

Sodium metavanadate catalyzed direct hydroxylation of benzene to phenol with hydrogen peroxide in acetonitrile medium

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Abstract

The homogenous liquid-phase direct catalytic oxidation of benzene to phenol was performed at room temperature in acetonitrile solvent using sodium metavanadate as the catalyst and hydrogen peroxide as the oxidant. The effects of various reaction parameters, such as acidity of the system, reaction temperature, reaction time and the amount of hydrogen peroxide used, were studied. Under the optimized conditions, a phenol yield of 13.5% with a selectivity of 94% was obtained. The variation of vanadium species during the reaction was studied by in situ $^{51}\text{V-NMR}$ method. It was found that vanadium species existed as VO_2^+ before the reaction. In the presence of hydrogen peroxide, VO_2^+ species might be transferred to peroxovanadate species, such as $\text{HVO}(\text{O}_2)_2$, $\text{VO}(\text{O}_2)^+$, which oxidized benzene to phenol exerting the catalytic performance. A catalytic cycle involving the above mechanism was proposed.

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Keywords: Benzene; Sodium metavanadate; Hydroxylation; In situ $^{51}\text{V-NMR}$

1. Introduction

Phenol is an important intermediate for the production of antioxidants, agrochemicals and polymers. More than 90% of the world production of phenol is obtained by the multi-step cumene process, which has several disadvantages: low one-pass yield of phenol [1], high energy cost, an explosive intermediate (cumene hydroperoxide), and requirement to treat the by-product of acetone with 1:1 molar ratio. Thus, the direct hydroxylation of benzene to phenol with high atomic efficiency and high selectivity becomes one of the most challenging tasks and has attracted much attention. In the past decades, this interesting work has been extensively studied in both liquid- and gas-phase, and several catalysts, such as Fenton reagent [2], metal oxides [3–5], Pd membrane [1,6], ZSM-5 zeolites [7,8], heteropolymolybdates [9–12] and so on have been investigated.

Among the reported vanadium-containing catalysts, the V-substituted heteropolyacids especially, showed high activities and vanadium was found to be necessary for the reaction. It was found that the vanadium species existed in the Keggin structure

and as VO_2^+ in solution are all catalytically active, but acted differently [9,12]. To our knowledge, there is scarcely detailed mechanistic study on the activation of C–H bond by directly using sodium metavanadate as the catalyst. In an attempt to explore the performance of vanadium species existed in solution for the benzene hydroxylation, the catalytic oxidation of benzene was carried out using sodium metavanadate in the present work.

2. Experimental

2.1. Materials

All chemicals were of analytical grade and were used without further purification. Benzene, *o*-cresol, and sodium metavanadate, were purchased from Shanghai Chemical Co. Ltd. Hydrogen peroxide, glacial acetic acid, alcohol, acetone, acetonitrile, nitrous acid, sulfuric acid, hydrochloric acid, and sodium hydroxide were from Chengdu Chemical Co. Ltd.

2.2. Typical oxidation procedure and products analysis

The oxidation of benzene was carried out in a two-necked 50 mL round bottom flask placed in a water bath. HNO_3

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(1 mol/L) and NaOH (1 mol/L) were used to adjust the acidity of the solution. In a typical procedure, 0.2 mmol NaVO_3 and 1 mL (11.3 mmol) benzene were added into 15 mL acetonitrile with certain amount of nitrous acid added to adjust the acidity, and then 2 mL (19.4 mmol) H_2O_2 (30%) was added into the above mixture. The reaction was performed comparatively under stirring by a magnetic stirrer (600 rpm) or without stirring for about 13 h. Then, the products were analyzed by gas chromatography (Varian, GC-960 equipped with hydrogen flame detector and a capillary column). *o*-Cresol was used as an internal substance to quantify the phenol formed. The main product of the reaction was further identified by coupled gas chromatography and mass spectroscopy (GC-MS, Agilent 5973 Network 6890N) to be phenol, with a very small amount of benzoquinone. The yield of phenol was calculated as mmol phenol/mmol initial benzene. Selectivity of phenol was calculated as mmol phenol/(mmol all products) [12]. The catalytic turnover number (TON) was estimated as mmol phenol/mmol initial vanadium.

2.3. In situ ^{51}V -NMR study

In situ ^{51}V -NMR was carried out to investigate the variation of vanadium species during the whole reaction process. The ^{51}V -NMR signals were obtained on a Bruker DRX-300 spectrometer operating at 78.9 MHz using a 10 mm broadband probe, at 295 ± 0.5 K. Chemical shifts were externally referenced to VOCl_3 at 0 ppm. The ^{51}V -NMR acquisition parameters were: 98 kHz spectral width, 0.15 s acquisition time and 30 Hz line broadening. And the ^{51}V -NMR signals were scanned every 5 min and accumulated four times to output.

3. Result and discussion

3.1. Identification of the catalytically active species in the reaction

To explore the active vanadium species, the reaction was carried out at different pH. The result is shown in Table 1. No phenol formed when the pH was above 2. Only when the pH was below 2, especially around 1, phenol was detected in the solution. Further rise in acidity of the medium did not result in a higher phenol yield.

It is known that the distribution of vanadium species in solution is significantly influenced by the pH of the solution [13,14]. That is, in high pH ($\text{pH} > 9$), vanadium species mainly exist as VO_4^{3-} , HVO_4^{2-} , and H_2VO_4^- . Near the pH of 7, $\text{V}_4\text{O}_{12}^{4-}$ is predominant, with a small amount of $\text{V}_5\text{O}_{15}^{5-}$. When the pH is lower than 6, $\text{V}_{10}\text{O}_{28}^{6-}$ begins to appear and becomes predominant over the pH range of 4.1–3.0, in the pH of 2.0, VO_2^+ and V_{10} coexist. Only VO_2^+ exists at the pH below 1.0.

Table 1
Phenol yield in the media with different pH

pH	0.65	0.75	0.85	1.09	1.75	2.65	3.92	4.45	7.0	10.8	14.0
Phenol (%)	6.84	7.06	7.25	7.91	4.25	–	–	–	–	–	–

Experimental conditions: 0.2 mmol NaVO_3 ; 1 mL (11.3 mmol) of benzene; 2 mL (19.4 mmol) of H_2O_2 and 15 mL of CH_3CN ; H_2O_2 dropwisely for an hour; stirring (600 rpm); 298 K; 4 h.

Table 2
Yield of phenol in different solvents

Solvents	pH	Yield (%)	Selectivity (%)	TON
Alcohol	1	0.67	100	0.39
Alcohol	7	Trace	–	–
Acetone	1	1.76	100	0.99
Acetone	7	Trace	–	–
Acetonitrile	1	11.25	91	6.36
Acetonitrile	7	Trace	–	–
Acetic acid	0.9	8.90	90	5.03

Experimental conditions: 0.2 mmol NaVO_3 ; 1 mL (11.3 mmol) of benzene; 2 mL (19.4 mmol) of H_2O_2 ; H_2O_2 dropwisely for an hour; stirring (600 rpm); 298 K; 13 h. Yield of phenol calculated as mmol phenol/mmol initial benzene. Selectivity of phenol calculated as mmol phenol/(mmol phenol + mmol benzoquinone). Turnover number calculated as mmol phenol/mmol initial vanadium.

The ^{51}V -NMR spectrum with a chemical shift of -543 ppm in the present experimental conditions (Fig. 1a) confirmed the sole existence of VO_2^+ in the catalytic system before hydrogen peroxide was added [15], revealing that VO_2^+ is responsible for the hydroxylation of benzene, and other vanadium species might not exhibit catalytic performance for the titled reaction under the reaction conditions investigated. This is consistent with the result reported by Nomiya et al. [9], where sodium metavanadate was found to be capable of catalyzing the conversion of benzene to phenol in the presence of acid. The induction period observed [9] may be caused by the transformation of vanadium species in the presence of hydrogen peroxide.

3.2. Effect of the solvent

Alcohol, acetone, acetonitrile and glacial acetic acid were used as the solvents for the reaction. The result is shown in Table 2. When alcohol, acetone, and acetonitrile were used as the solvent directly, only a trace amount of phenol was detected, indicating that the neutral surrounding was unfavorable for phenol formation. When the solvents were adjusted to be acidic with pH around 1, phenol formed predominantly. It should be pointed out that the present reactions were all carried out homogeneously, that is, NaVO_3 dissolved in the three solvents when hydrogen peroxide was added into the solvents. The feasibility of the reaction media for the hydroxylation could be expressed as the following order: acetonitrile > acetone > alcohol.

As reported by Conte et al. [16], the nature of the coordination sphere of the peroxovanadium complexes exerts a marked effect on their oxidative ability. Alcohol, acetone, and acetonitrile were three typical solvents, and the order of the oxidative ability of complex in different solvent is acetonitrile > acetone > alcohol. Thus the different catalytic performance of vanadium in different solvents may be caused by the coordination of the solvent

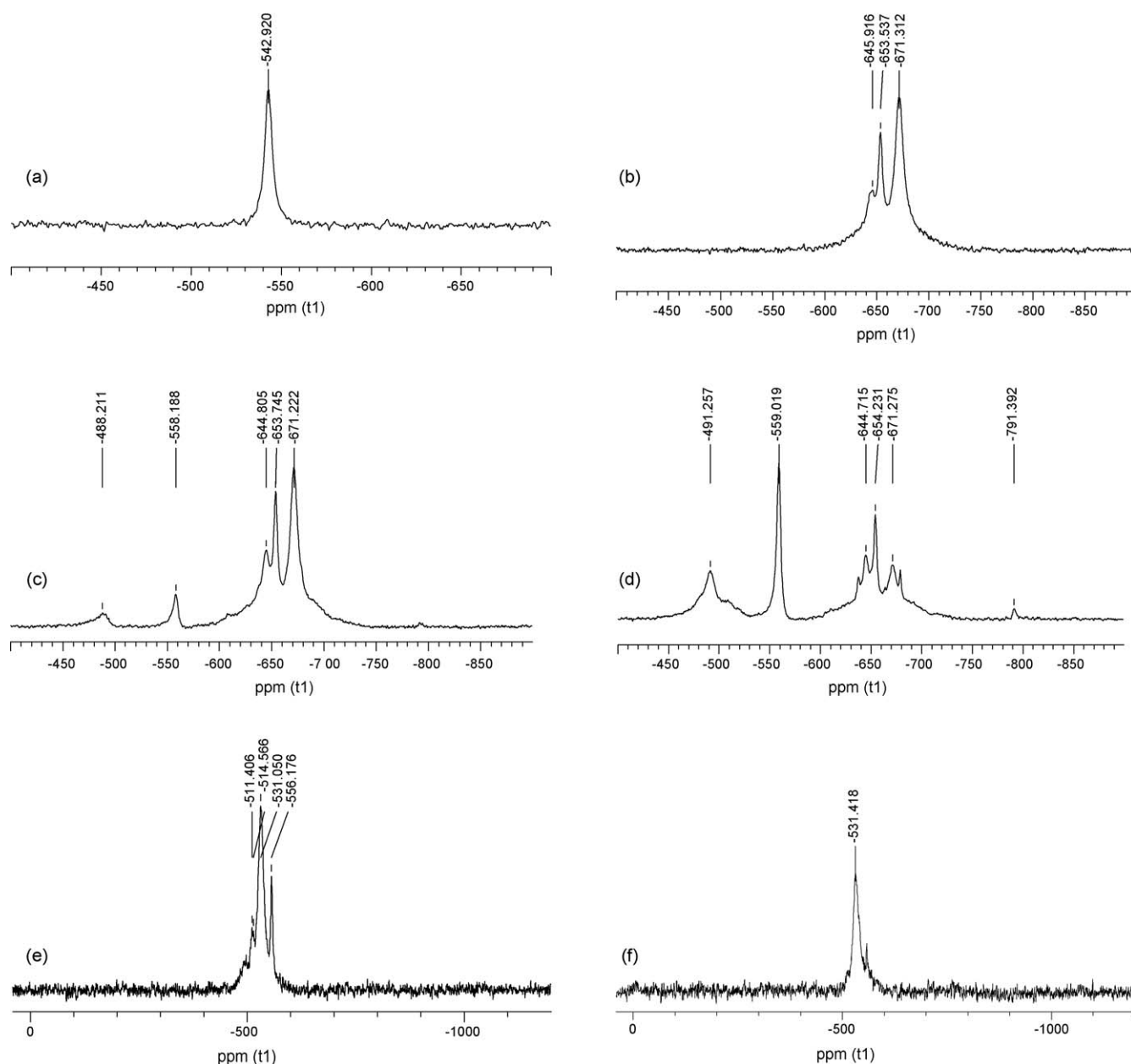


Fig. 1. ^{51}V -NMR signals of the samples after certain reaction time. (a) Solution of $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (4:1, v/v) containing NaVO_3 ; (b) 20 min; (c) 220 min; (d) 600 min; (e) 740 min; (f) 760 min.

molecular to the peroxovanadium species and then the oxidative potential is altered.

For comparison, the reaction was carried out in glacial acetic acid with a pH of 0.9 and a phenol yield of 8.9% was obtained. The yield was slightly lower than that obtained in acidic acetonitrile. Although acetic acid may provide an acidic surrounding, the coordination of acetic acid to vanadium species may affect the oxidative ability, and then decreased the yield of phenol. Subsequently, we focus our attention on acetonitrile as the solvent.

3.3. Effect of the amount of vanadium used

The dependence of the catalytic performance on the amount of NaVO_3 used was investigated and the result is plotted in Fig. 2.

No phenol was detected without the use of NaVO_3 , which indicated that the presence of vanadium was essential for performing the oxidation. The amount of phenol increased with the increase of the amount of vanadium, and reached a constant yield of 11.3% with a selectivity of 90% when the amount of the catalyst used ranged from 0.2 to 0.3 mmol. Further increase in the amount of the catalyst could not bring a higher yield of phenol and even decreased the activity abruptly when 0.6 mmol NaVO_3 was used. This could be attributed to the accelerated self-decomposition of hydrogen peroxide by the excess amount of vanadium [12]. The same tendency was observed in acetic acid system where the phenol yield increased with the increase of the amount of metavanadate, and a phenol yield of 8.6% and a TON of 10 were obtained when 0.2 mmol metavanadate was

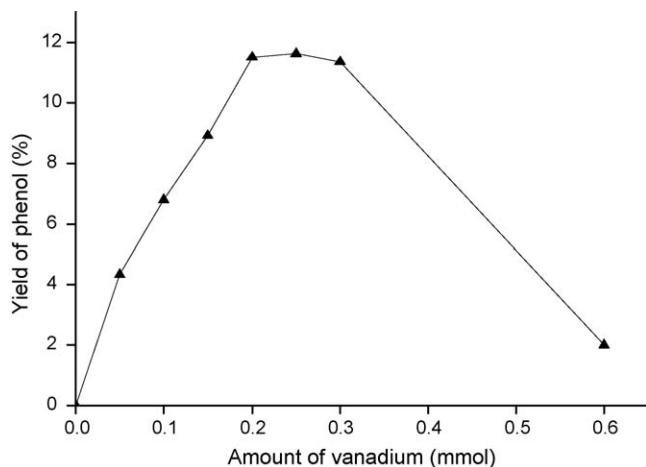


Fig. 2. Yield of phenol as a function of the amount of vanadium used. Experimental conditions: 1 mL (11.3 mmol) of benzene; 2 mL (19.4 mmol) of H_2O_2 and 15 mL of CH_3CN ; H_2O_2 dropwisely for an hour; stirring (600 rpm); 298 K; 13 h.

used [12]. In the model hydroxylation of Nomiya et al. [9] using metavanadate directly as the catalyst, the yield of 1.7% to phenol with TON of 19 was obtained. The difference may be caused by different reaction conditions.

3.4. Effect of different acid

The acidity of the solution has a significant effect on the yield of phenol, and the decomposition of H_2O_2 is reduced in the acid medium. To investigate the effect of the different acid on the reaction, besides nitrous acid, sulfuric acid and hydrochloric acid were also used to adjust the pH to around 1. The result is shown in Fig. 3, and the catalytic performance with different acid exhibits the following order: $\text{HNO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$.

When using the three inorganic acids, the difference is quite small. The phenol yield is slightly higher using nitrous acid. This may be attributed to the fact that when sulfuric acid and

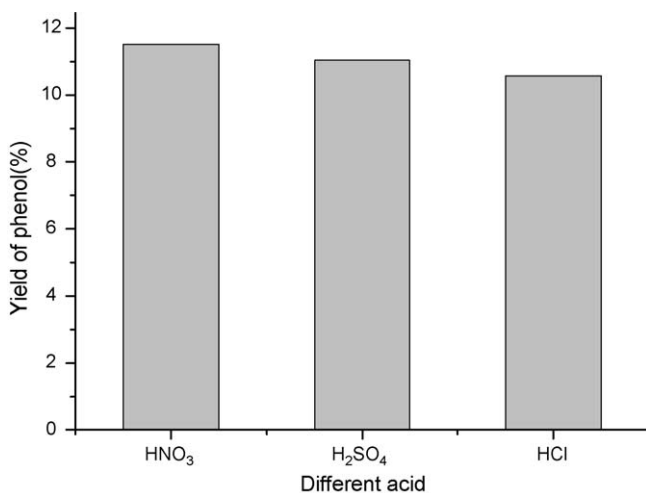


Fig. 3. Yield of phenol with different acids used to adjust acidity. Experimental conditions: 0.2 mmol NaVO_3 ; 1 mL (11.3 mmol) of benzene; 2 mL (19.4 mmol) of H_2O_2 and 15 mL of CH_3CN ; H_2O_2 dropwisely for an hour; stirring (600 rpm); 298 K; 13 h.

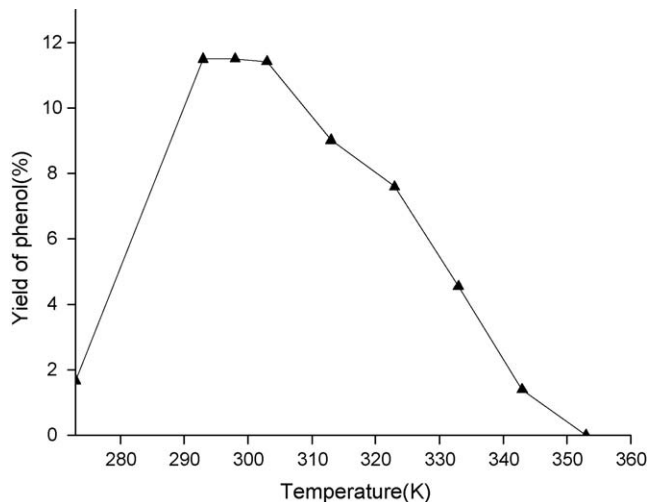


Fig. 4. Yield of phenol at different temperature. Experimental conditions: 0.2 mmol NaVO_3 ; 1 mL (11.3 mmol) of benzene; 2 mL (19.4 mmol) of H_2O_2 and 15 mL of CH_3CN ; H_2O_2 dropwisely for an hour; stirring (600 rpm); 13 h.

hydrochloric acid were used, the reaction mixture was not as uniform as when nitrous acid was used after a period of reaction time.

3.5. Effect of the reaction temperature

The effect of the reaction temperature on the yield of phenol is shown in Fig. 4. It was indicated that at 273 K, only 1.7% yield of phenol was obtained, showing a very slow reaction. When the reaction temperature was raised to 293 K, a sharp increase of the phenol yield was observed, and the variation of reaction temperature from 293 to 303 K did not affect the yield of phenol much because of the competition between the increase of the reaction rate and the decomposition of hydrogen peroxide. Further increase in temperature caused the remarkable decrease of phenol yield, and nitrobenzene and nitrophenol were observed as by-products. It was known that the typical nitration reaction of benzene occurred at about 333 K [17]. The above data indicate that the competitive nitration of benzene occur at above 303 K. So, higher temperatures are in favor of the production of nitrobenzene and nitrophenol in addition to the self-decomposition of hydrogen peroxide. Thus the temperature range over 293–303 K is suitable for the present hydroxylation reaction. This is in agreement with the literature [12,18].

3.6. Effect of the amount of H_2O_2

H_2O_2 was added dropwisely with stirring, added totally with stirring, and added totally without stirring to perform the reaction. The result is shown in Fig. 5. It can be seen that when H_2O_2 was added totally without stirring, the highest yield of phenol was obtained, while phenol was relatively higher when H_2O_2 is added totally with stirring. This may be caused by the influence of different manners of stirring on the decomposition of H_2O_2 and the mechanism preserved further detailed investigations.

The effect of the amount of H_2O_2 on the yield of phenol is shown in Table 3. No phenol was obtained without the use of

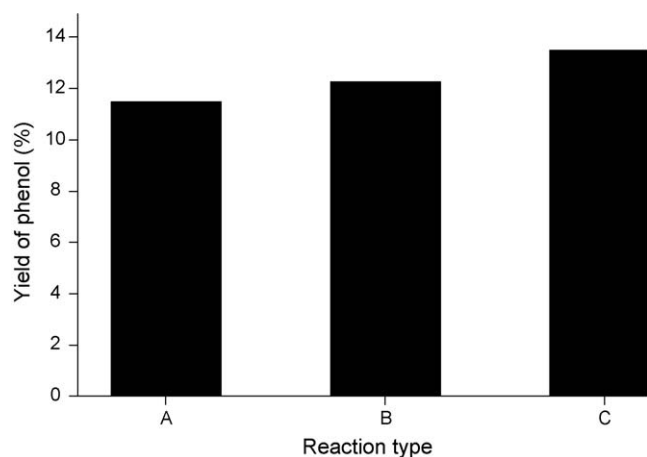


Fig. 5. Yield of phenol under different added manners of H₂O₂. Experimental conditions: 0.2 mmol NaVO₃, 1 mL (11.3 mmol) of benzene, 2 mL (19.4 mmol) of H₂O₂ and 15 mL of CH₃CN; (A) H₂O₂ dropwisely for an hour; stirring (600 rpm); (B) dropwisely for an hour; without stirring; (C) added totally without stirring; 298 K; 30 h.

H₂O₂. With the increase of the amount of H₂O₂, the yield of phenol as well as the TON based on vanadium increased but the efficiency of hydrogen peroxide decreased simultaneously. When 2 mL H₂O₂ was used, the yield of phenol and its efficiency were relative higher, and the utilization of H₂O₂ reached 8%, which is better than our previous work (5%) [12]. Nevertheless, the utilization of H₂O₂ is still quite low; thus, how to enhance the effective use of H₂O₂ in the present reaction system preserves also a challenge.

3.7. Effect of the reaction time

The reaction mixture sampled at certain interval during the reaction period was analyzed by GC–MS. Fig. 6 shows the yield and the selectivity of phenol as a function of reaction time. The amount of phenol formed increased with time firstly, and after 13 h of reaction, it did not vary. The in situ ⁵¹V-NMR showed that after about 13 h, the vanadium species returned to VO₂⁺ with the consumption of hydrogen peroxide.

3.8. Mechanistic study

Till now, many catalysts involving vanadium had been used in the direct hydroxylation, and different reaction mechanisms were proposed. It was proposed that the Milas and Sussman

Table 3
Yield of phenol with different amount of H₂O₂ used

Amount (mL)	Yield (%)	TON	Efficiency (%)
0	–	–	–
1.2	9.22	5.20	9.22
2	13.5	7.61	7.85
3	14.6	8.23	5.72
4	15.5	8.74	4.54

Experimental conditions: 0.2 mmol NaVO₃; 1 mL (11.3 mmol) of benzene and 15 mL of CH₃CN; 298 K; 13 h; without stirring. Efficiency calculated as mmol phenol/mmol initial H₂O₂.

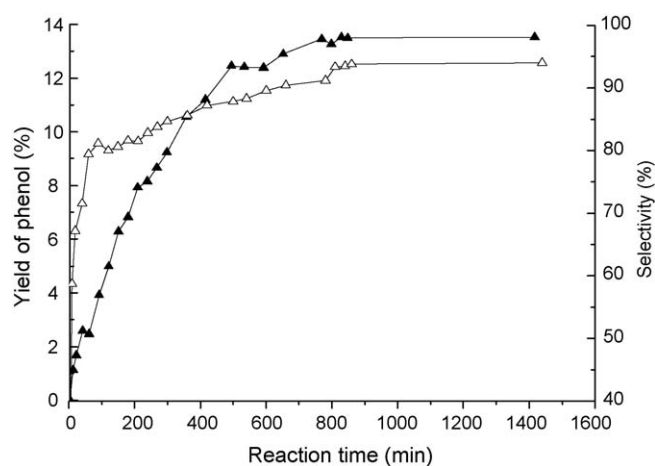


Fig. 6. Yield and selectivity of phenol as function of the reaction time. Experimental conditions: 0.2 mmol NaVO₃, 1 mL (11.3 mmol) of benzene, 2 mL (19.4 mmol) of H₂O₂ and 15 mL of CH₃CN; 298 K; without stirring (▲, yield; △, selectivity).

reagent [19] consisting of V₂O₅ and aqueous H₂O₂ acted similarly as Fenton reagent. For the monovanadium-substituted phosphomolybdate catalysts, a mechanism involving vanadium(V) peroxy intermediate species which formed with hydrogen peroxide on the skeleton of the Keggin-type polyanion to perform oxygen transfer was proposed by Alekar et al. [20]. Besides, the vanadium(V) peroxy complexes have been also used as oxygen transfer agent. Depending on the nature of the ligand coordinated to the metal and the experimental conditions, the vanadium(V) peroxy complexes act either as electrophilic oxygen transfer reagents or as radical oxidants. And the oxidation of alcohols and the hydroxylation of aromatic hydrocarbons are examples of homolytic reactivity [21]. For example, the bidentate picolinic acid anion (PIC) as ligand to peroxovanadate in the noncoordinating solvent such as C₆H₆, CH₃NO₂, CH₃CN may stabilize the active species and inhibit the electrophilic reactivity and enhance the homolytic one, while in the coordination solvent such as CH₃OH and DMF, its reactivity is suppressed [22].

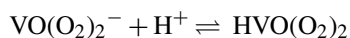
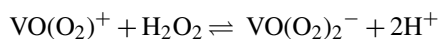
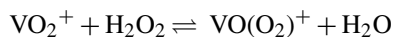
To investigate the essential states of the homogenous vanadium catalyst as a function of time during the whole reaction process, the reaction mixture was surveyed by means of in situ ⁵¹V-NMR.

Before the addition of hydrogen peroxide, the CH₃CN–H₂O solution containing a small amount of sodium metavanadate (below 0.01 mol/L of vanadium) exhibited only one peak at –543 ppm (Fig. 1a) which should be attributed to VO₂⁺. According to the literature [15], the chemical shift of VO₂⁺ in aqueous solution is –545 ppm, and the little difference should be caused by the solvent.

Hydrogen peroxide was added to the solution and the ⁵¹V-NMR was carried out immediately to identify the vanadium species. The typical NMR spectra are shown in Fig. 1b–f.

It is reported that VO₂⁺ in aqueous solution has the equilibrium between vanadium (V) and hydrogen peroxide in acidic aqueous solution, and this equilibrium can be described by the following two equations to form monoperoxy VO(O₂)⁺,

diperoxo $\text{VO}(\text{O}_2)_2^-$ species sequentially [15], and at low pH the anionic diperoxo vanadium species undergoes protonation yielding a neutral derivative [23]:



In the present work, the amount of hydrogen peroxide used was about 100-fold excess to vanadium. In situ ^{51}V -NMR suggested that all products should be evolved from the interaction of hydrogen peroxide with vanadium species in the solution to form monoperoxo and diperoxo vanadium species.

At the beginning 3 h of the reaction, when H_2O_2 exceeded too much, the ^{51}V -NMR spectrum of the sample exhibited three peaks at -646 , -654 , and -671 ppm, respectively (Fig. 1b). These peaks did not vary significantly during the 3 h, indicating the amount of the corresponding vanadium species kept constantly during the initial 3 h. As reported by Slebodnick and Pecoraro [24], the state of vanadium species existed in solution depended on the pH, the concentration, the percentage of water contained in acetonitrile and the temperature. In $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ mixture (v/v, 1/4), the peak of $\text{VO}(\text{O}_2)_2^-$ shifted downfield about 20 ppm from that in aqueous solution. The change of chemical shift may be caused by the variation of chemical environment around the vanadium center by solvent. Thus, the observed three peaks were attributed to derivatives of $\text{VO}(\text{O}_2)_2^-$ by the effect of the solvation. According to the literature [23], $\text{VO}(\text{O}_2)_2^-$ may be protonized at low pH. The exact types of the three vanadium species were not identified. After the initial 3 h, a phenol yield of 6.8% was reached.

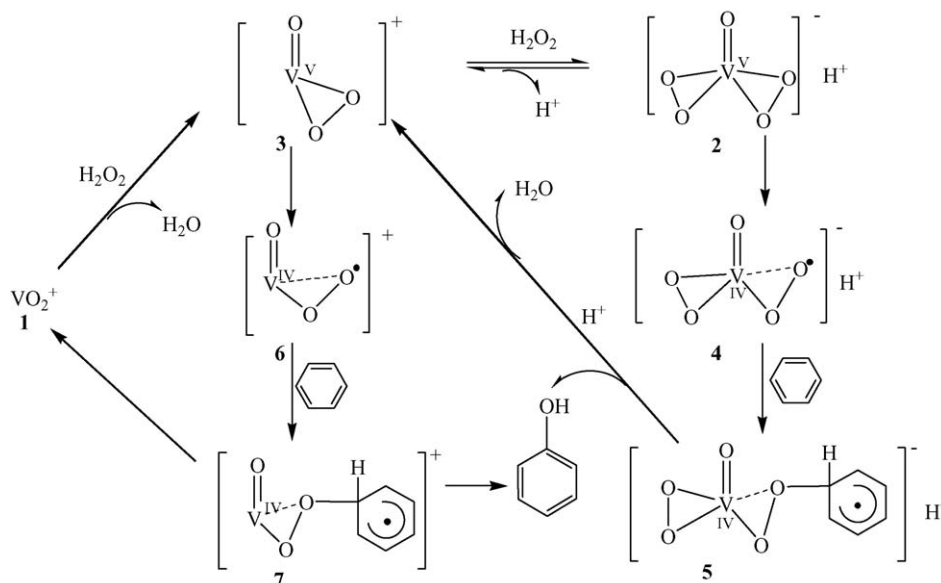
As the reaction proceeded (Fig. 1c and d), besides the three peaks at -646 , -654 and -671 ppm, two new peaks appeared at -488 and -558 ppm, respectively. According to the litera-

ture [24], the peak of $\text{VO}(\text{O}_2)^+$ shifted downfield 50 ppm from -545 ppm in 20% $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ in aqueous solution. That is, the peak at -488 ppm may be attributed to $\text{VO}(\text{O}_2)^+$. And the peak at -558 ppm was not exactly identified from literature and it existed only as an intermediate during the reaction process. We predict it should be assigned to derivative of $\text{VO}(\text{O}_2)^+$. Due to the complexity of the reaction, small amount of other vanadium species also appeared, as seen from Fig. 1d, the unidentified peaks existed at 791 ppm. The ^{51}V -NMR spectra of the reaction mixtures from 3 to 12 h show a tendency of the elimination of $\text{VO}(\text{O}_2)_2^-$ species and the increase of the new species of monoperoxo vanadate species. After 12 h of reaction, the phenol yield reached 12.9%.

Then, the two peaks at 491 and 559 ppm disappeared in the following 40 min, accompanying the appearance of two small peaks at -511 and -514 ppm (Fig. 1e), and the two peaks only existed for a short time, these two peaks may be attributed to the derivatives of $\text{VO}(\text{O}_2)^+$. When the reaction was finished, the above two peaks disappeared and only one peak at -532 ppm could be observed, indicating the recovery of VO_2^+ (Fig. 1f). The final phenol yield increased from 12.9 to 13.5%.

As mentioned above, the formation of phenol is affected by the solvent, that is, the presence of alcohols is disadvantageous for the phenol production. In addition, the existence of alcohols is not beneficial for the radical process [22]. Based on the in situ ^{51}V -NMR analysis and experimental results in the system, a radical mechanism has been proposed for the present vanadium-catalyzed hydroxylation of benzene to phenol and is shown in Scheme 1.

The initial vanadium species exists as VO_2^+ (species 1) without the addition of hydrogen peroxide in the acidic $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ medium. With the excess use of hydrogen peroxide in the system, diperoxo vanadate species 3 forms predominantly, followed by the cleavage of V–O bond to generate peroxo diradical intermediate 4 accompanied with the reduction of V(V) to V(IV). The



Scheme 1. The proposed mechanism for the hydroxylation of benzene to phenol catalyzed by NaVO_3 with H_2O_2 as oxidant.

peroxy diradical species then attack the benzene ring and yield the intermediate 5. The cleavage of O–O bond in species 5 results in the formation of phenol and accompanied by the protonation and dehydration of vanadium species giving rise to monoperoxovanadate species 2. The species 2 undergoes the similar variation, producing phenol and accompanied by the regeneration of VO_2^+ (species 1), which complete the catalytic cycle. Obviously, the diperoxovanadate species 3 and monoperoxovanadate species 2 are responsible for the present hydroxylation of benzene to phenol. Thus, the exhaustion of hydrogen peroxide in the system resulted in the loss of the active hydroxylation species, which leads to the termination of the reaction.

The presence of species 1 has been confirmed by its ^{51}V -NMR (Fig. 1a). The variation of the amount of diperoxovanadate species 3 and monoperoxovanadate species 2 has been shown in Fig. 1b–d. The species 3 refers to the derivatives from $\text{VO}(\text{O}_2)_2^-$ while species 2 relates to the derivatives from $\text{VO}(\text{O}_2)^+$. The final existence of VO_2^+ (species 1) has shown in Fig. 1f.

The oxidation of toluene was carried out under the same conditions and the products were analyzed by GC–MS. It was found that benzaldehyde was a major product and benzyl a minor product, *o*-, *m*- and *p*-cresol were also detected, and the amount of the by-products is as the following order: *o*-cresol > *m*-cresol \gg *p*-cresol, which confirmed that the vanadium-catalyzed process was a radical process. The distribution of products is similar to the literature [25], which confirms that the active species in the process may be $\text{V}^{\text{IV}}\text{—O—O}^\bullet$.

4. Conclusion

Sodium metavanadate could be used directly to catalyze the hydroxylation of benzene to phenol with high selectivity under relatively moderate conditions. The optimized experimental conditions are as the following: 0.2 mmol NaVO_3 , 1 mL (11.3 mmol) benzene, 15 mL acetonitrile, pH around 1, 2 mL (19.4 mmol) H_2O_2 (30%), reaction time of 13 h and without stirring. Under these conditions, a phenol yield of 13.5% with a selectivity of 94% is obtained. VO_2^+ is found to be the catalytic precursor. Diperoxovanadate species and monoperoxovanadate species form with the addition of hydrogen peroxide, and they are all responsible for the hydroxylation. They may present as $\text{V}(\text{IV})\text{—O—O}^\bullet$ during the reaction process, and the vanadium returns to VO_2^+ in the end to accomplish a catalytic cycle.

Acknowledgements

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