

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: Light-Induced Efficient Hydroxylation of Benzene to Phenol by Quinolinium and Polyoxovanadate-based Supramolecular Catalysts

Authors: Yongge Wei, Yaqi Gu, Qi Li, Dejin Zang, Yichao Huang, and Han Yu

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202011164

Link to VoR: https://doi.org/10.1002/anie.202011164

WILEY-VCH

RESEARCH ARTICLE

Light-Induced Efficient Hydroxylation of Benzene to Phenol by Quinolinium and Polyoxovanadate-based Supramolecular Catalysts

Yaqi Gu, ^[a] Qi Li, ^[a] Dejin Zang, ^[a] Yichao Huang, ^[a] Han Yu^{[a],*} and Yongge Wei ^{[a,b],*}

Abstract: Direct Hydroxylation of benzene to phenol with high yield and selectivity has been the goal of phenol industrial production. Photocatalysis can serve as a competitive method to realize the hydroxylation of benzene to phenol owing to its cost-effective and environmental friendliness, however it is still a forbidding challenge to obtain good yield, high selectivity and high atom availability meanwhile. Here we show a series of supramolecular catalysts based on alkoxohexavanadate anions and quinolinium ions for the photocatalytic hydroxylation of benzene to phenol under UV irradiation. We demonstrate that polyoxoalkoxovanadates can serve as efficient catalysts which can not only stabilize quinolinium radicals but also reuse H_2O_2 produced by quinolinium ions under light irradiation to obtain excellent synergistic effect, including competitive good yield (50.1%), high selectivity (> 99%) and high atom availability.

Introduction

Phenol, as an important chemical raw material, still has many limitations in its industrial production, such as cumbersome synthesis steps, high energy consumption, low yield and low selectivity.^[1] One-step production of phenol with low energy consumption, high yield and high selectivity has always been the goal of researchers. Many progresses have been made in direct hydroxylation of benzene to phenol.^[2-6] In the field of chemical catalysis, a series of vanadium silicalite zeolites were reported which can catalyze the hydroxylation of benzene to phenol in 30.8% yield and high selectivity of 99 % with H₂O₂ as the sole $\mathsf{oxidant}.^{[4]}\;\mathsf{H}_2\mathsf{O}_2$ is the most commonly used green oxidizer of benzene oxidation to phenol to date.^[3-6] Compared with H₂O₂, O₂ is more attractive because it is cheaper and much more safety. However, oxygen-participated benzene oxidation generally requires additional redox agents (for example, CO and H₂),^[7,8] redox agents-free catalytic systems were less reported and most of them usually need noble metal catalysts or non-noble metal catalysts under harsh reaction conditions or accomplished in the low selectivity.^[2, 9-11, 15] Besides thermochemical catalysis, the method of electrocatalysis has also been proposed for the direct hydroxylation of benzene to phenol.^[12] Yet, due to its costeffective and environmental friendliness, photocatalysis has attracted more and more attention recently in the synthesis of compared with thermochemical catalysis and phenol electrocatalysis.^[13-18] Developing novel photocatalytic systems

[a] Dr. Y. Gu, Mr. Q. Li, Dr D. Zang, Dr Y. Huang, Prof. Dr. H. Yu, * Prof. Dr. Y. Wei* Key Lab of Organic Optoelectronics & Molecular Engineering of

Ministry of Education, Department of Chemistry Tsinghua University

Haidian District, Beijing, 100084, P. R. China

E-mail: hanyu0220@tsinghua.edu.cn; yonggewei@tsinghua.edu.cn [b] Prof. Dr. Y. Wei*

State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100191, P.R. China. E-mail: ygwei@pku.edu.cn with O_2 as the oxidant might be the most promising method for hydroxylation of benzene.

Some important photocatalysts for the photocatalytic oxidation of benzene to phenol with O_2 as the oxidant have been reported.¹³⁻¹⁸ Among them, DDQ-O₂-TBN/HNO₃ photocatalytic systems were reported with the highest yield (93 %) and selectivity (98 %) of phenol to date, however, as mentioned above, additional oxidants TBN/HNO₃ were essential to oxidize DDQH₂ to DDQ under aerobic conditions in the catalytic cycle.^{13,14} There are also several systems need no additional redox agents, besides noble metal contained catalysts,¹⁵ the reported TiO₂/silicate (with 77.6 % benzene conversion and 22.7 % phenol selectivity) and quinolinium ion catalysts also show appreciable activity of benzene oxidation to phenol.^{2, 16-18}

Quinoline itself has photocatalytic activity for the oxidation of benzene to phenol.^[16-18] Under light conditions, it can catalyse the formation of phenol and hydrogen peroxide from benzene, water and oxygen gas.^[16] But quinolinium ion catalysts are less reported till now. Some efforts have been made to analyse the effects of substituents (-CH₃/-H/-CN) on quinolinium rings,^[16] the kind of counter anions (SO₄²⁻, Cl⁻, NO₃⁻) and co-catalyst on the catalytic performance of hydroxylation of benzene, ^[17,18] while the reuse of generated hydrogen peroxide has been totally neglected.

Polyoxometalates (POMs) form a unique class of metal-oxide clusters of the early transition metals (usually Mo, W, V) generally in their highest oxidation states with diversity of structures and properties. POMs are widely used in the catalytic systems, especial for the catalytic oxidation due to their electron reservoir abilities and the activity of their diverse reduced forms.^[19] The catalytic activity of POMs in the hydroxylation of benzene to phenol has also been confirmed these years,^[20,21] however the yield of phenol is rather low and the kinds of POMs are very limited. Developing POM-based catalytic systems with high phenol yield and selectivity is still a formidable challenge. H₂O₂ is the most commonly used oxidant for POM-based catalytic systems,^[19] and here POMs might be suitable candidates for the reuse of hydrogen peroxide generated in a photocatalytic system of quinolinium ions. Supramolecular photocatalytic systems constructed from POM anions and quinolinium ions may behave efficiently synergistic catalytic activity of phenol preparation via the hydroxylation of benzene. Recently, one example of phosphotungstic anion-countered quinolinium salt (named as C16Qu-PW) was reported with relatively low phenol yield (20.9 %),[22] furthermore, even though the C₁₆Qu-PW showed a higher yield of phenol (20.9 %) than $C_{16}Qu$ and PW alone (14.1 % for $C_{16}Qu$ and <0.1 % for PW, respectively), the synergistic effect between C₁₆Qu and PW was not very obvious, and the reported mechanism explanation is

RESEARCH ARTICLE

WILEY-VCH

Figure 1. Molecular structures of the supramolecular catalysts: $(C_4-Quin)_2V_6$ (a), $(C_8-Quin)_2V_6$ (b), $(C_{16}-Quin)_2V_6$ (c) and $(C_8-Quin-NH_2)_2V_6$ (d). The solvent molecules are omitted for clarity. Color code: V - orange, O - red, N - blue and C - grey.

unsuitable for the reuse of hydrogen peroxide generated during the photocatalytic process.

In this supramolecular catalysts: article. four $[C_9H_7N(C_4H_9)]_2[V_6O_{13}{(OCH_2)_3CCH_2OH}_2]$ 3CH₃CN $(C_4-Quin)_2V_6$, CCDC: (abbreviated 1957103), as $[C_9H_7N(C_8H_{17})]_2[V_6O_{13}{(OCH_2)_3CCH_2OH}_2]$ (4/3)CH₃CN CCDC: (abbreviated $(C_8-Quin)_2V_6$, 1957107), as $[C_9H_7N(C_{16}H_{32})]_2[V_6O_{13}{(OCH_2)_3CCH_2OH}_2]$ · (5/4)CH₃CN $C_4H_{10}O$ (abbreviated as $\ (C_{16}\mbox{-}Quin)_2V_6,\ CCDC:\ 1057109)$ and $[NH_2C_9H_6N\ (C_8H_{17})]_2[V_6O_{13}\{(OCH_2)_3CCH_2OH\}_2]$ (abbreviated as $(C_8$ -Quin-NH₂)₂V₆, CCDC: 1057110) were constructed from the perspectives of improving atomic availability by a strategy of molecular self-assembly based on alkoxohexavanadate anion $[V_6O_{13}{(OCH_2)_3CCH_2OH}]^{2-}$ (abbreviated as V₆) and a series of quinolinium bromide, including $C_9H_7N(C_4H_9)Br$, $C_9H_7N(C_8H_{17})Br$, $C_9H_7N(C_{16}H_{33})Br$ and $NH_2C_9H_6N(C_8H_{17})Br$. These four catalysts were characterized by single crystal X-ray diffraction, ¹H NMR and FT-IR. Their UV-visible absorption spectra were also determined. The influence of assembly structure, substituents in quinolinium ring and the acidity of reaction system on the synergistic catalytic effect was focused on, the possible involved mechanisms of synergistic catalysis were proposed.

Results and Discussion

Synthesis of supramolecular catalysts $C_9H_7N(C_4H_9)Br$ (abbreviated as (C₄-Quin)Br), $C_9H_7N(C_8H_{17})Br$ (abbreviated as (C₈-Quin)Br), $C_9H_7N(C_{16}H_{33})Br$ (abbreviated as (C₁₆-Quin)Br) were synthesized by mixing quinoline with excess brominated alkanes (bromobutane, *n*-octyl bromide, 1-Bromohexadecane) at 80 °C for 24h. Because of the activity of amino group, $NH_2C_9H_6N$ (C_8H_{17})Br (abbreviated as (C_8 -Quin- NH_2)Br) cannot be obtained by the direct reaction of 6-aminoquinoline with *n*octyl bromide. It was obtained by more complex steps, as showed in **Scheme S1**. Related compounds involved here were confirmed by ^{1}H NMR (Figs. S1-S6). $[(C_4H_9)_4N]_2[V_6O_{13}{(OCH_2)_3CCH_2OH}_2]$ (abbreviated as $(TBA)_2V_6$) was prepared according to a previously reported procedure.^[23] The crystals of these four supramolecular catalysts were obtained by diffusion method and used for single crystal X-ray diffraction analysis subsequently. Their complete molecular structures and crystal data were provided in Fig. S22 and Tab. S3, respectively. The molecular structures of supramolecular catalysts without solvents were given in Figure 1, each molecule includes two quinolinium ions and one alkoxohexavanadate anion, with or without co-crystallized solvents. In particular, hydrogen bond interactions between anions in $(C_4$ -Quin)₂V₆ was found (shown in Fig. S21 and Tab. S2). Besides, ¹H NMR spectra (Figs. S7-S10) and FT-IR (Figs. S11- S14) spectra of these supramolecular catalysts after dried were also provided.

Photocatalytic hydroxylation of benzene under conditions without H2SO4 and the reaction mechanism. Considering the supramolecular catalysts all have absorption at 365 nm, 365 nm Led lamps were chosen as light source to perform photocatalytic experiments (Fig. S23). The photocatalytic experiments were performed under UV-light (25 °C, 10 W led lamp) irradiation of various catalysts in water-acetonitrile mixtures containing benzene and dodecane (internal standard) (Table 1). GC-MS were used for the detection and quantification of phenol. No phenol was detected without catalysts (Table 1, Entry 11) or without light irradiation (Table 1, Entry 9-10). No phenol was detected by $(TBA)_2V_6$ with O_2 or H_2O_2 as the oxidant (**Table 1**, Entry 12, 13), it reflected that the alkoxohexavanadate V₆ alone could not catalyze O_2 or H_2O_2 to oxidize benzene to phenol here. Only small amount of phenol was detected by (C₄-Quin)Br, (C₈-Quin)Br and (C₁₆-Quin)Br with 1 %, 1.3 %, 1.0 % phenol yield, respectively, while the reaction can be catalyzed efficiently by (C₄-Quin)₂V₆, (C₈-Quin)₂V₆ and (C₁₆-Quin)₂V₆ with 14.0 %, 21.7 % and 22.5 % phenol yield, respectively, much higher than V₆ itself and their corresponding quinolinium bromides. Considering the produced H₂O₂ by quinolinium rings under photocatalytic

RESEARCH ARTICLE

conditions here cannot be exploited by V_{6} , a mechanism of hydrogen peroxide reuse is not involved. EPR measurements were performed then to further understand the role of V₆ in photocatalytic system. Signals attributed to DMPO-OOH (DMPO: 5,5-dimethyl-1-pyrroline N-oxide, spin trap) derived from O2⁻⁻ (Fig. S15 (a), $A_N = 1.3 \text{ mT}$, $A_{H\beta} = 1.0 \text{ mT}$, $A_{H\gamma}=0.16 \text{ mT}$, g = 2.0042) were captured on irradiation of a reaction system containing (C₄-Quin)Br, while signals mainly attributed to carbon-centered radicals (Fig. S15 (b), $A_N = 1.5$ mT, $A_{H\beta} = 2.1$ mT, g = 2.0047) were captured on irradiation of a reaction system containing (C4-Quin)₂V₆. Consider no carbon-centered compounds other than quinolinium ions were introduced into the EPR testing system, the captured carbon-centered radicals most likely belong to the quinolinium radical c (Scheme 1). A reported photocatalytic mechanism of quinolinium ions is as follow^[16]: quinolinium ions (shorted as QuCN⁺) can transform into excited state (shorted as QuCN**) under photo irradiation, and then transforms into radicals (shorted as QuCN ') via seizing an electron from benzene which forms the benzene cation correspondingly due to the loss of an electron, QuCN can reduce O2 to produce O2. followed by protonation of O2: to afford HO2: (as shown in Fig. S16). Compared the EPR spectra of the reaction system of (C₄-Quin)Br with that of (C₄-Quin)₂V₆, the disappearance of DMPO-OOH derived from O2 and the appearance of species c (Scheme 1) in (C₄-Quin)₂V₆ system's EPR spectra suggests that the introduction of V₆ limits the formation of O₂-and helps to stabilize species c. DFT simulations reveals that the absorption energy between c (R=H, n=2) and V₆ is -18.6309 Kcal/mol, while the absorption energy between c and Br is -3.9868 Kcal/mol (The models for V_{6} - c and Br- c were shown in Fig. S17). The DFT simulations further confirm V₆ is beneficial for stabilizing quinolinium radicals. The catalytic mechanism of supramolecular catalysts, O2 and H2O under light irradiation conditions was proposed at last (Scheme 1). The quinolinium ions (a) can transform into excited state (b) under irradiation, and then transforms into radicals (c) accompanied by the formation of benzene cation. The hydrogen abstraction of c, which is stabilized by V₆, from the OH-adduct radical generated from benzene cation and water molecule affords phenol and d. d can be oxidized by V_6 (**e**) and regenerates **a**. The reduced V_6 (**f**) can be oxidized back to e by O2. The higher catalytic efficiency of supramolecular catalysts than their corresponding quinolinium bromide may be associated with the simpler way of benzene oxidation. Beside, V₆ may also promote the generation, separation and transport of the photo-induced carriers. [22,24,25]

As can be seen from **Table 1**, the yield of phenol increases with the increase of carbon chain length of quinolinium ions in supramolecular catalysts. $(C_{16}$ -Quin)_2V_6 and $(C_8$ -Quin)_2V_6 show much enhanced catalytic efficiency than $(C_4$ -Quin)_2V_6. The assembly structure of supramolecular catalysts in solid may be associated with this phenomenon (**Figure 2**). The size of channels/pores in these three supramolecular catalysts influence the final catalytic effect seriously. The larger the pore size, the easier the contact between catalyst and reactant, and the higher the catalytic efficiency. The orderly accumulation of carbon chains in $(C_{16}$ -Quin)_2V_6 leads to a one-dimensional channel with 5.8 Å maximum diameter (**Figure 2**(c)). Carbon chains in $(C_8$ -Quin)_2V_6 is long enough to bring big pores with 4.6 Å maximum diameter (**Figure 2**(b)). Conversely, the carbon

chains in $(C_4$ -Quin)₂V₆ is too short to bring big channels or pores and only pores with 3.2 Å maximum diameter are obtained (**Figure 2**(a)). It is worth mentioning that the phenol selectivity of $(C_{16}$ -Quin)₂V_6 > (C_8-Quin)₂V_6 > (C_4-Quin)₂V_6 is also related to the assembly structures, the larger the pore/channel size of supramolecular catalysts, the better the separation of phenol and the prevention of excessive oxidation of phenol on the surface of catalysts. The result is that the longer carbon chains of quinolinium ions, the larger channels/pores formed in supramolecular catalysts, the higher catalytic efficiency and good phenol selectivity obtained.

Entry	Catalyst	Phenol Yield (%)	Sel. (%)	
1 ^{ace}	(C4-Quin)Br	1.0 %		
2 ^{ace}	(C ₈ -Quin)Br	1.3 %	>99 %	
3 ^{ace}	(C ₁₆ -Quin)Br	1.0 %	>99 %	
4 ^{ace}	(C ₈ -Quin-NH ₂)Br	No detected	-	
5 ^{ade}	(C ₄ -Quin) ₂ V ₆	14.0 %	97.5 %	
6 ^{ade}	(C ₈ -Quin) ₂ V ₆	21.7 %	98.6 %	
7 ^{ade}	(C ₁₆ -Quin) ₂ V ₆	22.5 %	99 %	
8 ^{ade}	$(C_8$ -Quin-NH ₂) ₂ V ₆	No detected	-	
9 ^{bce}	(C ₁₆ -Quin)Br	No detected	-	
10 ^{bde}	$(C_{16}-Quin)_2V_6$	No detected	-	
11 ^{ae}	No catalyst	No detected	-	
12 ^{ade}	(TBA) ₂ V ₆	No detected	-	
13 ^{adf}	(TBA) ₂ V ₆	No detected	-	

All the experiments were carried out in a mixed solutions (H₂O/CH₃CN, 3:17 = v:v) containing substrate (0.5 mmol) and internal standard (dodecane, 44 µmol) for 12 h at 25°C. The other details are show as below: a, with UV-light irradiation. b, in dark. c, the catalyst dosage is 0.025 mmol. d, the catalyst dosage is 0.0125 mmol. e, with O₂ as oxidant. f, with H₂O₂ as oxidant. Entry. 1-4, 9, 11-13 are homogeneous system and Entry. 5-8, 10 are heterogeneous system.

No phenol was detected by (C8-Quin-NH2)Br and no enhanced catalytic efficiency from (C₈-Quin-NH₂)₂V₆ to (C₈-Quin-NH₂)Br was observed (Table 1, Entry 4, 8), much lower than the obviously enhanced catalytic efficiency from (C₈-Quin)₂V₆ to (C₈-Quin)Br. There are three main reasons behind this phenomenon. The first is the difference between (C₈-Quin-NH₂)Br and (C₈-Quin)₂V₆ in assembly structure. Rectangular channels with 3.3 x 1.5 Å² cross-sectional area was found in $(C_8-Quin-NH_2)_2V_6$ (**Figure 2**(d)), smaller than $\pi \times 2.3 \times 2.3 \text{ Å}^2$ of $(C_8$ -Quin)₂V₆. The second reason maybe lies in strong electron donation properties of amino groups in C₈-Quin-NH₂, similar to the reported work by Prof. Shunichi Fukuzumi, catalytic efficiency of quinolinium ions with different substituents behaves as QuCN⁺ > QuMe⁺ > QuH⁺.^[16] Finally, the alkalescence of -NH₂ group may also lead to the low catalytic efficiency. Alkaline condition of reaction solution caused by -NH₂ limits the reoxidation of the reduced V₆ anion and reduces the yield of phenol at last. From this viewpoint, acidic environment with abundant H⁺ is more conducive to the reaction. A new photocatalytic system was then constructed with concentrated H₂SO₄ as additive to maintain acidic environment (Table 2).

RESEARCH ARTICLE



Scheme 1. The proposed mechanism of hydroxylation of benzene by supramolecular catalysts, O_2 , H_2O/CH_3CN system under light irradiation conditions (R=H, n= 2, 6, 14). The Color code in e and f: V - orange, O - red, C - black and H – grey.

Photocatalytic hydroxylation of benzene under conditions with H₂SO₄ as additive and the reaction mechanism. The catalytic system of supramolecular catalysts becomes homogeneous after the introduction of H₂SO₄. UV-vis spectra were obtained first to confirm the supramolecular interaction between alkoxohexavanadate anions and quinolinium ions (Fig. S18), the different absorption intensity of (TBA)₂V₆ and (C₄- $Quin)_2V_6$ at 387 nm in the acidic catalytic system reflects the existence of energy transfer phenomenon between alkoxohexavanadate anions and quinolinium ions. (C8-Quin-NH₂)₂V₆ performed improved catalytic activity with H₂SO₄ than without H₂SO₄ (Table 2, Entry 21). Interestingly, (TBA)₂V₆ show much higher catalytic efficiency with H₂SO₄ than without H₂SO₄ in the presence of H₂O₂ (Table 2, Entry 23, 24), while still no phenol was detected by (TBA)₂V₆ with H₂SO₄ under O₂ conditions (Table 2, Entry 22). It means both acid and H₂O₂ are essential to produce catalytic active species for benzene oxidation to phenol by (TBA)₂V₆. (C₄-Quin)Br, (C₈-Quin)Br, (C₁₆-Quin)Br and (C₈-Quin-NH₂)Br show improved phenol yield with H₂SO₄ than without H₂SO₄(**Table 2**, Entry 14, 15, 16, 17), caused by the following two reasons. The first, the introduction of SO₄²⁻ bringing more Mulliken charge population on [Cn-Quin-H]²⁺ or [C₈₋ Quin-NH₃]²⁺ cation^[17] The second, abundant H⁺ provided by H₂SO₄ makes the formation of HO₂ become much easier. (C₄- $Quin)_2V_6$, $(C_8-Quin)_2V_6$, and $(C_{16}-Quin)_2V_6$ show obviously enhanced catalytic activity with H₂SO₄ than without H₂SO₄ under O₂ conditions (Table 2, Entry 18, 19, 20), and the calculated highest TON was 19.8 by (C8-Quin)₂V6. The transition from heterogeneous system to homogeneous system is one of the EPR reasons for the increase of catalytic efficiency. measurements were performed then to further understand catalytic mechanism of H₂SO₄ photocatalytic system. Signals attributed to DMPO-OOH derived from O_2^{-} (Fig. S19, $A_N = 1.3$ mT, $A_{\beta H} = 0.9$ mT, g = 2.0049) were captured on irradiation of $(C_4$ -Quin)₂V₆ with H₂SO₄, it means H₂O₂ can be produced by the hydrogen abstraction of HO2' from the OH-adduct radical I (Scheme 2) then. The related performance was exhibited with that the yield of H₂O₂ and phenol were improved simultaneously by quinolinium ions photocatalysis.[16] Therefore, the other reason for the improvement of catalytic efficiency in H2SO4 system is that H₂O₂ produced by quinolinium ions can be used further to oxidize benzene to phenol catalyzed by the polyoxoalkoxovanadate anion. The slight difference in catalytic effect of (C₄-Quin)₂V₆, (C₈-Quin)₂V₆, and (C₁₆-Quin)₂V₆ resulted from the difference in emulsification of the catalyst themselves. With the increase of carbon chain length on quinolinium ions, the emulsification increased first and then decreased.

In order to understand the photocatalytic mechanism more comprehensively, the mechanism of thermochemical catalytic hydroxylation of benzene by V₆, H₂O₂, H₂SO₄ was also studied. Radical scavenger test was first performed to verify whether the hydroxylation of benzene by V₆, H₂O₂ and H₂SO₄ without light irradiation is a free radical reaction or not. No deactivation happened in the presence of butylated hydroxytoluene (BHT, scavenger for various radicals) reflects the process is non-radical route (Table 2, Entry 25). In-situ EPR measurements were performed at last. No signals were captured on V₆ in CH₃CN, while V^{4+} signals were captured with the adding of H_2SO_4 (Fig. S20). It reflects V^{5+} is turned into V^{4+} in the presence of H₂SO₄. As the previous works confirmed,^[4, 26] the newly formed V⁴⁺ species (Scheme 2 (b), f) can react with H₂O₂ to form highly active species (Scheme 2, g, h) and realize the hydroxylation of benzene. A possible involved mechanism of hydroxylation of benzene by supramolecular catalysts, O₂, H₂O and H₂SO₄ under light irradiation conditions was proposed at last, as shown in Scheme 2. In summation, the whole photocatalytic mechanism of supramolecular catalysts includes: 1) phenol and hydrogen peroxide are produced by quinolinium ions under photocatalytic conditions first (**Scheme 2**, (a))^[16]. 2), the produced H_2O_2 is then exploited further by the catalytic activation of alkoxohexavanadate anion to hydroxylate benzene again (Scheme 2, (b)). Besides, as mentioned before, V₆ may also promote generation, separation and transport of the photoinduced carriers here. [22, 24, 25]

RESEARCH ARTICLE



Figure 2. Packing structures of $(C_4-Quin)_2V_6$ (a), $(C_8-Quin)_2V_6$ (b), $(C_{16}-Quin)_2V_6$ (c), $(C_8-Quin-NH_2)_2V_6$ (d) in the crystals. The solvent molecules and H atoms are omitted for clarity. Color code: V – orange, O – red, N – blue, C – gray and H – white.

Entry	Catalyst	Oxidant	H_2SO_4	Light	Catalytic systems	Phenol Yield (%)	Sel. (%)
14 ^{ac}	(C₄-Quin)Br	O ₂	V	\checkmark	Homogeneous	1.7 %	>99 %
15 ^{ac}	(C ₈ -Quin)Br	O ₂	\checkmark	\checkmark	Homogeneous	5.0 %	> 99 %
16 ^{ac}	(C ₁₆ -Quin)Br	O ₂	\checkmark	\checkmark	Homogeneous	1.9 %	>99 %
17 ^{ac}	(C ₈ -Quin-NH ₂)Br	O ₂	\checkmark	V	Homogeneous	1.0 %	> 99 %
18 ^{ad}	$(C_4-Quin)_2V_6$	O ₂	\checkmark	V	Homogeneous	45.0 %	> 99 %
19 ^{ad}	$(C_8$ -Quin) ₂ V ₆	O ₂	\checkmark	V	Homogeneous	50.1 %	> 99 %
20 ^{ad}	$(C_{16}\text{-}Quin)_2V_6$	O ₂	~	V	Homogeneous	47.2 %	> 99 %
21 ^{ad}	$(C_8$ -Quin-NH ₂) ₂ V ₆	O ₂	V	\checkmark	Homogeneous	4.0 %	> 99 %
22 ^{ad}	(TBA) ₂ V ₆	O ₂	V	\checkmark	Homogeneous	No detected	—
23 ^{bd}	(TBA) ₂ V ₆	H_2O_2	N	\checkmark	Homogeneous	17 %	>99 %
24 ^{ad}	(TBA) ₂ V ₆	H ₂ O ₂	1	×	Homogeneous	26.7 %	>99 %
25 ^{ade}	(TBA) ₂ V ₆	H ₂ O ₂	V	×	Homogeneous	26.2 %	>99 %

All the experiments were carried out in a mixed solution (H₂O/CH₃CN, 3:17 = v: v) containing substrate (0.5 mmol), internal standard (dodecane, 44 µmol) and H₂SO₄ (0.288 mmol) at 25 °C. The other details are show as below: a, the reaction time is 12 h. b, the reaction time is 4 h. c, the catalyst dosage is 0.025 mmol. d, the catalyst dosage is 0.0125mmol. e, BHT (1 mmol) was added to the reaction system.

The influence of the substituents in benzene ring on catalytic reactions was investigated by changing the kind of substrates. As shown in Tab. S1, the introduction of Cl, Br, NO₂ and OCH₃ groups in benzene all decreases the reaction efficiency. The conversation of chlorobenzene to p-chlorophenol (20.8 %) is higher than bromobenzene to p-bromophenol (4.9 %), and no oxidation products were detected in the case of nitrobenzene and methoxybenzene as substrates. Because the electron-withdrawing ability of substituents is NO₂ >Cl >Br >OCH₃, we conclude that the electron-withdrawing ability of substituents is not the only factor affecting the reaction efficiency are still under consideration in our laboratory.

Conclusion

In conclusion, a series of supramolecular catalysts based on an alkoxohexavanadate anion and several quinolinium ions for photocatalytic hydroxylation of benzene to phenol have been developed from the perspective of improving atomic availability by the strategy of molecular self-assembly. The influence of assembly structure, substituents in quinolinium ring and the acidity of reaction system on the synergistic catalytic effect of alkoxohexavanadate anion and quinolinium ions have been

JUSCLI

RESEARCH ARTICLE



Scheme 2. The proposed mechanism of hydroxylation of benzene by supramolecular catalysts, O2, H2O/CH3CN and H2SO4 under light irradiation conditions. The colour code in e, f, g and h: V - orange, O - red, C - black and H - grey.

uncovered. In the heterogeneous catalytic case without H₂SO₄, the longer the carbon chain of quinolinium ions, the larger the holes/ channels of the assemblies, the more conducive to the improvement of catalytic efficiency. The electron donor group/alkaline substituent group on quinolinium ring is harmful to the catalytic reaction. The acidity of the catalytic system helps to improve catalytic efficiency. The introduction of H₂SO₄ not only improves the solubility of supramolecular catalysts in the system, but also contributes to the formation of H2O2 and V-peroxo compound, improving the synergistic catalytic efficiency at last. In the photocatalytic case with H₂SO₄ as an additive, (C₈- $Quin)_2V_6$ exhibits the highest phenol yield (50.1 %) and selectivity (> 99 %) by using O_2 as the sole oxidant, much higher than $(TBA)_2V_6(0)$ and C_8 -Quin (5.0 %) alone. The 50.1 % phenol yield surpasses all the POM-based catalysts reported for the hydroxylation of benzene to phenol to date and at the leading level of photocatalytic synthesis of phenol from benzene using O₂ as the sole oxidant without extra redox agents.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21971134, 21631007 and 21225103), Doctoral Fund of Ministry of Education of China No. 20130002110042, Tsinghua University Initiative Foundation Research Program No. 20131089204 and the State Key Laboratory of Natural and Biomimetic Drugs K20160202. We thank Ms Ye Bi, Mr. Han Wu, Dr. Bin Yuan, Mr. Xianjin Zhu and Mr. Guoyong Dai for discussions and supports.

Conflict and interest

The authors declare no competing financial interests.

Keywords: supramolecular photocatalysis, polyoxovanadates, quinolinium, hydroxylation of benzene, synergistic catalysis

- [1] S.-I. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba, F. Mizukami. Science, 2002, 295, 105-107.
- [2] Y. Ide, M. Torii, T. Sano. J. Am. Chem. Soc. 2013, 135, 11784-11786.
- [3] Y. Pan, Y. J. Chen, K. L. Wu, Z. Chen, S. J. Liu, X. Cao, W. -C Cheong, T. Meng, J. Luo, L. R. Zheng, C. G. Liu, D. S. Wang, Q Peng, J. Li, C. Chen. Nat. Commun. 2019, 10, 4290. [4] Y. Zhou, Z. P. Ma, J. J. Tang, N. Yan, Y. H. Du, S. B. Xi,; K. Wang, W.
- Zhang, H. M. Wen, J. Wang. *Nat. Commun.* 2018, 9, 2931. [5] X. F. Chen, J. S. Zhang, X. Z Fu, M. Antonietti, X. C. Wang. *J. Am. Chem.*
- Soc. 2009, 131, 11658-11659.

[6] T. Tsuji, A. A. Zaoputra, Y. Hitomi, K. Mieda, T. Ogura, Y. Shiota, K. Yoshizawa, H. Sato, M. Kodera. Angew. Chem. Int. Ed. 2017, 56, 7779-7782. [7] M. Tani,; T. Sakamoto,; S. Mita,; S. Sakaguchi,; Y. Ishii. Angew. Chem., Int. Ed. 2005, 44, 2586-2588.

- [8] R. Dittmeyera, L. Bortolottob. Applied Catalysis A: General, 2011, 391, 311-318.
- [9] L. S. Wang, S. Yamamoto, S. Malwadkar, S. Nagamatsu, T. Sasaki, K. Hayashizaki, M. Tada, Y. Iwasawa. ChemCatChem, 2013, 5, 2203-2206.
- [10] S. S. Shang, H. Yang,; J. Li, B. Chen, Y. Lv, S. Gao. ChemPlusChem, 2014, 79, 680-683.
- [11] a) T. Dong, J. Li, F. Huang, L. Wang, J. Tu, Y. Torimoto, M. Sadakata, Q. X. Li. Chem. Commun. 2005, 21, 2724-2726; b) N. B. Castagnola, A. J. Kropf, C. L. Marshall. Applied Catalysis A: General, 2005, 290, 110-122
- [12] B. Lee, H. Naito, M. Nagao, T. Angew. Chem. Int. Ed. 2012, 51, 6961-6965.
 [13] K. Ohkubo, A. Fujimoto, S. Fukuzumi. J. Am. Chem. Soc. 2013, 135, 5368-5371
- [14] L. E. Hofmann, L. Mach, M. R. Heinrich. J. Org. Chem. 2018, 83, 431-436.
- [15] Y. Aratani, K. Oyama, T. Suenobu, Y. Yamada, S. Fukuzumi. Inorg. Chem. 2016, 55, 5780-5786.
- [16] K. Ohkubo, T. Kobayashi, S. Fukuzumi. Angew. Chem. 2011,123, 8811-8814.
- [17] Z. Y. Long, L. M. Sun, M. J. Zhang, Y. D. Zhang, C. H. Zong, Z. L. Xue, T. Y. Wang, G. J. Chen. Catalysis Communications. 2019, 121, 1-4.
- [18] Y. -W. Zheng, B. Chen, P. Ye, K. Feng, W. G. Wang, Q. Y. Meng, L. Z. Wu, C. H. Tung. J. Am. Chem. Soc., 2016, 138, 10080-10083.
- [19] S. S. Wang, G. -Y Yang. Chem. Rev. 2015, 115, 4893-4962
- [20] C. Y. Yuan, X. H. Gao, Z. S. Pan, X. L. Li, Z. G. Tan. Catalysis Communications, 2015, 58, 215-218.
- [21] F. X. Gao, R. M. Hua. Applied Catalysis A: General, 2004, 270, 223-226. [22] L. Y. Zhang, Q. Hou, Y. Zhou, J. Wang. Molecular Catalysis, 2019, 473, 110397
- [23] P. F. Wu, J. K. Chen, P. C. Yin, Z. C. Xiao, J. Zhang, A. Bayaguud, Y. G. Wei. Polyhedron, 2013, 52, 1344-1348.
- [24] R. W. Liang, R. Chen, F. F. Jing, N. Qina, L. Wu. Dalton Trans. 2015, 44, 18227-18236.
- [25] J. -Z. Liao, H. -L. Zhang, S. -S. Wang, J. -P. Yong, X. -Y. Wu, R. M. Yu, C. -Z. Lu. *Inorg. Chem.* 2015, 54, 4345-4350.
 [26] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, R. Weissl. *J. Am.*
- Chem. Soc. 1983, 105, 3101-3110.

RESEARCH ARTICLE

TOC



The readily available series green V supramolecular catalysts can catalyze the hydroxylation of benzene to phenol with high conversion, selectivity and atom efficiency.

