# Novel "ship-in-the-bottle" type catalyst: evidence for encapsulation of 12-tungstophosphoric acid in the supercage of synthetic faujasite

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A new type of "ship-in-the-bottle" catalyst has been obtained by encapsulation of heteropolyacid $H_3PW_{12}O_{40}$ in the supercage of faujasite. As shown by XRD and IR, the structure of zeolite Y after encapsulation is retained. $^{31}P$ MAS NMR reveals that the signal at −14.4 ppm, assigned to the Keggin unit, is in the case of the encapsulated catalyst much broader than the line observed for a sample containing the heteropolyacid adsorbed on the zeolite. The broadening is due to interaction between phosphorus and aluminium from zeolite. Highly active catalysts are formed by encapsulation, as exemplified here by strongly increased activity and modified selectivity in isomerization and disproportionation of *m*-xylene.

**Keywords:** heteropolyacid in zeolite; faujasite with $H_3PW_{12}O_{40}$; encapsulation of $H_3PW_{12}O_{40}$ in faujasite; *m*-xylene conversion

Heteropoly oxometalates with the Keggin structure are well known as oxidation and acid catalysts, in which the redox and acid–base properties may be tailored by choosing different heteroatoms, different atoms of the addenda or substituting the addenda with altervalent ions [1]. A few processes which utilize heteropoly compounds as catalysts have already been implemented on an industrial scale. One of the compounds which in recent years attracted considerable interest because of its very strong acidity accompanied by redox properties is 12-tungstophosphoric acid $H_3PW_{12}O_{40}$ ($PW_{12}$) [1]. Its application as heterogeneous catalyst is, however, hindered by its low thermal stability and a very high solubility in water, the catalyst being thus decomposed or taken away from the reactor by the flow of the reactants.

It seemed that the shortcomings of heteropoly compounds as catalysts would be eliminated while their virtues strengthened by designing a novel catalytic system using the encapsulation and thus immobilisation of the Keggin units in a zeolitic matrix. In this paper we will demonstrate that 12-tungstophosphoric acid ($PW_{12}$) can be not only *adsorbed*, but also *encapsulated* in the supercage of faujasite type zeolite (FAU). $PW_{12}$ in the solid state displays an acidity stronger than −8.2 in $H_0$ [2,3]. Of about 85 structures known [4], faujasite has been chosen as a zeolitic matrix, since its channel system consists of large nearly spherical cavities (supercages or $\alpha$-cages). The building blocks of zeolite Y, a synthetic analogue of the rare mineral faujasite, are truncated octahedra joined together via hexagonal biprisms, thereby yielding supercages. Each supercage is linked, in a diamond-like arrangement, to four others by the smaller 12-membered ring openings (ca. 7.4 Å). The primary structure of the $PW_{12}$ consists of Keggin heteropoly anions with diameter of ca. 12 Å (fig. 1). As the diameter of the faujasite supercage is only slightly larger than that of the anion, it seemed that, due to geometrical considerations, the $PW_{12}$–FAU system would constitute an ideal choice for attempts aimed at encapsulation of the Keggin unit in the faujasite supercage. Indeed, computer graphics show that the Keggin unit [$PW_{12}O_{40}$] fits well in the supercage of FAU (fig. 2) [#1].

As-prepared zeolite Y, typically with Si/Al ratio of 2.5, is unstable in strong acid solutions, which attack its framework yielding an amorphous product. We have therefore prepared a number of faujasitic solids with the silicon-enriched framework, by using $SiCl_4$, $H_4EDTA$ and $(NH_4)_2SiF_6$ treatments [5]. During the dealumination of zeolite Y some tetrahedral aluminium ions are being extracted from the framework to yield solids with increased Si/Al ratio, while preserving the structure of faujasite.

Zeolite Na-Y, highly crystalline according to X-ray studies, with Si/Al = 2.47 and Na/Al = 1.09 as determined by atomic absorption (AA), was used as the parent material. As the lithium-exchanged samples were superior over Na-Y for dealumination with $SiCl_4$ [6,7], the zeolite was ion-exchanged with 10 wt% lithium nitrate solution at 353 K (sixfold), washed until $NO_3^-$ free and dried. The resulting Li,Na-Y was dehydrated overnight and dealuminated in a fixed-bed quartz reactor by silicon tetrachloride vapour in nitrogen stream at 670 K. The stabilised sample was cooled, washed with distilled water and dried. The $(Si/Al)_F$ of the sample was 41. Another part of zeolite Na-Y was dealuminated chemically by means of ethylenediaminetetra-acetic acid

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[#1] Fig. 1 was drawn by using the graphical program BALSAC, for which we are indebted to Professor Klaus Hermann from the Fritz Haber Institute of the Max Planck Society, Berlin.

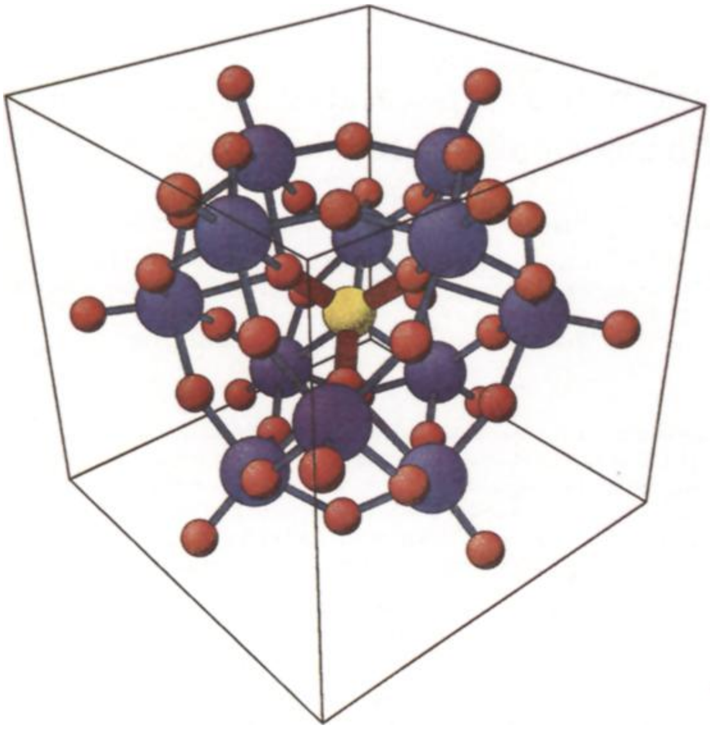

Fig. 1. The structure of the Keggin heteropolyanion $(PW_{12}O_{40})^{3-}$. Phosphorus is yellow, tungsten deep blue and oxygen red.

($H_4$EDTA). Dealumination proceeds stoichiometrically so that the desired aluminium content may be readily obtained by using the calculated amounts of $H_4$EDTA. The degree of dealumination by $H_4$EDTA was chosen to extract about 50% of the framework aluminium. The rate of $H_4$EDTA addition, essential to reduce amorphization of the zeolite, was kept low at 0.01 g $H_4$EDTA per 1 g zeolite per 1 h. Dealumination was carried out under

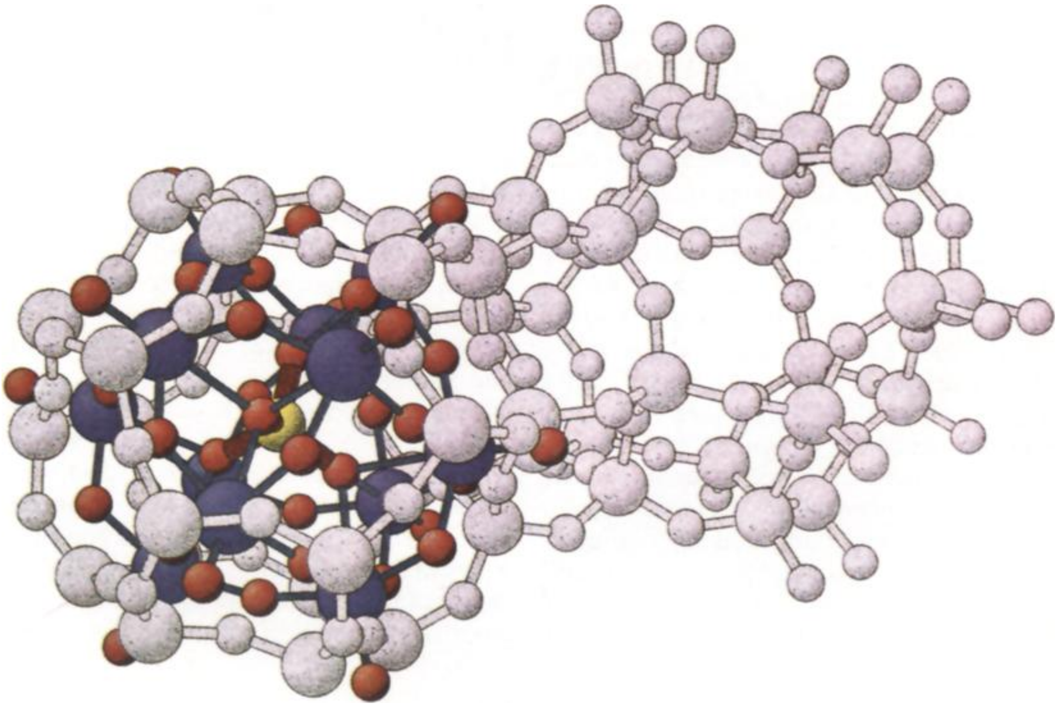

Fig. 2. The Keggin anion $(PW_{12}O_{40})^{3-}$ encapsulated in one of the two faujasite supercages shown. Atoms are coloured as in fig. 1.

stirring at 360 K and the process was continued for 4 h after all the acid had been added. The dealuminated sample was washed with hot distilled water, dried and ion-exchanged with 10 wt% $NH_4Cl$ solution. Its Si/Al framework ratio was 4.86, and the sample contained, except micropores, a secondary pore system with the diameter of 15 Å. Removal of some sodalite cages (truncated octahedra) is responsible for the formation of mesopores. It is known that attack of bulky $H_4EDTA$ acid on faujasite proceeds from the rim to the core of the crystal, leaving the external parts of crystals more siliceous, while their diameter is unaffected by the treatment [8].

Pure 12-tungstophosphoric acid has been synthesised from sodium phosphate, sodium tungstate and purified [9]. IR spectrum of the acid is shown in fig. 3a. Four absorption bands at 1080, 982, 892 and 789 $cm^{-1}$ are typical of the Keggin unit. The lines at 1080 and 982 $cm^{-1}$ are assigned to P–O and W=O groupings, while the two other are due to W–O–W vibrations. The spectrum is similar to that published earlier by Rocchiccioli-Deltcheff et al. [10].

A zeolitic matrix for encapsulation was prepared by treating zeolite Y with the silicon tetrachloride vapour, followed by intensive washing with distilled water. Fig. 3b shows its IR spectrum. Encapsulation of the $PW_{12}$ acid in the matrix has been performed [11] to yield the sample labelled $PW_{12}$/FAU(enc). Evidence of encapsulation, in contrast to *adsorption* and *deposition* of $PW_{12}$ on the external surface of zeolite (cf. the text below), comes from FT IR and $^{31}P$ solid-state MAS NMR studies. In fig. 3c the IR spectrum of $PW_{12}$/FAU(enc) is given. As seen, all the lines characteristic of zeolite (fig. 3b) remained unaffected, thus we did not observe the collapse of its lattice upon contact with the very strong acid $PW_{12}$. The lines of $PW_{12}$ at 1080 and 789 $cm^{-1}$ overlap with those of the zeolite matrix, in the spectrum one can notice an increased intensity of the line at 789 $cm^{-1}$, and also a new broad band at 953 $cm^{-1}$. The latter one may be assigned to the stretching vibrations of the W=O groups sticking out of the Keggin unit and hence shifted from 982 $cm^{-1}$ due to interaction with the supercage of faujasite.

We have also prepared, for comparison, a number of solids obtained via impregnation of the 12-tungstophosphoric acid, from various solutions, on the faujasite matrix dealuminated by $H_4EDTA$ acid, followed by evaporation of the solvent. In fig. 4b a typical spectrum of $PW_{12}$ adsorbed on the dealuminated zeolite is shown. In the spectrum three bands typical of the $PW_{12}$ bulk crystalline phase can be discerned, at 805, 895 and a shoulder at 983 $cm^{-1}$. The fourth band is hidden under the intense line of the Si–O asymmetric stretching vibrations of the support.

NMR is an indispensable tool for further characterisation of the novel catalyst. In fig. 5 the $^{31}P$ magic-angle-spinning NMR spectra of the samples are visualized.

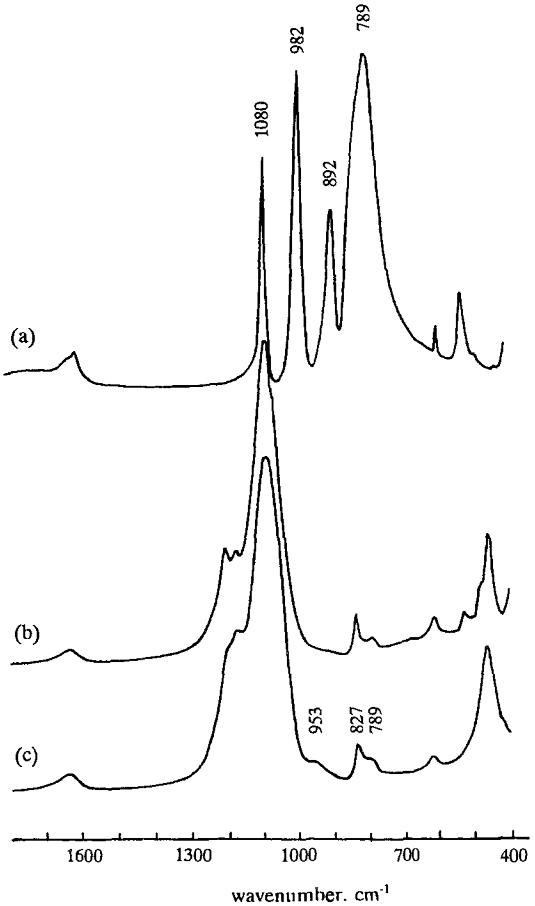

Fig. 3. FT IR spectra of pure 12-tungstophosphoric acid ($PW_{12}$) (a), the zeolitic matrix dealuminated with $SiCl_4$ treatment (b), and $PW_{12}$ *encapsulated* in the faujasitic matrix $PW_{12}$/FAU(enc) (c).

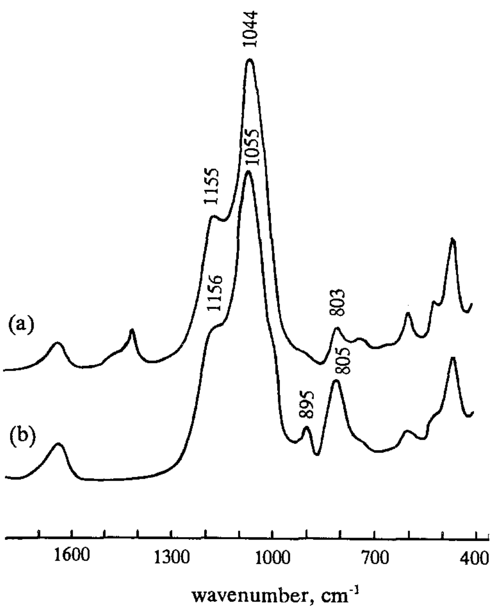

Fig. 4. FT IR spectra of zeolite Y dealuminated with ethylenediaminetetra-acetic acid ($H_4EDTA$) (a) and $PW_{12}$ *adsorbed* on the dealuminated matrix from ethyl ether solution (b).

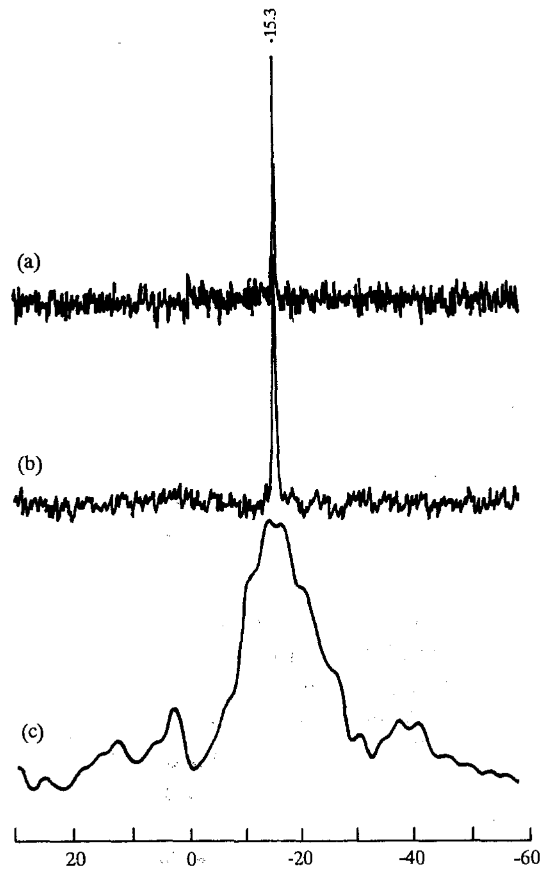

Fig. 5. Solid-state $^{31}P$ MAS NMR spectra of pure 12-tungstophosphoric acid ($PW_{12}$) (a), and $PW_{12}$ adsorbed (b) and encapsulated (c) in the faujasitic matrix. The spectra were recorded on a Bruker MSL-300 spectrometer; the rotors were spun at 4 kHz. For details see text.

Pure crystals of the 12-tungstophosphoric acid give a line at −15.3 ppm, with a small splitting seen at −15.6 ppm (fig. 5a). The origin of the latter is not yet known. The linewidth is ca. 1 ppm. Upon adsorption of $PW_{12}$ onto zeolite again one signal from phosphorus nuclei at the same position is seen (fig. 5b). While the width is slightly broader, it remains essentially the same (ca. 1.2 ppm). This points to the lack of interaction between the zeolite and the acid, and the latter behaves as a bulk compound (XRD does not, however, reveal the presence of a separate heteropoly acid phase). The spectrum of $PW_{12}$/FAU(enc) is dramatically different (fig. 5c). The spectrum is much broader (ca. 14.5 ppm), with the chemical shift at −14.4 ppm. This broadening is due to the heteronuclear second-order dipole/quadrupolar interaction cross term [12] between phosphorus atoms of the Keggin anion and aluminium in the zeolitic matrix. Such interaction is proportional to the dipole–dipole coupling between $^{31}P$ and $^{27}Al$, to the quadrupolar coupling constant of aluminium, and inversely proportional to the Larmor frequency. We note that the anisotropy of this term is not removed by magic-angle spinning, because of different spatial symmetry. The spectrum constitutes therefore a direct proof that: (i) the Keggin units are indeed present in the sample; and (ii) there is an interaction between the host and the guest. Such an interaction was not observed in the sample prepared via standard impregnation and *adsorption* of the heteropoly compound on the faujasitic matrix.

Catalytic properties of the novel $PW_{12}$–FAU hybrid catalysts have been examined in the isomerisation and disproportionation of *m*-xylene. The course of the reaction depends on the strength of Brønsted acid sites and the geometry of zeolite [13]. In particular, acid sites with higher strength are needed for disproportionation of dialkylbenzenes. Development of the strong acidity of the catalyst containing encapsulated and isolated Keggin units can be easily demonstrated by comparing the low conversion of *m*-xylene on the pure zeolite matrix (7.5–9.5%) with a very high conversion 23.7–52.6% observed on the $PW_{12}$–FAU(enc) catalyst at 573–648 K (fig. 6). Residual activity of the matrix is due to few Brønsted acid centres present in the sample (note that the matrix contains few tetrahedral aluminium atoms per unit cell). Moreover, disproportionation of *m*-xylene to toluene and trimethylbenzenes (TMB) is hindered on the matrix, while large amounts of toluene and TMB were found on the hybrid catalysts (cf. table 1). Such a selectivity points to the presence of very strong acid sites in the catalyst.

To conclude, we have demonstrated, for the first time, that a novel highly acidic ship-in-the-bottle type catalyst can be obtained by encapsulation of 12-tungstophosphoric acid in the supercages of zeolite Y. The guest–host interaction has been revealed by using solid-state $^{31}P$ MAS NMR. The novel catalyst displays high activity in the conversion of alkylaromatics, exemplified

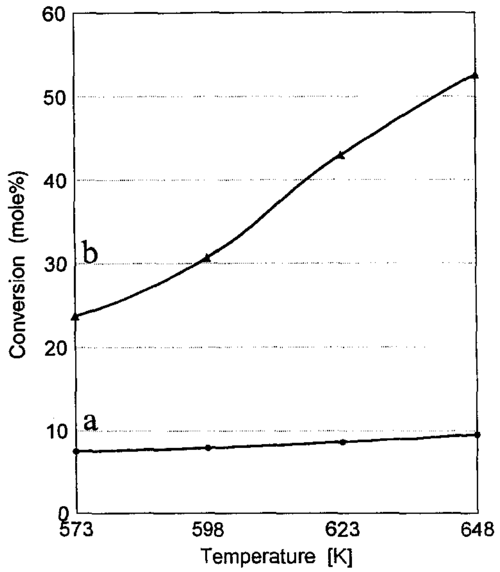

Fig. 6. Overall conversion of *m*-xylene (mol%) on the zeolitic matrix (a) and $PW_{12}$/FAU(enc) catalyst (b). The conversion was measured in a pulse mode microreactor, connected on-line to a GCHF gas-chromatograph, equipped with a TCD detector.

Table 1

Selectivity of *m*-xylene conversion towards toluene and trimethylbenzenes on pure faujasite matrix and 12-tungstophosphoric acid encapsulated in the zeolitic support

| Catalyst | Selectivity towards toluene + trimethylbenzenes (%) | | | |
|---|---|---|---|---|
| | 573 K | 598 K | 623 K | 648 K |
| faujasitic matrix (FAU) | 3.84 | 5.42 | 9.13 | 16.65 |
| $PW_{12}$/FAU(enc) | 51.29 | 53.58 | 57.54 | 59.87 |

here by isomerisation and disproportionation of *m*-xylene.

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