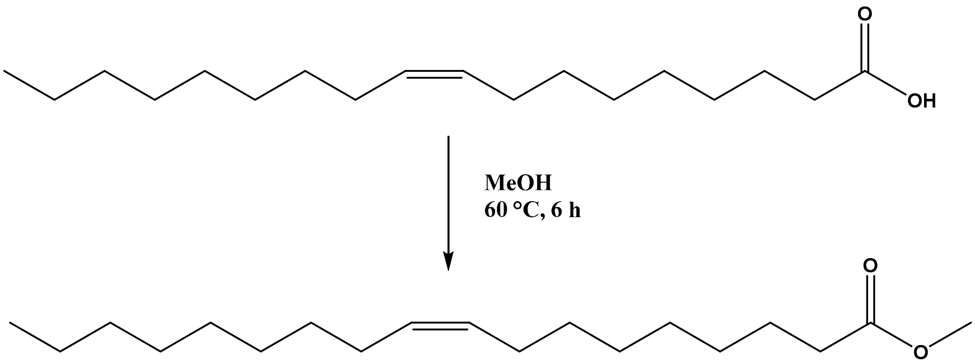
Finally, the same authors reported the synthesis of cesium salts of PW_{12} supported on dealuminated US-Y and their use in the hydroisomerization of *n*-heptane [45]. For that purpose, the desired amount of cesium was first deposited by impregnation of Cs_2CO_3 on the zeolite, followed by drying and calcination at 550 °C. The desired amount of PW_{12} and platinum were then introduced by the same methods as above. The solids obtained were characterized by the same techniques as listed above, and additionally NH_3 TPD analysis. The key result was the confirmation of the presence of the cesium salt of PW12 by X-ray diffraction. These solids were also active in hydroisomerization of *n*-heptane with high activity and selectivity (for example, at 310 °C 76.2% conversion was observed with a selectivity to isomerization of 92.2%).

Kostova *et al.* prepared Mo-containing β-zeolite by use of PMo_{12} and a mechanochemical approach [46]. The solid was characterized by infrared spectroscopy and Temperature Programmed Reduction (TPR) analysis. It was then used in the hydrodesulfurization of thiophene. The activity was 50% higher than that of a sample prepared by classical impregnation.

5.3. Applications in Organic Chemistry

While the above section was devoted to the transformation of apolar molecules (if one accepts thiophene), where the heteropolyacid is not soluble, the following applications involve polar molecules where it is highly soluble. Some examples which are not from purely organic chemistry but involving polar substrates will also be included here.

Patel *et al.* studied the esterification of oleic acid with methanol catalyzed by HPW_{12} supported on Hβ zeolite [47]. Heterogeneous acid catalysts comprised of 12-tungstophosphoric acid (10%–40%) and zeolite Hβ were synthesized by classical impregnation from an aqueous solution of HPW_{12} and subsequent drying at 100 °C. The 30 wt % loaded catalyst was characterized by various physicochemical techniques. The use of this catalyst was explored for biodiesel production by esterification of a free fatty acid, oleic acid, with methanol (Scheme 5). The effect of various reaction parameters such as catalyst concentration, acid/alcohol molar ratio, and temperature were studied to optimize the conditions for maximum conversion. The catalyst showed high activity in terms of high conversion (84%) and high turnover number, 1048. A kinetic study, as well as a Koros−Nowak test were carried out, and it was found that esterification of oleic acid followed first order kinetics with a calculated activation energy E_a of 45.2 $kJ \cdot mol^{-1}$ and a pre-exponential factor A of 5.4×10^4 min^{-1}. As the reaction occurred in methanol, where the heteropolyacid is highly soluble, the question of recycling was very important. The catalyst showed potential for being used as a recyclable catalytic material, with simple regeneration and no significant loss in conversion after recycling observed. As an application, preliminary studies were carried out for biodiesel production from waste cooking oil and using jatropha oil as feedstock.

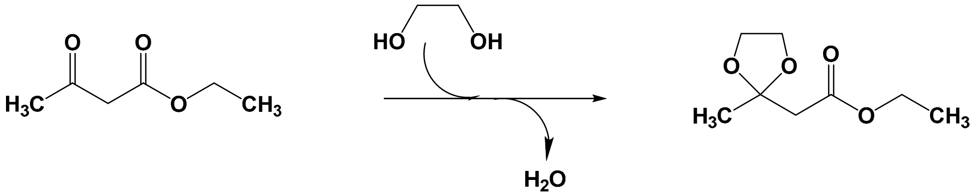


Scheme 5. Esterification of oleic acid by methanol.

Later, the study was extended to $HSiW_{12}$ supported on the same Hβ zeolite [48]. The catalyst was also used for the *trans*-esterification of soybean oil with methanol. Recycling studies were performed and did not show any deactivation of the catalyst.

Srinivas *et al.* prepared catalysts by impregnation of 12-tungstophosphoric acid on Y zeolite [49]. Unfortunately, the Si/Al ratio of the zeolite used for these experiments was not given. The PW_{12} loading varied from 10 to 25 wt %. The solids were characterized by BET analysis, X-ray diffraction, infrared spectroscopy and NH_3 TP. They were used for the etherification of glycerol with *t*-butanol. The highest conversion (84%) and highest selectivity to the mono-ether were achieved on the sample containing 20 wt % PW_{12}, which had also been shown to be the most acidic by TPD of ammonia. The reusability was studied by recovering the catalyst at the end of the reaction by filtration, washing it with methanol and drying at 100 °C for 2 h. No appreciable variation of activity was detected after four cycles. Another important point is that the filtrate of the reaction mixture did not contain tungsten, proving that the polyoxometalate was well anchored on the surface. However, as the Si/Al ratio of the starting zeolite was not given, one cannot exclude a partial decomposition of the zeolite by the polyoxometalate, resulting, for example, in an insoluble aluminium salt of PW_{12}.

Zhang *et al.* prepared a series of catalysts by immobilization of 12-tungstophosphoric acid and its cesium salt on ultra-stable Y zeolite and its dealuminated form (DUS-Y) and silica materials. The acid was deposited by impregnation while the cesium salts were obtained by a two-step protocol: the desired amount of cesium was first introduced by impregnation of cesium carbonate followed by calcination, after which the polyacid was then introduced by a second impregnation. The different materials were characterized by various physicochemical methods including X-ray powder diffraction, BET surface area analysis, ^{31}P and ^{29}Si MAS NMR spectroscopy and SEM. The early work reported that they were tested in the liquid-phase esterification of acetic acid with butanol [50]. They were then used in the synthesis of fructone by acetalization of ethylacetoacetate with ethylene glycol [51–53] (Scheme 6).



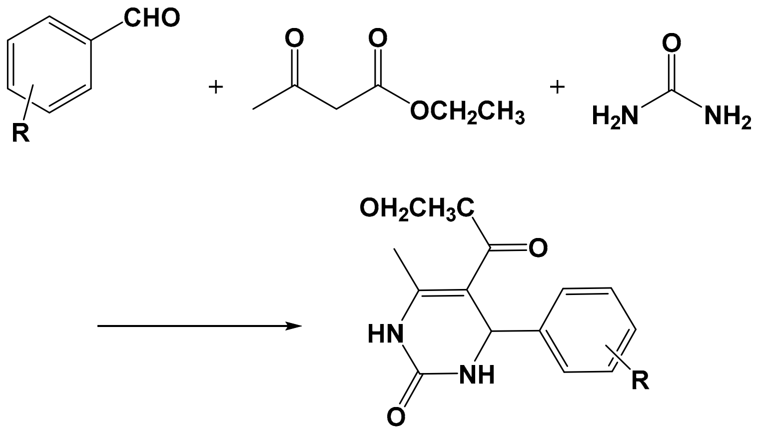
Scheme 6. Synthesis of fructone by acetalization of ethylacetoacetate with ethylene glycol.

Various parameters were studied (amount of PW_{12}, of Cs, reaction conditions, *etc.*). The best systems were those based on the Cs salts of PW_{12} supported on dealuminated US-Y zeolite and a conversion as high as 98.7% with a selectivity of 97% to fructone could be achieved over 30%

$Cs_{2.5}H_{0.5}PW_{12}$/DUS-Y. A study of leaching by treatment with water showed that the systems based on the pure heteropolyacid were not stable, with most of the Keggin units being released in water. In contrast, those based on the cesium salt did not show a significant leaching.

The same authors also studied the synthesis of fructone-B by acetalization of ethylacetoacetate with 1,2-propanediol and observed similar results, the Cs salts being active with minimal leaching [54]. In another paper [55], they used these catalysts for the liquid-phase esterification of acetic acid with *n*-butanol. The conversion was higher than that observed when using the zeolite or the polyoxometalate alone. Again, the supported cesium salts exhibited only minimal leaching, leading to only a small decrease of the catalytic activity upon recycling.

Moosavifar reported the use of heteropolyacids supported on Y zeolite for the synthesis of dihydropyrimidinones by the Biginelli reaction [56] (Scheme 7). PMo_{12}, PW_{12} and SiW_{12} were deposited on a Y zeolite dealuminated by treatment with $HClO_4$. Good yields were obtained for all three systems within a few hours and the catalysts could be recycled after washing with hot water and ethanol. Such behavior is surprising, as the heteropolyacids are highly soluble in these polar solvents. However, the catalytic reaction involves urea, which is probably protonated by the polyacid, leading to the formation of an insoluble salt. The synthesis of such a species has been reported recently [57]. Due to the great size of the molecules, polyacids encapsulated in Y zeolite such as those described in [20,22,23] were inactive for this reaction.



Scheme 7. Synthesis of dihydropyrimidinones by the Biginelli reaction.

More recently, Narkhede and Patel studied this reaction over HPW_{12} and $HSiW_{12}$ supported on Hβ zeolite [58]. The catalysts were those reported previously [47,48] and led to higher yields in smaller times (for example a 98% yield in 15 min instead of a 97% yield in 360 min). The reaction was then extended to other substrates (Table 3).

Nandiwale *et al.* prepared a catalyst based on HPW_{12} supported on desilicated H-ZSM-5 and studied it in the esterification of levulinic acid by ethanol, in view of the synthesis of ethyl levulinate, which can be used as diesel miscible biofuel [59]. The desilification was performed by treatment with NaOH at various concentrations (from 0.2 to 1.5 M) during 30 min at 65 °C. The resulting solids possessed an increased surface area with a high number of mesopores where HPW_{12} could be deposited by the incipient wetness technique. These solids were used in the esterification of levulinic acid and various parameters were studied (relative amounts of reactants, of catalyst, temperature, speed of agitation, *etc.*) including the recycling of the catalyst (reused directly after filtration). Unfortunately, no study of leaching was made and even if a kinetic law was proposed, the high conversions (more than 80%) prevented some conclusions to be made.

Table 3. Synthesis of various dihydropyrimidones on $PW_{12}/H\beta$ and $SiW_{12}/H\beta$ [58].

Catalyst	**R–C(=O)H, R =**	**R′C(=O)CH$_2$C(=O)CH$_3$, R′ =**	**NH$_2$–C(=X)NH$_2$, X =**	**Reaction Time (min)**	**Yield (%)**
$PW_{12}/H\beta$	C_6H_5	$–OC_2H_5$	O	15	98
$SiW_{12}/H\beta$	C_6H_5	$–OC_2H_5$	O	15	95
$PW_{12}/H\beta$	C_6H_5	$–OC_2H_5$	S	17	90
$SiW_{12}/H\beta$	C_6H_5	$–OC_2H_5$	S	20	92
$PW_{12}/Hv\beta$	C_6H_5	$–OCH_3$	O	14	92
$SiW_{12}/H\beta$	C_6H_5	$–OCH_3$	O	12	94
$PW_{12}/H\beta$	C_6H_5	$–OCH_3$	S	15	97
$SiW_{12}/H\beta$	C_6H_5	$–OCH_3$	S	15	96
$PW_{12}/H\beta$	4-ClC_6H_4	$–OC_2H_5$	O	30	89
$SiW_{12}/H\beta$	4-ClC_6H_4	$–OC_2H_5$	O	28	90
$PW_{12}/H\beta$	4-$NO_2C_6H_4$	$–OC_2H_5$	O	32	82
$SiW_{12}/H\beta$	4-$NO_2C_6H_4$	$–OC_2H_5$	O	30	92

5.4. Applications in Photocatalysis

5.4.1. Systems without Titanium

Marchena *et al.* [60] prepared two series of materials based on HPW_{12} immobilized on NH_4Y and NH_4ZSM-5 and prepared by wet impregnation of aqueous solutions. The concentration of HPW_{12} was varied in order to obtain PW_{12} contents of 5, 10, 20 and 30 wt % in the solid. The materials were characterized by N_2 adsorption–desorption isotherms, X-ray diffraction, infrared spectroscopy, ^{31}P MAS-NMR spectroscopy, thermogravimetry, and Diffuse Reflectance UV–Visible spectroscopy, with the acidic behavior studied by potentiometric titration with *n*-butylamine.

The specific surface area (S_{BET}) decreased as the polyoxometalate content was increased, as a result of zeolite pore blocking. The X-ray diffraction patterns of the solids modified with PW_{12} showed the characteristic peaks of NH_4Y and NH_4ZSM-5 zeolites, and an additional set of peaks assigned to the presence of $(NH_4)_3PW_{12}O_{40}$ formed by exchange of the protons of the polyacid with the ammonium ions of the zeolite. By interpretation of the infrared and ^{31}P NMR spectra, the main species present in the samples was the $[PW_{12}O_{40}]^{3-}$ anion, which was partially transformed into $[P_2W_{21}O_{71}]^{6-}$ during the synthesis and drying steps. The thermal stability of these materials was similar to that of the parent zeolites. Moreover, the samples with the higher PW_{12} content had band gap energy values similar to those reported for TiO_2.

These systems were highly active in the photocatalytic degradation of 4-chlorophenol and they could be reused at least three times with minimal decreases in the degree of degradation of 4-chlorophenol attained. This stability was probably related to the formation of the ammonium salt of PW_{12}, which is insoluble. An increase of the photocatalytic activity was observed when the amount of PW_{12} increased, showing its direct participation in the degradation of the organic substrate (Equations (2) to (4)) and/or in the production of the $\cdot$OH reactive species (Equation (5)) that participates in the degradation of the organic substrate S (Equation (6)).

$$PW_{12} + hv \rightarrow PW_{12}*, \tag{2}$$

$$PW_{12}* + S \rightarrow PW_{12}^{-} + S^{+}, \tag{3}$$

$$PW_{12}^{-} + O_2 \rightarrow PW_{12} + O_2^{-}, \tag{4}$$

$$PW_{12}* + H_2O \rightarrow PW_{12}^{-} + \cdot OH + H^{+}, \tag{5}$$

$$\cdot OH + S \rightarrow \text{oxidation products}. \tag{6}$$

Additionally, the increase in the catalytic activity may be due to the lower band gap values of the samples with higher PW_{12} contents, which would increase the capacity to absorb higher wavelength radiation.

Later, the same authors used the catalysts prepared on Y zeolite for the photodegradation of methyl orange [61] and those prepared on ZSM-5 for the photodegradation of waste water containing azo dyes [62]. The highest photocatalytic activity was obtained for a 30 wt % HPW_{12} loading. The catalyst separated by filtration and treated at 400 °C for 2 h could be reused without significant decrease of the conversion.

Ozer *et al.* studied the photocatalytic oxidation of aqueous solutions of 1,2-dichlorobenzene by polyoxometalates supported on NaY zeolite [63]. Three different polyoxometalates were used, $H_2NaPW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$. The catalysts were prepared *in situ* by the polyoxometalate, the zeolite and the solution of dichlorobenzene mixing in the reactor. Preliminary experiments had shown that there was adsorption of the polyoxometalate on the zeolite but, unfortunately, no characterization data was presented, with only the catalytic performances being reported. However, even if they did not characterize their catalysts, the authors pointed out their complexity.

Very recently, Marchena *et al.* reported the synthesis and characterization of $HSiW_{12}$ supported on NH_4Y and NH_4ZSM-5 and its use in the photodegradation of methyl orange [64]. The catalysts were prepared by wet impregnation at 80 °C with polyoxometalate loading varying between 5 and 30 wt %. The Si/Al ratio of the zeolites was 2.47 for NH_4Y and 17 for ZSM-5. The samples were characterized by various methods, but the most important results were obtained by XRD, which showed some additional peaks compared to those of the starting zeolite. These peaks were due to the presence of the ammonium salt of SiW_{12}. The formation of this new phase can be easily understood, as in solution there is an exchange between the ammonium ions of the zeolite and the protons of the polyoxometalate. This reaction is in equilibrium, but, as the ammonium salt of SiW_{12} is insoluble, it drives the equilibrium to yield the ammonium salt. The only limitation could be the ammonium content of the zeolite, but even for ZSM-5, which had the highest Si/Al ratio with the highest SiW_{12} loading, there are more than two ammonium ions per proton of the polyoxometalate. A kinetic study of the photocatalytic degradation of methyl orange showed a linear dependence of the reaction rate on the amount of SiW_{12} in the solid, due to its direct participation in the catalytic cycle. As with the previous studies by the same authors with PW_{12}, the catalyst could be reused without any problems.

5.4.2. Systems with Titanium

Rayalu and coworkers developed the synthesis of photocatalytic systems based on heteropolyacids, TiO_2 and Y zeolite [65–70]. The zeolite used for these studies was the commercial faujasite with a Si/Al ratio of 2.5. TiO_2 was first introduced by reaction of titanium isopropoxide with the Y zeolite, followed by calcination at 500 °C. In some cases, titanium was introduced by other ways [66]. The $HPMo_{12}$ heteropolyacid was then introduced by a classical impregnation. In some cases, partial replacement of the zeolite cations by exchange with Co^{2+} was conducted prior to the reaction with the polyoxometalate. These materials were characterized by infrared and UV–Visible spectroscopies, XRD and chemical analysis. They were first tested in the photocatalytic reduction of methyl orange in aqueous solution with ethanol as a sacrificial electron donor [66,68]. The composite containing cobalt photoreduced methyl orange to an extent of about 4.11 mg/g TiO_2 and showed a better photocatalytic activity as compared to the same catalyst without cobalt, showing the role of transition metal ions.

A mechanism was proposed based on these considerations:

- A charge separation is created in the TiO_2 species upon irradiation by the UV component of the light source.
- The electron from the conduction band of TiO_2 is transferred to the polyoxometalate, which is reduced to a visibly active species PM_{12}^{-}.

- This reduced species is excited by the visible radiation leading to an excited PM_{12}^{*} species, which is able to transfer the excited electrons to the transition metal in the zeolite. This transfer is not direct but occurs via the Lewis acid sites of the zeolite.
- The excited species PM_{12}^{*} can also be formed by direct excitation of the polyoxometalate by the UV radiation followed by a reduction via the sacrificial electron donor.
- Finally, the substrate reacts with the transition metal.

A study of the effect of the method used for the introduction of phosphomolybdic acid was reported in [69]. Three different methods were used: adsorption, impregnation and encapsulation. For the adsorption procedure, the zeolite was treated with a solution containing PMo_{12} for one hour and then isolated by filtration. The adsorption cycle was repeated three times. Impregnation was made by the procedure already outlined above. Encapsulation was made by using the method of Mukai *et al.* but starting from commercial Y zeolite (Si/Al = 2.5). The amounts of Mo observed in these materials were (in mg/g of catalyst) 0.88 for adsorption, 42.42 for impregnation and 4.31 for encapsulation, while the conversion of methyl orange was 12%, 51% and 19%, respectively. It was concluded that the sample prepared by impregnation was the most active and a study as a function of the PMo_{12} loading showed that at lower and higher loadings the efficiency was lower. However, it is interesting to note that the materials prepared by adsorption and encapsulation were also active, but with Mo loadings which are at least 10 times lower than those achieved by impregnation.

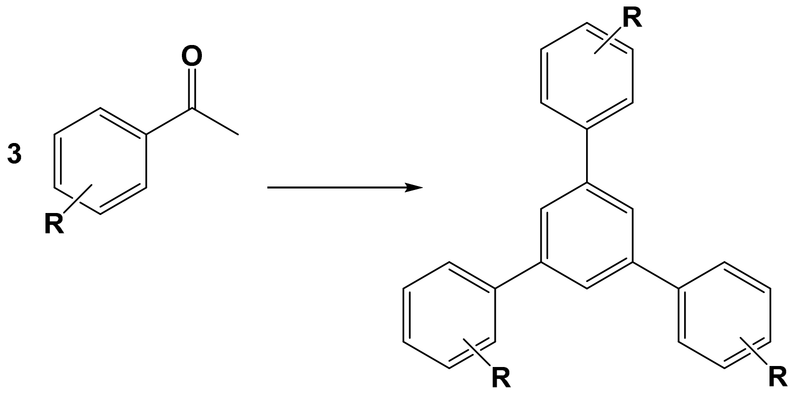
Three sets of material were prepared by the impregnation procedure, starting from Y zeolite, dealuminated Y zeolite (Si/Al = 80) and β zeolite (Si/Al = 15), were also tested in the water splitting reaction for the production of hydrogen [65,67]. Only the samples prepared from classical Y zeolite were active for both the methyl orange photoreduction and the water splitting reaction. As above, the introduction of cobalt enhanced not only the visible light absorption of the material but also its photocatalytic efficiency. In the absence of cobalt, the hydrogen yield was about 3000 μmol/h/g TiO_2 when illuminated in the UV range, a value quite low as compared to those reported in the literature. In the presence of cobalt, the hydrogen yield was 2300 μmol/h/g TiO_2, but in the visible range, a value which is high for these illumination conditions. In other publications, various parameters were studied in order to optimize the hydrogen yield [70,71], for example, the nature of the zeolite (Y zeolite, ultrastable Y zeolite, titanium silicalite, β zeolite) and the method of introduction of the polyoxometalate (impregnation, direct encapsulation by *in situ* synthesis). In these studies, again only the system obtained on Y zeolite through impregnation of the polyoxometalate led to hydrogen evolution.

Najafabadi and Taghipour [72,73] prepared composites by a similar protocol: First of all, TiO_2 was synthesized on/in the zeolite by hydrolysis of titanium isopropoxide. Cobalt was then introduced by exchange with the cations of the zeolite and, finally, the polyoxometalate ($HPMo_{12}$) was introduced by impregnation. The solids were characterized by Energy Dispersive X-ray Spectroscopy (EDX), nitrogen adsorption, Scanning Electron Microscopy (SEM) and UV–Vis reflectance spectroscopy. In the first paper [72], the zeolites studied were NaY (Si/Al = 2.55) and Na-mordenite (Si/Al = 6.5). In the second paper, HY (Si/Al = 15) and Hβ (Si/Al = 12.5) were also used [73]. These materials were used for the photocatalytic degradation of 2,4-dichlorophenoxyacetic acid and the photocatalytic hydrogen evolution. An effect of the remaining anion of the cobalt salt used for the exchange was evidenced, with nitrate leading to a 30% lower hydrogen production than chloride. The hydrogen production was also higher with the sodium-exchanged zeolites. This was explained by the pH dependency of the TiO_2 band edges. In these solids, TiO_2 was the semiconductor, cobalt ions were the hydrogen evolution sites and the heteropolyacid was the multifunctional solid acid with significant excitability under visible light. This interpretation is quite similar to that of Rayalu.

6. Other Polyoxometalates Supported on Zeolites

Other polyoxometalates have also been supported on zeolites. Typically, these compounds were lacunary Keggin species, although a few studies with alternate structures have also been reported.

Very recently, Tayebee *et al.* prepared heteropolyacids on nanoclinoptilolite and studied them in the cyclotrimerization of aryl methyl ketones [74] (Scheme 8). Various heteropolyacids were used, $HPMo_{12}$, HPW_{12}, $HPW_{10}V_2$ and $H_6P_2W_{18}O_{62}$. Only the sample with this late polyacid was fully characterized, as it was the most active system. Clinoptilolite is a zeolite containing two types of channels, those composed of eight and 10 membered rings, respectively [75]. The maximum diameter of a sphere that can be included in its framework is 5.97 Å [11], so polyoxometalates cannot be incorporated within it and can, therefore, only be deposited on its external surface. In order to increase the sorbed amount, nanocrystals (size *ca.* 40 nm) were used, with the cations initially replaced by protons through exchange with ammonium and subsequent calcination. A study of the adsorption of $H_6P_2W_{18}O_{62}$ showed that it follows a Langmuir isotherm with adsorption of 200 mg of polyacid per gram of clinoptilolite. This value is compatible with an adsorption of the external surface of the zeolite as it corresponds to a surface of *ca.* 40 m^2 per gram of zeolite. The solid was characterized by various methods including X-ray diffraction, infrared and UV–Visible spectroscopies and SEM. It was used in the cyclotrimerization of various aryl methyl ketones and shown to be recycled without a noticeable loss of activity.

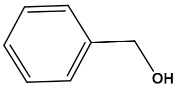
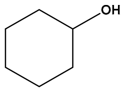
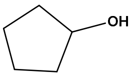
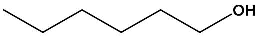
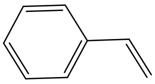
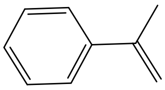
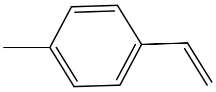


Scheme 8. Cyclotrimerization of aryl methyl ketones.

Narkhede and Patel reported the synthesis of a recyclable catalyst comprising a monolacunary silicotungstate $[SiW_{11}O_{39}]^{8-}$ (SiW_{11}) supported on zeolite Hβ [76]. The polyoxometalate was as a sodium salt (acidic or not, no data were given about this point) and it was deposited on Hβ zeolite by impregnation. Various loadings between 10 and 40 wt % were prepared. The impregnated materials were treated with 10% 0.1 M HCl and then washed with distilled water. As SiW_{11} is not stable in these conditions, this treatment has probably transformed part of it into SiW_{12} and/or has replaced some sodium ions by protons. An interesting point is the presence of mesopores in this zeolite (diameter 2.48 nm), whose diameter decreases after adsorption of SiW_{11} (to 1.71 nm) proving that the polyoxometalate is located inside them. The acidity was determined by *n*-butylamine titration and the solids were used in the esterification of oleic acid by methanol and the transesterification of soybean oil. The reaction is purely heterogeneous and the catalyst can be reused without loss of activity or leaching. As the cations are composed solely of protons and sodium ions, the absence of leaching is surprising. One explanation should be that the negative charges of SiW_{11} are partially compensated by protons of the zeolite, leading to a cation/anion interaction that stabilizes it. Note that this interaction is more stable than that occurring when a polyacid is deposited on silica [36]. These authors have recently used these catalysts for the valorization of glycerol via acetalization and carboxylation reactions [77].

Later, the same group reported the synthesis of PMo_{11} supported on the same zeolite Hβ and its use in the aerobic oxidation of alcohols and alkenes [78]. The preparation was quite similar to that reported above but no treatment with HCl was conducted. The catalyst loading varied from 10 to 40 wt %. The system with 30 wt % PMo_{11}, which displayed the highest catalytic activity, was fully characterized. Differential Thermal Analysis showed an increase of the thermal stability of the polyoxometalate upon deposition on the zeolite (from *ca*. 300 to 350 °C). Infrared and Raman spectroscopy, as well as XRD, were in full agreement with the conservation of the structure of the polyoxometalate, but the ^{31}P MAS NMR spectrum showed unambiguously that a partial degradation occurred upon impregnation, with formation of PMo_{12} (peak at -4.3 ppm) and an unknown species (peak at +2.6 ppm). The catalysts were used in the catalytic oxidation by oxygen of benzyl alcohol or styrene at 80 and 90 °C, respectively. A small amount of *t*-butyl hydrogen peroxide was added to initiate the reaction. The major reaction product in the two cases was benzaldehyde (the selectivity was 90% when starting from benzyl alcohol). Very high turnover numbers (TON) were achieved (*ca*. 10,000 for the alcohol and more than 20,000 for styrene). The catalyst could be reused at least two times without any loss of activity and no leaching was observed. Finally, the study was extended to other alcohols and alkenes (see Table 4).

Table 4. Catalytic oxidation of various substrates by oxygen catalyzed with $PMo_{11}/H\beta$ [78] [a].

Substrate	Conversion (%)	Selectivity (%)	TON
	25.5	90	9551
	21	>99	8590
	20	>99	8171
	9	>99	3745
	57	72	20,975
	59	70	22,099
	50	67	18,728

[a] Reaction conditions: For alcohols $T = 90$ °C and $t = 24$ h; for alkenes $T = 80$ °C and $t = 8$ h, catalyst amount *ca*. 0.2 wt %.

7. Conclusions

As shown in this review, there are different ways to obtain composites based on polyoxometalates and zeolites: (i) The polyoxometalate can be synthesized in the presence of the zeolite; (ii) the zeolite can be synthesized in the presence of the polyoxometalate and (iii) the zeolite and the polyoxometalate can be contacted, for example, by impregnation.

When the polyoxometalate is synthesized in the presence of the zeolite, encapsulation can occur only in the case of faujasite. For all other zeolites, the polyoxometalate will be located on the exterior of the crystal. The effect of the Si/Al ratio of faujasite is also very important, as encapsulation seems to proceed only for dealuminated samples, although some recent reports describe a preparation with low Si/Al ratios, full characterization of these materials remains unpublished. Another consideration is the identity of the cation in the zeolite. As ammonium and cesium lead to insoluble salts of the Keggin polyoxometalates, their presence favors the formation of catalysts that can be recycled in polar solvents. However, dealuminated Y zeolite contains small mesopores where the polyoxometalate can be localized and it is difficult to determine if the preparation will lead to a purely encapsulated Keggin ion (located in the supercage) or if it will be located in these mesopores. The main conclusion of all these studies is that, in the majority of cases, either no encapsulation or only partial encapsulation occurs.

When the zeolite is synthesized in the presence of the polyoxometalate, the zeolite is always faujasite, the aim being to obtain encapsulation. However, the preparation method involves the introduction of the polyoxometalate in a very basic medium, in which it is not stable. Surprisingly, at the end of the reaction, it has been reformed but its exact location remains controversial.

Finally, the last method, which is also the easiest, allows for the preparation of catalysts that can have similar properties to those prepared by the two above procedures. The major advantage is that many parameters can be varied easily, such as the polyoxometalate loading, the nature of the zeolite, its cations, *etc.* Recyclability in polar solvents can be achieved by the introduction of cations such as ammonium or cesium. This can be done by using a zeolite containing these cations or by introducing them by impregnation, after the impregnation of the polyoxometalate. However, these cations will preclude the use of these systems for reactions requiring a Brönsted acid, in which case encapsulation remains the best proceedure.

In concluding this review, we wish to report a new method, which is completely different from those described above and which is very original, that is the synthesis of HPW_{12} in the hollow voids of silicalite [79]. Silicalite-1 is first treated by tetrapropylammonium hydroxide, leading to the creation of regular hollow voids in the interior of the crystals, the thickness of the shell being about 10–20 nm. HPW_{12} is then synthesized from Na_2WO_4, Na_2HPO_4 and HCl in the suspension of the hollow zeolite in water at pH = 1.0. As Na_2WO_4 and Na_2HPO_4 are smaller than the pore size of silicalite-1, they can enter and exit the hollow nanospheres through the micropores of the zeolite. They react then inside the hollow nanospheres, leading to the formation of HPW_{12}, which cannot escape as they are too large to pass through the microporous channels of the shell. After washing with water 6–10 times, the solid is used in a model reaction, the esterification of acetic acid with ethanol. No deactivation is observed even after five recycle runs. This method could be applied to other zeolites—for example, faujasite—and could allow for the obtention of catalysts combining the activity of the polyacid and the separation properties of the zeolite. Due to the law of micro-reversibility, this method could lead to unexpected selectivities.

Conflicts of Interest: The author declares no conflict of interest.

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