



Studies on the selective two-electron photo-oxidation of benzene to phenol using polyoxometalates, water and simulated solar radiation

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ABSTRACT

The direct one-step oxidation of benzene to phenol with the vanadium tungsten polyoxometalate $\text{NaH}_3\text{PW}_{11}\text{VO}_{40}$ was investigated under various reaction conditions. Photochemical substrate transformations were followed both under continuous wave photolysis with cut-off filtered mercury lamp light and under simulated solar light conditions. For comparison, potential dark reactions were also studied in control experiments. It could be shown that benzene is very selectively photo-oxidized to phenol in the course of a near UV and visible-light driven reaction. This process is accompanied by a reduction of the $\text{NaH}_3\text{PW}_{11}\text{VO}_{40}$ catalyst as indicated by a rapid color change from yellow to violet-blue and the formation of a vanadium(IV) multiline EPR signature. Different strategies for the re-oxidation of the reduced polyoxometalate photocatalyst have been investigated in order to further increase the observed turnover numbers for substrate conversion.

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1. Introduction

From a chemical and environmental point of view, the photocatalytic hydroxylation of organic substrates using sunlight as the sole energy source is of considerable interest [1,2]. In this context, the selective formation of phenol from benzene avoiding further oxidation by-products represents an important research topic. While this problem can be addressed by various strategies [3–7], the partial oxidation of aromatic compounds with an efficient and sustainable catalyst system working under mild conditions remains a highly desirable challenge.

Due to their excellent long-term stability, favourable electron-acceptor properties and the presence of easily accessible metal-oxo functionalities, polyoxometalates in their oxidized form (POM_{ox}) comprise a versatile class of redox reagents for both thermal and photochemical transformations of organic substrates including aromatic compounds [8–14]. Especially the thermodynamically driven tendency of POMs to assemble and self-repair in aqueous solution under turnover conditions, which has been reported for several transition-metal substituted polytungstates, makes these compounds very attractive for the design of robust oxidation catalysts [15]. For the present study, we have chosen deriva-

tives containing the Keggin-type polyoxovanadotungstate anion $[\text{PW}_{11}\text{VO}_{40}]^{4-}$ (Scheme 1) and tested them for the direct aerobic conversion of benzene to phenol under various irradiation conditions.

2. Experimental

2.1. Materials

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ hydrate p.a. grade, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ p.a. grade, V_2O_5 purest grade and benzene p.a. grade were purchased from Merck. NaVO_3 (96%) with a minimum of 38% vanadium was purchased from AlfaAesar. H_3PO_4 (85%) p.a. grade and HNO_3 (65%) p.a. grade were obtained from J.T Baker. Anhydrous CuCl_2 was purchased from Janssen Chimica. Acetonitrile p.a. grade was purchased from VWR. All chemicals were used as received.

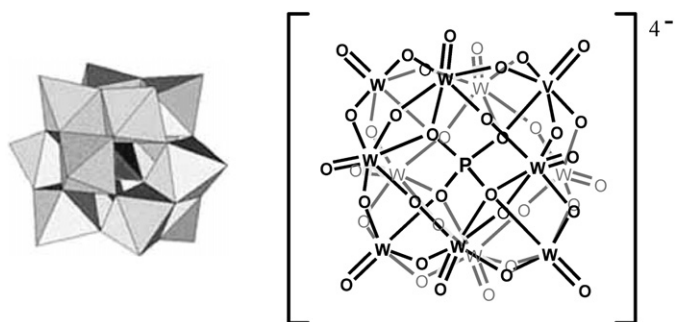
2.2. Synthesis of vanado-tungsto-phosphate salts

The vanadium(V) site-substituted heteropolyacid catalysts (POM_{ox}) were prepared as the sodium salts starting from phosphotungstic acid hydrate and vanadate. Appropriate stoichiometric amounts of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, NaVO_3 and H_3PO_4 were reacted in water according to the following net equation (Eq. (1)):



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Scheme 1. Structural representation of the $[PW_{11}VO_{40}]^{4-}$ heteropolyanion.

An aqueous vanadate solution was first acidified with phosphoric acid and then poured into a tungsten polyoxometalate solution. The resulting mixture was equilibrated at 80 °C for 3 h. UV–Vis and IR spectra were measured and compared with published data to confirm the formation of the desired product according to the literature [16,17].

2.3. Analytical methods

Electronic spectra were recorded on a Jasco V-670 UV-VIS-NIR spectrophotometer. IR spectra were measured on a Shimadzu Affinity-1 FT-IR spectrophotometer equipped with a Specac Golden Gate™ single reflection diamond ATR accessory. X-band (9.48 GHz) EPR spectra of the photogenerated vanadium(IV) species were obtained with a Bruker Elexsys E 580 electron paramagnetic resonance spectrometer. Solid samples were scanned at room temperature. The microwave power was 5 mW. Product analysis was performed on a PerkinElmer 8500 gas chromatograph equipped with a split/splitless injector, a FID detector, and several different columns: a 25 m long fused silica column, a 25 m long DB-wax column and a 27.5 m long PoraPlot Q column all with a diameter of 0.32 mm. In the case of very low product concentrations, a colorimetric quantification of phenol was additionally performed with the NANOCOLOR phenol test 1–75 kit from Macherey–Nagel, which is based on the azo coupling of phenoles to a 4-nitroaniline derivative.

2.4. General reaction conditions

Substrate transformation processes were performed both in homogeneous aqueous solution and in biphasic solvent mixtures containing the polyoxometalate catalyst (POM_{ox}). A typical homogeneous reaction mixture consisted of water that was saturated under aerobic conditions with approximately 1.7×10^{-2} M of benzene substrate, while the catalyst concentration was chosen in the range of 3–7 mM. Biphasic reaction mixtures typically were composed from an aqueous catalyst solution (3–7 mM) and an organic benzene solution in a volume ratio of 1:5 or 1:10 to ensure that more than 90% of the phenol produced are transferred to the organic phase (the partition coefficient of phenol for a benzene/water mixture is 2). The reaction time of the experiments, which were carried out under permanent magnetic stirring, was varied from 3 to 74 h. Reaction vessels in general consisted of borosilicate glassware except for the investigations of wavelength dependent reactions, where spectroscopic quartz glass cuvettes have been chosen. Hydrogen peroxide in the millimolar range was detected semi-quantitatively by a specific colorimetric test kit based on peroxidase as a catalyst (Merck).

2.5. Electrochemical experiments

The redox properties of the POM catalyst $NaH_3PW_{11}VO_{40}$ as well as Fe^{3+} and Cu^{2+} salts in different acetonitrile water mixtures were investigated by cyclic voltammetry. All measurements were performed under nitrogen atmosphere with 0.9 M sulfuric acid as the bulk electrolyte. For the desired H_2O/CH_3CN ratio, acetonitrile was added step by step in appropriate amounts. A platinum disc electrode was applied as the working electrode and platinum wire as a counter electrode. All measurements were referenced against a Ag/AgCl electrode (Bioanalytical systems).

2.6. Photochemical and photocatalytic experiments

For the light-driven substrate transformations, different irradiation sources were tested including cut-off filtered medium pressure mercury lamps (100 W or 150 W) and simulated AM 1.5 solar light generated with an adjustable power 300 W xenon lamp installed in a Luzchem photoreactor equipped with a SolSim filter combination. Details on the individual series of photocatalytic tests are provided below.

2.7. Basic photoreaction of POM_{ox} with benzene

Continuous wave irradiation (150 W Hg lamp) of a biphasic mixture of 1 ml aqueous catalyst solution (3.1×10^{-3} M) and 5 ml of neat benzene in a 12 ml borosilicate culture glass vessel was carried out at 25 °C for 5 h in the presence of atmospheric oxygen.

2.8. Photoreaction of POM_{ox} in the presence of HNO_3

A biphasic reaction mixture consisting of 0.4 ml aqueous catalyst solution (5.8×10^{-3} M), 0.1 ml concentrated HNO_3 and 5 ml benzene was irradiated with the full light of a 100 W Hg lamp at an oxygen pressure of 8 bar at 40 °C for 74 h.

2.9. Photocatalytic reactions with cut-off filtered light

In these reactions, different filter combinations were applied to eliminate certain spectral regions from the excitation source output. The other reaction conditions were kept constant in each experiment. As the light source, an Osram HBO 100 W medium pressure Hg-lamp was used. The air saturated reaction mixtures consisted of 3 ml of 5.8×10^{-3} M aqueous POM_{ox} catalyst solution (17.4 μ mol $NaH_3PW_{11}VO_{40}$) and 4.5 μ l of neat benzene (50.7 μ mol). All reactions were carried out in quartz glass cuvettes and kept at room temperature by continuous air-cooling with a fan. The following Schott glass cut-off filters were applied: 200 nm (quartz glass), 280 nm, 295 nm, 305 nm, 360 nm, and 435 nm. After 4 h of irradiation in each case, the quantification of products was carried out with the NANOCOLOR phenol test 1–75 kit (Macherey–Nagel).

2.10. Solar photocatalytic reactions

A Luzchem photoreactor simulating the solar spectral irradiance reaching the earth's surface under ambient conditions was used for following photoreaction: 1 ml of a 7.2×10^{-3} M aqueous solution of the POM_{ox} catalyst and 5 ml of benzene were irradiated for 4.5 h in the solar simulator adjusted to an output of approximately 22,500 lx at the sample position, which corresponds to 92% of AM 1.5 conditions (ASTM International Air Mass 1.5 Global Tilt Standard).

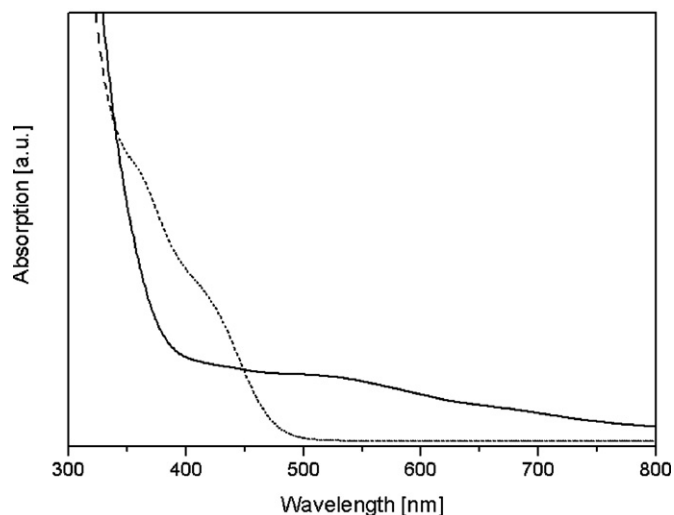


Fig. 1. UV-Vis absorption spectra of the oxidized (---) and photoreduced (—) forms of the polyoxovanadotungstate catalyst ($c = 3.15 \times 10^{-3}$ M) in aqueous solution.

2.11. Photoreactions in the presence of Fe^{3+} /acetonitrile

Under aerobic conditions, a mixture of 2 ml of aqueous catalyst solution (7.2×10^{-3} M), 2 ml acetonitrile, 0.12 ml benzene and 9 mg $FeCl_3 \cdot 6H_2O$ was irradiated in a borosilicate culture glass vessel at $30^\circ C$ for 20 h (Luzchem SolarSimulator, 34,200 lx).

2.12. Photoreactions in the presence of free VO_2^+

1 ml of aqueous catalyst solution (7.2×10^{-3} M) containing $NaVO_3$ (8.2×10^{-3} M) and 5 ml benzene was irradiated in a borosilicate culture glass vessel at $30^\circ C$ for 20 h (Luzchem SolarSimulator, 34,200 lx).

3. Results and discussion

The redox transformation of substrates mediated by the oxidized polyoxometalate catalyst $NaH_3PW_{11}VO_{40}$ (POM_{ox}) is accompanied by a gradual increase of various spectral features which are diagnostic for the generation of a reduced form of the polyoxometalate catalyst (POM_{red}). The progress of such a reaction can be readily monitored by characteristic variations in the UV-Vis spectra (Fig. 1). The colour changes from orange to violet-blue observed in the course of the redox process are typical for the formation of metal-based mixed-valent species carrying at least one additional electron within the polyoxometalate core [18].

The nature of the photoreduction product of the $[PW_{11}V^VO_{40}]^{4-}$ heteropolyanion could be clearly identified as a $[PW_{11}V^{IV}O_{40}]^{5-}$ species by means of EPR spectroscopy (Fig. 2). Solid samples of the violet-blue polyoxometalate material isolated from reaction mixtures of photocatalytic substrate conversion experiments display a typical eight-line EPR signal corresponding to a single electron reduced species (POM_{red}) with d^1 electron configuration, where the additional unpaired electron is trapped at the vanadium(IV) oxo site [19].

These results are also confirmed by solid state ^{31}P NMR measurements of photolyzed samples, which display a significant broadening of the signal corresponding to the central phosphorus atom of the catalyst.

Benzene was investigated as a substrate for the photocatalytic experiments under different irradiation conditions (see Section 2). A very selective transformation of benzene into phenol could be observed in many cases as indicated by gas chromatographic anal-

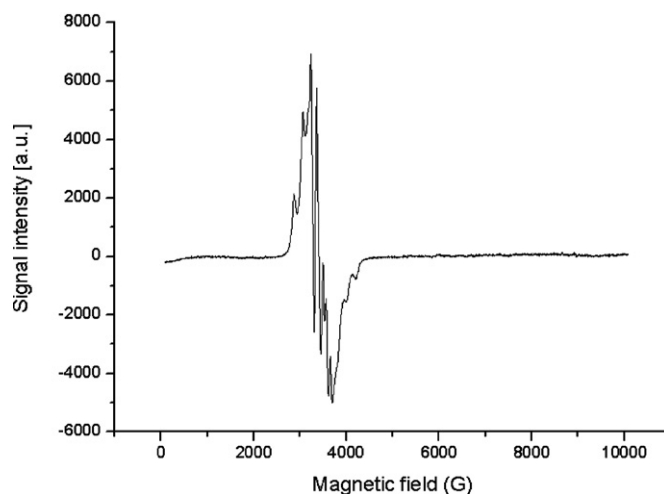


Fig. 2. EPR spectrum of the one-electron photoreduced polyoxovanadotungstate catalyst recorded at room temperature in the solid state.

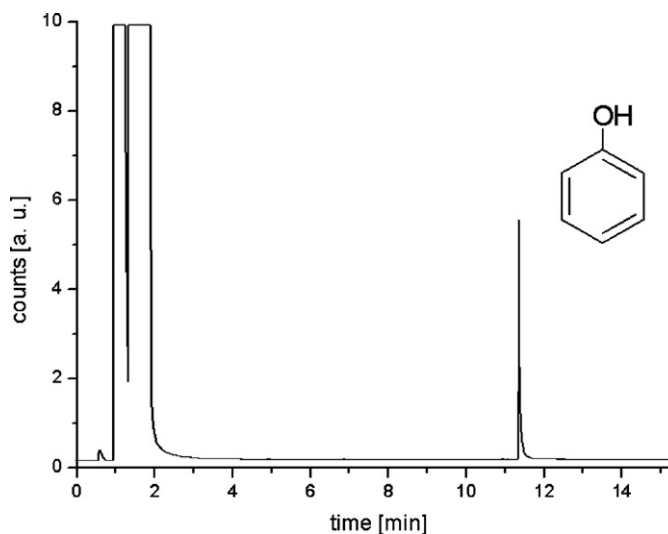


Fig. 3. GC-FID data demonstrating the selective photo-oxidation of benzene to phenol in the presence of 3.15×10^{-3} M polyoxometalate catalyst $NaH_3PW_{11}VO_{40}$ in a biphasic 2:2:1 water/acetonitrile/benzene mixture after 5 h of irradiation with a 100 W medium pressure mercury lamp filtered through borosilicate glass. The phenol signal at 11.5 min is absent in unreacted samples. Additional peaks between 1 and 2.5 min retention time are due to acetonitrile solvent and excess of benzene, respectively.

ysis. As an example, a typical chromatogram showing excellent selectivity is given above (Fig. 3).

Irradiation experiments with appropriate cut-off filter combinations revealed that the photocatalytic conversion of benzene to phenol is a wavelength dependent process (Fig. 4). While typically only less than 10% of the substrate molecules are transformed into phenol upon short-term irradiation of the long-wavelength polyoxometalate absorption bands, the yields strongly increase up to almost 40% of conversion with excitation energies in the UV-spectral region (Fig. 4).

Under these latter conditions, however, the otherwise excellent selectivity of the process may be partially lost due to secondary photolyses of the phenol product or other undesired side reactions such as the formation of biphenyl or open chain oxidation products from benzene. The increasing risk of potential side reactions is clearly reflected by studying the wavelength-dependent selectivity properties of the photocatalytic phenol production process,

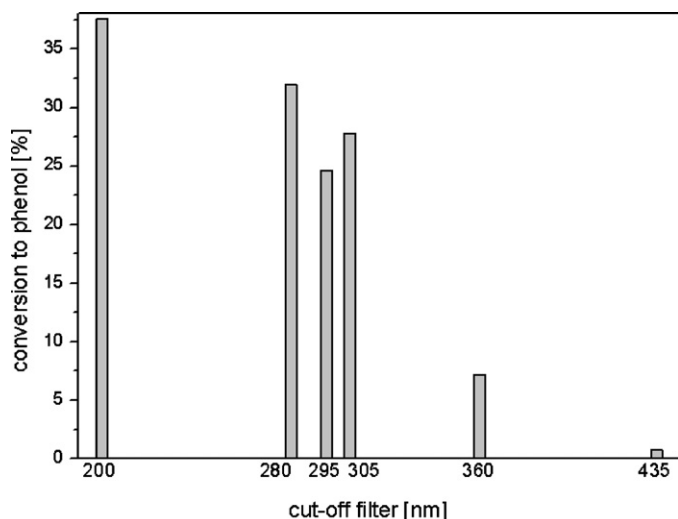
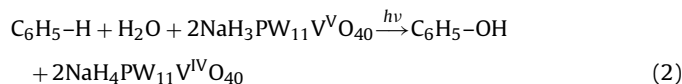


Fig. 4. Photocatalytic conversion of benzene to phenol in homogeneous aqueous solution using different cut-off filters (200 nm, 280 nm, 295 nm, 305 nm, 360 nm) and a 100 W medium pressure mercury lamp; irradiation times 4 h, catalyst concentration: 3.15×10^{-3} M, benzene concentration: 1.58×10^{-3} M.

which demonstrates a gradual drop of selectivity with increasing excitation energies (Fig. 5).

Quantitative analysis of the corresponding reactions under stoichiometric conditions confirmed that the conversion of benzene to phenol, which corresponds to a net two-electron oxidation process, leads to the formation of two one-electron reduced polyoxometalate molecules, each with single site vanadium (IV) spin density distribution (Fig. 2). The substrate conversion was studied under anaerobic and aerobic conditions, as well as under more drastic reaction conditions with 8 bar of dioxygen pressure and prolonged irradiation times. The results of these experiments strongly indicate that dioxygen is not directly involved in the redox process and that the oxygen atom incorporated into the phenol product most probably originates from solvent water molecules according to the following overall equation (Eq. (2)):



As the only further reaction intermediate, the formation of significant amounts of hydrogen peroxide has been observed in the irradiated samples. While a direct hydrogen peroxide production from neat water would require vacuum UV-radiation [20], it is well established that photoexcited polyoxometallates can also promote the formation of hydroxyl radicals (HO^\bullet) in aqueous solution [21]. Therefore, the peroxide detected in our photolyzed samples might originate from a recombination of hydroxyl radicals generated in situ. Further control experiments with the Keggin-type phosphotungstate polyoxometalate anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ revealed that the vanadium site is obviously required for the selective transformation of benzene to phenol under our reaction conditions.

At the present stage of the investigations, no oxygen isotope labeling experiments or other efforts to confirm the origin of the phenol O-atom and the nature of the active vanadium species involved have been carried out. Therefore, the detailed mechanism of the substrate conversion process still remains unknown. Nevertheless, in agreement with the literature, our results seem to indicate an important role of a vanadium peroxo species, which is supposed to be formed as the active oxidant in different thermal polyoxometalate substrate conversion processes, which are based on an excess of hydrogen peroxide added as an additional reagent [13,22,23]. Since in our case, however, no H_2O_2 was ini-

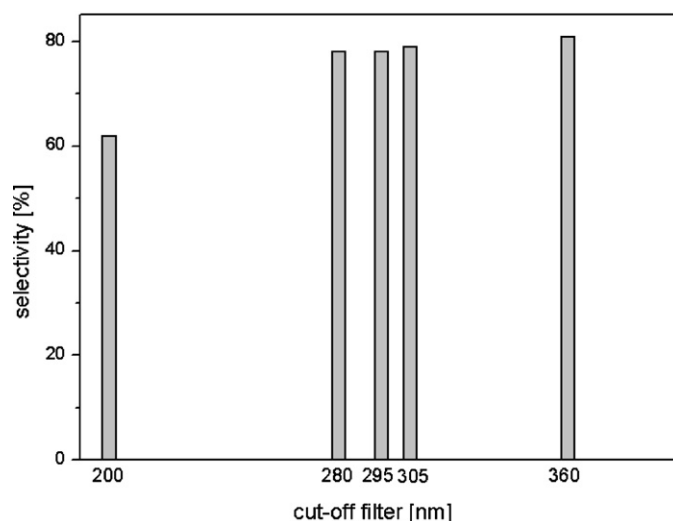
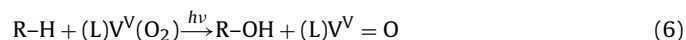
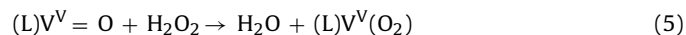
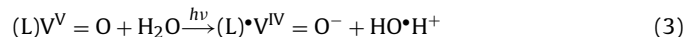


Fig. 5. Wavelength-dependent selectivity profile of the photocatalytic conversion of benzene to phenol in the presence of the polyoxometalate catalyst $\text{NaH}_3\text{PW}_{11}\text{VO}_{40}$ and water (cut-off filters: 200 nm, 280 nm, 295 nm, 305 nm, 360 nm, 100 W medium pressure mercury lamp; irradiation times 4 h, POM concentration: 3.15×10^{-3} M, benzene concentration: 1.58×10^{-3} M).

tially added and the potential intermediate peroxide formation from water molecules requires UV-light excitation, we tentatively assume that an in situ photogeneration of an active vanadium-peroxo species similar to the published thermal catalyst systems occurs. This assumption also allows to rationalize the initially unexpected results of a much higher phenol yield under shorter wavelength irradiation conditions (Fig. 4). Therefore, a plausible reaction sequence involving the vanadium site can be suggested (Eqs. (3)–(6)), which is in agreement with all the experimental results and also correctly describes the observed net stoichiometry (Eq. (2)) of the photocatalytic phenol production process (L = spectator ligands, $\text{R} = \text{C}_6\text{H}_5$):



According to this proposed reaction sequence, the selective C–H activation of the benzene substrate (Eq. (6)) should essentially take place in the coordination sphere of vanadium(V)-oxo and -peroxo species, similar to the mechanistic key-steps already postulated in a previous study on peroxide-dependent phenol production [22]. As a consequence, the formation of a vanadium(IV) radical species observed in our experiments would then correspond to the in situ photogeneration of hydroxyl radicals, which is thought to involve the LMCT excited state of the vanadium(V) oxo site (Eq. (3)). The vanadium(IV) species, on the other hand, is not directly involved in the following substrate conversion steps and should therefore gradually accumulate in the course of the reaction as actually observed (Fig. 1). In this context, it is interesting to note, that this behavior parallels the reactivity patterns of vanadium haloperoxidases, which contain a single vanadium site as their active center essentially remaining in the V(V) oxidation state during catalytic turnover. This active site is also thought to bind hydrogen peroxide prior to substrate oxidation ($\text{R} = \text{halide}$) and turns totally inactive, when the enzyme is reduced to the vanadium(IV) state [24].

From the net stoichiometry of this reaction sequence (Eq. (2)) it can be derived, that catalytic substrate turnover requires an additional re-oxidation process to preserve the active V(V) sites of the

polyoxometallate, since the electrons released in the course of the benzene oxidation reaction are otherwise efficiently trapped. As already discussed above, the O₂ content of the solutions under various irradiation conditions has no significant influence on the observed phenol formation. This is ascribed to the lack of an appropriate dioxygen activation mechanism that could provide peroxide for the substrate oxidation process (Eq. (5)), and also indicates that dioxygen is not able to directly re-oxidize the inactive violet-blue vanadium(IV) form of the catalyst (Fig. 1). Therefore, several additional reagents acting as electron acceptors have been added to the photocatalytic system and tested for their influence on substrate turnover (details of these investigations are provided in the supplementary material of this work). Indeed, analytical data clearly demonstrate that the otherwise stoichiometric reaction turns into a catalytic phenol production process under such conditions. As expected, the accumulation of vanadium(IV) species is significantly suppressed under steady state irradiation of the corresponding reaction mixtures. For example, upon addition of Fe³⁺ salts in acetonitrile water mixtures, the re-oxidation of vanadium(IV) sites takes place under photocatalytic turnover conditions (see supporting information). Similar results were obtained upon addition of vanadate ions. The redox potential of the polyoxometallate catalyst NaH₃PW₁₁VO₄₀ was determined as +0.85 V vs. NHE. From this value it can be derived, that inorganic anions such as nitrate might also be involved in the re-oxidation process of the photoreduced polyoxometallate. When HNO₃ was applied as an electron acceptor, however, the selectivity of the phenol production process was lost. Upon irradiation, several other products including biphenyl, nitrobenzene, *p*-benzoquinone and nitrophenol as the main product were detected.

In summary, we have presented a new photocatalytic system for the direct and very selective oxidation of benzene to phenol in aqueous solvent mixtures under ambient conditions using simulated solar light excitation. At present, the catalytic reaction is still hampered by a very low efficiency in terms of turnover numbers, which can be ascribed to the gradual formation of inactive vanadium(IV) sites in the course of the photolysis. Our results indicate that vanadium(V)-oxo and -peroxo species are directly involved in the benzene to phenol conversion process, while polyoxometallate reduction at the vanadium site occurs in an undesired side-reaction. Further efforts will therefore focus on a new strategy to couple the phenol formation steps mediated by the polyoxometallate catalyst with an established solar photocatalytic system for dioxygen activation and hydrogen peroxide formation under visible light excitation [25,26], in order to avoid UV-light dependent and hydroxyl radical mediated side-reactions leading to inactive vanadium(IV) species and to increase the efficiency of the system by a permanent peroxide supply from ambient air. This could open a

novel route towards a sustainable and environmentally benign formation of phenol from benzene based on water, dioxygen, sunlight and readily available catalyst components.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.07.011.

References

- [1] G. Knör, Chem. Eur. J. 15 (2009) 568.
- [2] B. Naik, K.M. Parida, G.C. Behera, ChemCatChem 3 (2011) 311.
- [3] S. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba, F. Mizukami, Science 295 (2002) 105.
- [4] A. Poater, X. Ribas, A. Llobet, L. Cavallo, M. Solà, J. Am. Chem. Soc. 130 (2008) 17710.
- [5] Z. Ding, X. Chen, M. Antonietti, X. Wang, ChemSusChem. 4 (2011) 274.
- [6] E.T. Farinas, M. Alcalde, F. Arnold, Tetrahedron 60 (2004) 525.
- [7] G. Zhang, J. Yia, J. Shimb, J. Leea, W. Choi, Appl. Catal. B: Environ. 102 (2011) 132, and refs. therein.
- [8] E. Papaconstantinou, Chem. Soc. Rev. 18 (1989) 1.
- [9] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171.
- [10] R. Neumann, Prog. Inorg. Chem. 47 (1998) 317.
- [11] H. Park, W. Choi, Catal. Today 101 (2005) 291.
- [12] C.L. Hill, J. Mol. Catal. A: Chem. 262 (2007) 1.
- [13] J. Arichi, M. Eternot, B. Louis, Catal. Today 138 (2008) 117.
- [14] A.C. Estrada, M.M.Q. Simões, I.C.M.S. Santos, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.M.V. Cavaleiro, ChemCatChem 3 (2011) 771.
- [15] Y.V. Geletii, Q. Yin, Y. Hou, Z. Huang, H. Ma, J. Song, C. Besson, Z. Luo, R. Cao, K.P. O'Halloran, G. Zhu, C. Zhao, J.W. Vickers, Y. Ding, S. Mohebbi, A.E. Kuznetsov, D.G. Musaev, T. Lian, C.L. Hill, Isr. J. Chem. 51 (2011) 238.
- [16] D.P. Smith, H. So, J. Bender, M.T. Pope, Inorg. Chem. Soc. 12 (1973) 685.
- [17] P.J. Domaille, J. Am. Chem. Soc. 106 (1984) 7677.
- [18] A. Hiskia, A. Mylonas, E. Papaconstantinou, Chem. Soc. Rev. 30 (2001) 62.
- [19] A. Selling, I. Andersson, J.H. Grate, L. Pettersson, Eur. J. Inorg. Chem. (2002) 743.
- [20] K. Azrague, E. Bonnefille, V. Pradines, V. Pimienta, E. Oliveros, M.-T. Maurette, F. Benoit-Marquié, Photochem. Photobiol. Sci. 4 (2005) 406.
- [21] P. Kormali, T. Triantis, D. Dimotikali, A. Hiskia, E. Papaconstantinou, Appl. Catal. B: Environ. 68 (2006) 139.
- [22] N.A. Alekar, V. Indira, S.B. Halligudi, D. Srinivas, S. Gopinathan, C. Gopinathan, J. Mol. Catal. A: Chem. 164 (2000) 181.
- [23] J. Ichihara, Y. Sasaki, Catal. Today 117 (2006) 120.
- [24] C.J. Schneider, J.E. Penner-Hahn, V. Pecoraro, J. Am. Chem. Soc. 130 (2008) 2712.
- [25] G. Knör, A. Vogler, Inorg. Chem. 33 (1994) 314.
- [26] G. Knör, ChemBioChem 2 (2001) 593.