

Heteropoly anion on carbon: characterization and use in 2,3,6-trimethylphenol oxidation

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Abstract

Heteropoly anion on modified carbon ($\text{PMo}_9\text{V}_3\text{O}_{40}^{6-}$) is an effective catalyst for the oxidation of 2,3,6-trimethylphenol with molecular oxygen in AcOH/ H_2O 95/5 vol%. The selectivity and activity of this catalyst relates to the carbon's surface modification. Heteropoly anions (HPAs) are strongly adsorbed to N-containing carbons. HPA adsorption can occur by coulombic attraction to protonated N-containing functional groups. HPAs retain the Keggin structure upon adsorption according to FTIR data. The solvent and the carbon surface chemistry determine the leaching of HPA, which is almost zero for N-containing carbon-supported HPA in acidic media.

Keywords: Heteropoly anion; Molybdovanadophosphate; Modified carbon; 2,3,6-Trimethylphenol; Oxidation; Molecular oxygen; FTIR spectroscopy

1. Introduction

Heteropoly anions (HPA) and activated carbons (C) offer a gainful combination to catalysis in organic chemistry; HPAs, on one hand, are versatile building blocks for catalytic systems, being able to act as Brønsted acids and as redox catalysts [1], carbons, on the other hand, are inert and stable carriers with an excellently accessible pore system that can host molecules of a wide range of sizes. We previously applied HPA/C in the esterification of phthalic anhydride with 2-ethylhexanol [2] and, present here its use, in the oxidation of 2,3,6-trimethylphenol (TMP).

Recently we described convenient chemical modification methods for the carbon surface [3,4], aiming amongst others at introducing surface functional groups as anchoring sites for HPAs. The interaction strength of HPA with C is

expected to depend on the functional group which is built into the surface of activated carbons. In the present paper the adsorption and desorption of $\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}$ (PMoV) is compared for carbons with a graphitic surface (C), carbons containing carboxylic acid functional groups (CN) and carbons with amide, imide and lactam functional groups (CAm and CNA). The integrity of the HPA structural unit (Keggin structure), when loaded on carbon, is shown through FTIR spectroscopy.

PMoV is an effective homogeneous catalyst in the synthesis of 2,3,5-trimethylbenzoquinone (TMBQ), which is an intermediate in the vitamin E synthesis. The vanadyl cation VO_2^+ was identified as the catalytic active species, which is effectively reoxidized by HPA. That V is predominantly present as V(V) indicates that the reoxidation step is fast [5]. One of the practised

TMBQ processes is the Mitsubishi GC process using copper chloride [6]. The present production methods may be improved with more stable catalysts and easier workup. Here we report the oxidation of TMP with O₂ to TMBQ over PMoV on modified carbon suspended in AcOH/H₂O 95/5 vol.%. The systems activity and selectivity towards the product may be improved by engineering the surface chemistry of the carbon.

2. Results and discussion

2.1. The surface chemistry effect of the carbon support on the adsorption and desorption of PMoV

As HPAs are known to exist in rapid equilibria in aqueous solution, exchanging Mo and V ions, the elements were monitored separately upon adsorption [7]. The PMoV adsorption isotherms, based on the element P, for several carbon modifications are given in Fig. 1. These adsorption isotherms were determined with very diluted PMoV solutions, to prevent disturbances by differences in the pH of the samples as adsorption progresses. It may be noted that the conditions in these experiments deviate substantially from those used in the regular loadings. The adsorption constants at low concentrations ($K_{\text{ads}}^{\text{X}} = nX_{\text{ads}}/[X]_{\text{aq}}$) are summarized in Table 1. At higher loadings K_{ads}

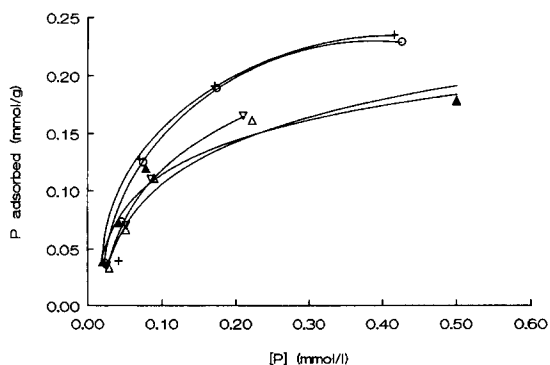


Fig. 1. P adsorption isotherms for the adsorption of HPMoV on parent carbons C (+, RA⁺0.8 and ∇, RH0.8), HNO₃ oxidized carbon CN (Δ, RA⁺0.8N01) and aminated carbons CNA (O, RA⁺0.8N01A01 and ▲, RH0.8N01A01) (150 mg carbon in 100 ml demineralized water with 15, 30, 50, 90 or 150 mg PMoV at pH 1.47 and 20°C).

Table 1

Adsorption constants for the individual elements P, Mo and V at very low HPMoV concentrations, derived from the adsorption isotherms on C, CN and CNA carbon modifications

Element	$K_{\text{ads}} (l \cdot g^{-1})$
P	1.4
Mo	5
V	0.2

[P] < 80 · 10⁶ M and P_{ads} < 120 · 10⁻⁶ mol · g⁻¹, [Mo] < 250 · 10⁻⁶ M and Mo_{ads} < 1500 · 10⁻⁶ mol · g⁻¹ and [V] < 500 · 10⁻⁶ M and V_{ads} < 120 · 10⁻⁶ mol · g⁻¹.

decreases for all elements. All activated carbons have an increasing affinity for the elements in the following series Mo > P > V, but the P, Mo and V isotherms are similarly shaped. For all elements the same order in the adsorbed amount onto the carbon is observed: RA⁺0.8 ≈ RA⁺0.8N01A01 > RA⁺0.8N01 > RH0.8 ≈ RH0.8N01A01. (also see sections 4.1 and 4.2; Nx is the code for nitric acid oxidation, portion x, and Ay is the code for NH₃ treatment, portion y). Both the porosity and the surface chemistry of these carbons are assumed to determine this order.

After continuous leaching with hot water C, CN and CNA are loaded with 23 wt.%, 19 wt.% and 27 wt.%. Leaching of PMoV on CAm (35 wt.%) with AcOH (continuous), 0.01 M HCl ($T = 50^\circ\text{C}$, batch) or AcOH/H₂O 95/5 vol% ($T = 50^\circ\text{C}$, batch) desorbed only 1 wt.% from the carbon. A second desorption step did not extract any further amount of HPA. In Table 2 a comparison is made between the leaching of various carbon modifications with water and acidic solvents. Before leaching the molar Mo/V ratio of the adsorbed PMoV is 3 for all carbons. It appears that with water Mo is preferentially leached whereas V is preferentially extracted with acidic media. After desorption CNA is comparatively rich in Mo (Mo/V = 2.3) and CN is comparatively V rich (Mo/V = 1.5; for C Mo/V = 1.9). In conclusion PMoV remains strongly adsorbed to carbon (CAm) in acidic media as warm as 50°C, but is easily partly leached from carbons C, CN and CNA by hot water. Protons are essential for the strong adsorption of HPA to carbons. Vanadium

Table 2
The desorption of PMoV/C with various solvents

Carbon	Desorption medium	PMoV loading/wt. %		Mo/V molar ratio in eluent
		before leaching	after leaching	
C	water/50°C	43	23	7.0
CN	water/50°C	34	19	6.5
CNA	water/50°C	53	27	3.9
CAm	100% AcOH/20°C	36	35	0.31
CAm	0.01 M HCl/50°C	34	34	0.31
CAm	95% AcOH(aq)/50°C ^a	34	33	2.1

For conditions see Section 4.2.

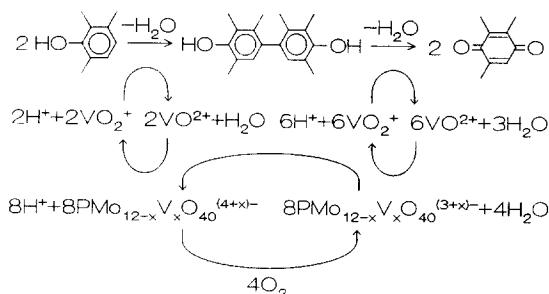


Fig. 2. The principle steps in the catalytic cycles of the oxidation of TMP over PMoV with O₂ in the presence of a water containing solvent. The formation of an intermediary biphenyl is one of the routes to TMBQ. The complete mechanism is very complicated [8].

Table 3
The turnover and formation frequencies of TMP and BP, upon TMP oxidation over the PMoV systems

Run ^a	TMP TOF(0) s ⁻¹	BP FF(0) s ⁻¹	Run	TMP TOF(0) s ⁻¹	BP FF(0) s ⁻¹
1 C	4.9 · 10 ⁻⁴	2.7 · 10 ⁻⁴	5 CAm	1.5 · 10 ⁻³	1.1 · 10 ⁻³
2 CN	5.3 · 10 ⁻⁴	0.0	6 HPMoV	1.5 · 10 ⁻²	– ^b
3 CNA	2.1 · 10 ⁻⁴	0.0	7 NaPMoV	5.6 · 10 ⁻³	1.2 · 10 ³
4 CAm	4.9 · 10 ⁻⁴	2.3 · 10 ⁻⁴			

For run conditions Sections 2.4, 2.5 and 4.3.

^a The turn-over and formation frequencies (TOF and FF) of TMP and BP (based on TMP equivalents converted into BP), respectively, over PMoV were determined at the initial stages of the reactions (60 min, 20 min for runs 6 and 7). The support applied in each run is given, runs 6 and 7 are homogeneous reactions.

^b This value was not determined.

retained better on acidic surfaces. The surface charge of activated carbons is an important factor determining the adsorption of HPA on activated carbon. Basic carbons contain relatively much proton sites at a certain pH and therefore adsorb HPAs stronger.

2.2. The characterization of PMoV on activated carbon

Absorption bands at 950 and 1050 cm⁻¹, observed by FTIR spectroscopy, can only be attributed to HPMoV/C and not to one of the oxides of the components. Interestingly the HPA seems to acquire a characteristic attributed to pure NaPMoV. A clear band is observed at 800 cm⁻¹. This indicates an interaction similar to that of sodium cations, which are incapable of forming delocalized bonds with HPA. The composition of the PMoV on carbon, with a typical Mo/V ratio = 2, is equal to that in NaPMoV.

2.3. TMP oxidation: the homogeneous versus the heterogeneous reaction

An important feature [8] of the TMP oxidation to TMBQ is the possible occurrence of the intermediary 4,4'-dihydroxy-bis-2,2',3,3',6,6'-hexamethylbiphenyl (BP, see Fig. 2). Special care was taken to prevent leaching; preleached catalysts were used in combination with a low-leaching solvent (see Table 2). At 50°C the activity (see Table 3) of PMoV/CAm run 5, a reused catalyst) is about ten times lower than that of homogeneous HPMoV (run 6) and comparable to that of homogeneous NaPMoV (run 7). The selectivity (see Table 4) of this supported system is higher than that of HPMoV, but less than that of NaPMoV. The CAm-supported system is promising as only BP and TMBQ form, BP may be further oxidized

Table 4
The conversion and selectivities to BP and TMBQ at 5 and 23 h

Run ^c	mol% ^a after 300 min ^b			mol% after 1380 min		
	Conversion	BP	TMBQ	Conversion	BP	TMBQ
1 C	80	21	32	100	5	55
2 CN	65	0	31	100	0	71
3 CNA	67	0	35	100	0	64
4 CAm	50	45	5	98	70	28
5 CAm	66	43	13	100	5	59
6 HPMoV	100	0	61	–	–	–
7 NaPMoV	100	1	82	–	–	–

For conditions Sections 2.4, 2.5 and 4.3.

^a The mol% are based on the amount of TMP found or converted into products (thus the actual molar amount of BP is half of the tabulated mol%).

^b The sampling time for runs 1 and 2 was 150 min.

^c The support applied in each run is given, runs 6 and 7 are homogeneous reactions.

to TMBQ in a relatively slow second step (at 25°C, run 4).

2.4. The influence of the surface chemistry of the carbon support on TMP oxidation

A comparison is made of four different supports: unmodified C RA⁺0.8 (run 1), HNO₃ oxidized C RA⁺0.8N01 (run 2), aminated C RA⁺0.8N01A01 (run 3) and ammoxidated C RH0.8Am13 (run 4). It appears that the CN-supported PMoV is more active than the CNA system in every respect. This leads to an earlier high level of TMBQ in the case of PMoV/CN. As is shown by Izumi et al. the acidic activity of supported HPAs depends on the acidity of the support [9]. The CAm system has the highest TMP TOF(0) (initial TMP turn-over frequency) and BP FF(0), but yields mainly BP instead of TMBQ as the consecutive step to TMBQ is slow. The system with C as the support has also a reasonably high TMP TOF(0) and BP FF(0) and also yields relatively much BP. CAm and C have a low density of functional groups at the surface compared to CN and CNA. CN and CNA will, therefore, adsorb water strongly to the carbon surface. This may be responsible for the observed effects. The high activity of the CAm-supported catalyst may be

partly due to its relatively high loading (34 wt.%, against 22 ± 3 wt.% for the others). At a high PMoV loading a relatively small part of the HPA interacts very strongly with the carbon. A strong PMoV–carbon interaction may decrease the PMoV activity. The relatively low activity of HPMoV supported on CNA (24 wt.%) is probably caused by the very strong interaction of HPAs with aminated carbon. On these carbons the HPAs bind through Coulombic attraction via the N-containing surface groups. The selectivities of these systems do, however, show considerable differences. The selectivity towards TMBQ is best for CN (71%, after 1260 min) and CNA (64%, after 1260 min), C still shows a reasonable selectivity (55%, after 1260 min) and CAm is highly selective but requires speeding up of the conversion of BP to TMBQ (30%, after 1260 min).

3. Experimental

3.1. Materials

PMoV acid was synthesized by adding stoichiometric amounts of H₃PO₄ (85 wt.%, >99% pure), MoO₃ (>99% pure, Janssen Chimica and Fluka Chimika) and NaVO₃ (>98% pure, Fluka Chimika) to an excess of Na₂CO₃(aq). The mixture was stirred at 50°C until the solution's color was deep red. The proton form of the HPA was obtained by the method of Drechsel [10]; H_{5,9}PMo_{0,1}V_{2,9}O₄₀·6.2H₂O, *M* = 1809, Mo/V ratio = 3.1. The sodium salt was prepared by evaporation of water from the deep red solution; Mo/V ratio = 2, the preparation contains some free H₃PO₄ and MoO₃ (IR). The molar ratio of Na-PMoV is: Na:P:Mo:V = 3.66:0.55:3.70:1.77. For IR characterization also a pure NaPMoV was prepared, by adding Na₂CO₃ to a solution of HPMoV until no more CO₂ evolved.

IR absorption bands are found at 720, 890, 960 and 1050 cm⁻¹ for HPMoV and, almost identical, at 800, 900, 960 and 1060 cm⁻¹ for purified NaPMoV and this is very similar to a reference spectrum of PMo₉V₃O₄₀.

The activated carbons used for this study are peat based, gas activated, microporous carbons extruded in 0.8×5 mm cylindrical shapes, encoded RH0.8 and RA⁺0.8 by the manufacturer (courtesy of NORIT NV, Amersfoort, Netherlands). HNO₃ oxidized C (code: CN) was prepared by boiling C in 30% HNO₃ during 3 h. Aminated C (CNA) was obtained by reacting CN with ammonia (excess flow of ammonia at 230°C during 21/2 hours). Ammoxidated C (CAm) was prepared by passing NH₃(g) and air, respective flow rates: 16 and 380 ml·min⁻¹, through a carbon bed of 3 g at 350°C during 20 min. The carbon was heated and cooled under a nitrogen flow. All carbon modifications were washed and dried according to a standard procedure [4]

3.2. Adsorption of HPAs on carbon

Adsorption isotherms were determined for the loading of HPMoV on C (RA⁺0.8 and RH0.8), CN and CNA (RA⁺0.8) and CAm (RH0.8). A carbon sample (150 mg) was shaken in 100 ml aqueous 0.0316 M HCl and 15, 30, 50, 90 or 150 mg PMoV for seven days at room temperature (pH 1.47 ± 0.03). PMoV loadings were calculated from the P, Mo and V concentrations in solution, which were determined by ICP.

The PMoV on carbon catalysts were prepared by adsorption onto 5 g of the following carbon modifications from a solution of 4.5 g HPMoV in 150 ml demineralized water (pH = 1.4): C, CN and CNA (C is RA⁺0.8). Similarly for CAm (C is RH0.8), in this case 1 g CAm was loaded with a solution of 1 g HPMoV in 33.3 ml demineralized water (pH = 1.4) in triplicate. The latter adsorption was repeated at a scale of 30 g carbon. All catalysts were leached before use (see Table 3). The catalysts were dried after loading at 100°C/0.4 mmHg.

The stability of HPMoV on C, CN and CNA catalysts was tested by leaching for 24 h with hot water with a Soxhlet extractor. HPMoV/CAm was extracted in three ways: (i) with AcOH in a Soxhlet extractor for 48 h, and batch-wise, (ii) with 100 ml 0.01 M HCl at 50°C and (iii) with

95/5 vol% AcOH/H₂O at 50°C, followed in each case by a leaching with 100 ml 0.01 M HCl for 96 h.

3.3. TMP oxidation

The TMP (Aldrich) oxidations were performed in a closed stirred reactor at 25°C in AcOH/H₂O 95/5 vol% (runs 5–7 at 50°C). The oxygen pressure above the oxygen saturated solution was 0.1 MPa. The catalyst (0.8–5.0 g) was allowed to become saturated with water for runs 1–3. TMP (0.25–5.43 g) and the internal standard, ± 0.5 g naphthalene (Merck) were added thereafter. For runs 4–7 such an accommodation period was not applied. The molar ratio TMP/V(V) ≈ 4 . A stainless steel stirrer was used for runs 13, 6 and 7 and a Teflon magnetic bar stirrer was used for runs 4 and 5.

3.4. Analysis

With FTIR spectroscopy the presence of PMoVs on carbon was proven. FTIR spectra were recorded on a Bruker IFS 66 spectrometer in KBr over the range of 600–1300 cm⁻¹ under atmospheric conditions without special precautions.

The reactions were monitored by HPLC (column: Nucleosil C18, eluent: MeOH:H₂O: trifluoroacetic acid 60:40:0.1, RI detection). The catalyst and solvents were removed from the samples and taken up in 1 ml MeOH. The HPLC was calibrated for TMP and TMBQ. The correction factor for BP was estimated. TMBQ was isolated and purified over a silica column (97.5% purity, GC and HPLC) and characterized by MS and ¹H NMR (mass peaks: 54, 68, 79, 96, 107, 122 and 150, NMR spectrum [δ (ppm), J (Hz)]: quartet [6.556, 1.6], doublet [2.039, 1.6], [2.030, 1.2] and [2.009, 1.2]).

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