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## Short Communication

# Insight into contributions to phenol selectivity in the solution oxidation of benzene to phenol with $H_2O_2$

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## ARTICLE INFO

## ABSTRACT

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## 1. Introduction

One of the most important intermediates in the chemical industry, phenol is utilized in the fabrication of polycarbonates and epoxy resins with more than 90% produced via the cumene process [1–4]. Significant efforts have been made towards more attractive routes to phenol with most focusing on reducing hazardous waste and raw material costs; the economic efficiency of the three-step cumene process is strongly dependent on the market price of propylene (raw material) and acetone (by-product). Towards this goal, gas-phase oxidants, including N<sub>2</sub>O [5-7] and molecular oxygen [8-10], have been explored for one-step routes, though these oxidants have struggled to gain commercialization. Molecular oxygen leads to selectivity problems as the high temperatures or strong catalysts required to activate O<sub>2</sub> lead to over-oxidation of benzene. While N<sub>2</sub>O oxidation of benzene via the Solutia Alphox<sup>™</sup> process leads to high phenol selectivities (97-100%) at complete N<sub>2</sub>O conversion [11], onpurpose production of N<sub>2</sub>O as a feedstock for this process is currently not economical, limiting application of this technology to operations with integrated N<sub>2</sub>O production processes such as the manufacture of adipic acid [12].

Due to the challenges in utilizing  $O_2$  and  $N_2O$  as oxidants, the development of a liquid-phase direct oxidation process with  $H_2O_2$  also stands as an attractive one-step route for the direct oxidation of benzene [13–15]. High selectivity to mono-oxidation of benzene to phenol is a critical parameter for the evaluation and utilization of

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A high selectivity to mono-oxidation of benzene to phenol is a critical parameter for the evaluation and utilization of catalysts for the one-step oxidation process to synthesize phenol The results presented herein indicate that the uncatalyzed oxidation of phenol with  $H_2O_2$  in solution is a key contributor to phenol oxidation (and, hence, phenol selectivity) in liquid phase oxidations of benzene with  $H_2O_2$ . Additives (ex. sulfolane, acetonitrile, certain inorganic salts) are capable of inhibiting the uncatalyzed phenol oxidation, leading to their potential utility in improving phenol selectivities for benzene oxidation with  $H_2O_2$ .

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catalysts for the oxidation of benzene with hydrogen peroxide. A challenge in the mono-oxidation of benzene is the lack of kinetic control due to the higher reactivity of phenol towards oxidation than for benzene, leading to substantial production of multiple-oxidation products of benzene (i.e. hydroquinone, benzoquinone, catechol) [16,17]. While numerous titanium-based materials have been investigated as liquid phase oxidation catalysts with hydrogen peroxide including Ti-MCM-41, Ti-Beta and Ti-SBA-15 [18-20], MFI-type zeolites have been the focus of significant research in benzene oxidation catalysis due to the fact that the pore size of the MFI lattice (5.5 Å) is similar to the diameter of the benzene molecule and may impart selectivity to mono-oxidation. However, catalytic studies in our lab of [Fe.Al]-MFI and TS-1 for the solution oxidation of benzene with hydrogen peroxide under the same conditions, have shown very different phenol selectivities (>98% for Fe and  $\leq$ 90% for Ti) for similar conversions under analogous reaction conditions [21]. Studies with TS-1 have also shown that the addition of a dialkyl sulfone (e.g. sulfolane) to batch reactions for oxidation of benzene with H<sub>2</sub>O<sub>2</sub> can dramatically improve phenol selectivity, limiting the formation of multiple-oxidation products [22]. Due to this improvement in phenol selectivity for TS-1 with an additive, we were interested in obtaining further insight into the factors influencing phenol selectivity, especially the selectivity difference between iron and titanium based MFI catalysts in order to develop a viable catalytic process for benzene oxidation with aqueous H<sub>2</sub>O<sub>2</sub> and MFI-based materials.

While a recent study published during the revision of this manuscript reports on factors contributing to TS-1 selectivities and possible roles of sulfolane in affecting phenol selectivity [23], the present study expands these experiments to iron-based materials and additional additives which enhance selectivity, and provides insight

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into the importance of the amount of  $H_2O_2$  remaining in reaction to phenol over-oxidation. The results herein provide insight on the nature of the differences in phenol selectivity for TS-1 and [Fe,AI]-MFI catalysts, and highlight the contribution of the uncatalyzed homogeneous reaction of phenol with hydrogen peroxide towards the production of undesired higher-oxidation products even at low reaction temperatures (i.e. 60 °C). The roles of potential additives for improving phenol selectivity are also discussed.

#### 2. Experimental

#### 2.1. Catalyst preparation

Microporous material, TS-1 was prepared following literature methods [24] by first mixing tetraethyl orthosilicate (302 g) and titanium (IV) butoxide (6.1 g) in a Teflon beaker under a blanket of nitrogen at room temperature. In a separate Teflon beaker tetrapropylammonium hydroxide (118 g of 40 wt.% TPAOH in water) and distilled water (287 g) were mixed. The TPAOH solution was then slowly added to the first solution with stirring at room temperature. An additional loading of distilled water (287 g) was added slowly with stirring until the solution became clear. The resulting solution was then transferred to a series of 125 mL Teflon liners which were placed into 125 mL Parr reactors inside a static oven. The reactors were heated at 160 °C for 96 h, cooled to ambient temperature, and the contents were combined. The pH was adjusted to 8 using 1 M nitric acid, and the mixture was centrifuged at 7500 rpm for 15 min. The solids were isolated, washed with distilled water, and centrifuged 3 times. The resultant solid was dried at 100 °C for 24 h, and then calcined first under nitrogen and then air. The calcination procedure involved heating to 230 °C under nitrogen at a rate of 1 °C/min, holding for 24 h, then heating to 540 °C at a rate of 1 °C/min, holding for 4 h, and then switching the gas feed to air and holding at 540 °C for 8 h before cooling to ambient temperature. The resulting calcined sample was analyzed by X-ray powder diffraction, with the spectrum indicative of an MFI-type lattice, UV/Vis and Ti content analysis (Supplementary data).

Microporous material, [Fe,Al]-MFI (1.04 mol% Fe, 1.25 mol% Al), was prepared by the method described above except iron(II) nitrate was utilized in place of the titanium source and aluminum hydroxide was included within the second addition of distilled water. The resulting calcined sample was analyzed by X-ray powder diffraction, with the spectrum indicative of an MFI-type lattice, UV/Vis and Ti content analysis (Supplementary data). TS-1 and [Fe,Al]-MFI were used for reaction testing without further treatment or activation.

#### 2.2. Oxidation reaction and products analysis

A Biotage-Argonaut Endeavor® reactor was utilized for phenol and benzene oxidation reaction screening. The Endeavor reactor utilizes eight stainless-steel beds (~10 mL volume each) with independent temperature and pressure control. These reactors permitted screening with high stir rates (1000 rpm) under high N<sub>2</sub> pressures (~300 psi), in addition to the ability to perform facile repetitions to reduce experimental error. In a typical phenol oxidation run, the total volume of the reactant mixture was approximately 5 mL, comprising phenol (0.95 g), H<sub>2</sub>O<sub>2</sub> (0.574 mL of 30 wt.% in water), water (0-3.5 mL), cosolvent (0-3.5 mL) and catalyst (0-80 mg). All reactions were run at 60 °C for 0.5-3 h. For reaction mechanism studies, catechol (5 mmol) or 2,6-di-tert-butyl-4-methylphenol (BHT, 0.1 mmol) were also added to the reaction mixture. Inhibition studies involved the use of acetonitrile or sulfolane as cosolvent or the addition of an inorganic salt (0-1 mmol) to the reaction mixture. Upon completion of a run, the liquid phase was homogenized with acetonitrile (15 mL) containing an internal standard (2 wt.% toluene), the solutions were filtered to remove catalyst and a sample of the diluted product mixture was analyzed by gas chromatography. Inclusion of the internal standard, toluene allowed for quantitative analysis of the diluted product mixture, and subsequent extraction of the product mixture concentrations pre-dilution. Diluted blanks, representative of the starting reactant mixture, were included in each GC analysis to provide an accurate measure of the initial phenol concentration in solution. Phenol conversion was calculated as the concentration of the oxidation products divided by the concentration of phenol in the original reactant mixture. An analogous procedure was utilized for benzene oxidation, where the total volume of the reactant mixture was approximately 5 mL, comprising benzene (1.4 mL), H<sub>2</sub>O<sub>2</sub> (0.6–3.6 mL of 30 wt.% in water), cosolvent (0–2 mL), inorganic salt (0–1 mmol) and catalyst (~80 mg). There was no evidence for the production of tars in the reaction screens performed. In addition to GC analysis, aliquots of the benzene oxidation diluted product mixture were removed for titration by the ceric sulfate method to determine the extent of  $H_2O_2$  consumption [25].

#### 3. Results and discussion

## 3.1. Uncatalyzed phenol oxidation in solution

The mechanism of oxidation reactions with H<sub>2</sub>O<sub>2</sub> over TS-1 have been extensively studied, including phenol oxidation, with a hydroperoxo titanium species generally accepted to be the active species involved in catalysis [26]. However, the potential contributions from an uncatalyzed homogenous reaction between phenol and hydrogen peroxide under the conditions employed for benzene oxidation with H<sub>2</sub>O<sub>2</sub> have not been as widely explored. Therefore, initial studies focused on the investigation of uncatalyzed phenol oxidation. The results of the batch reactor studies (60 °C, 3 h, phenol:  $H_2O_2 = 2$ ) are given in Table 1. In the presence of only H<sub>2</sub>O<sub>2</sub> and water, a phenol conversion of ~13% is observed, where the predominant products observed are hydroquinone and catechol in a ~2:1 ratio. This result is key to understanding higher-oxidation of benzene in the presence of a catalyst as it suggests that an uncatalyzed homogenous reaction between phenol and H<sub>2</sub>O<sub>2</sub> may contribute to further oxidation of phenol product under these conditions. To determine the possible effects of the catalyst support on this solution oxidation, analogous phenol reactions were performed with the addition of ZSM-5 (1.25% Al), silicalite and amorphous silica. In all cases, the observed phenol conversion was largely unchanged (~12%) indicating that the support surfaces did not inhibit or contribute further towards the uncatalyzed oxidation of phenol.

#### 3.2. Time course of phenol oxidation in solution

The uncatalyzed homogenous reaction of phenol with  $H_2O_2$ indicates that this undesired side reaction may be a key component of the overall phenol selectivity (i.e. extent of phenol oxidation) observed in MFI-type zeolite catalyzed oxidations of benzene with  $H_2O_2$  at 60 °C. The relative rate of the solution (uncatalyzed) phenol oxidation compared to the rate of catalyzed benzene oxidation to phenol is important in this evaluation. Hence, the oxidation of phenol in solution with  $H_2O_2$  (uncatalyzed) was determined as a function of time. From the results in Fig. 1A, phenol oxidation is minimal during the initial 1–2 h of reaction then increases dramatically with further

**Table 1**Phenol oxidation with  $H_2O_2$  in a batch reactor.

Additive	Phenol conversion (%)
None	12.8
ZSM-5 (1.25 mol% Al)	12.0
Silicalite	11.7
Amorphous silica (PQ MS-1733)	12.4



**Fig. 1.** Time course of uncatalyzed phenol oxidation with  $H_2O_2$ . (A) phenol oxidation (---) and with 5 mmol catechol (----) or 0.1 mmol BHT (----) added to the reaction and (B)  $H_2O_2$  consumption during phenol oxidation (-----) and with 0.1 mmol BHT added to the reaction (-----).

time. Importantly, the rate of H<sub>2</sub>O<sub>2</sub> consumption correlates to that of phenol oxidation (Fig. 1B), with an initial lag phase and higher  $H_2O_2$ consumption at longer reaction time. For this reaction, an autocatalytic mechanism could exist whereby the hydroxyphenol products catalyze the reaction of  $H_2O_2$  with phenol. To test this possibility, phenol oxidation reactions were performed with the addition of catechol to the reaction mixture. However, catechol addition (5 mmol) does not change the rate of phenol oxidation (Fig. 1A) indicating that an alternative mechanism must exist. Since some thermal H<sub>2</sub>O<sub>2</sub> decomposition occurs even at 60 °C over time in a batch reaction, it is possible that the active oxidant is part of the  $H_2O_2$ decomposition route - possibly a radical species. If a radical mechanism is present, the addition of a radical trap (2,6-di-tertbutyl-4-methylphenol, BHT) to the reaction should inhibit phenol oxidation. From Fig. 1A, the addition of 0.1 mmol BHT to the reaction substantially reduces phenol oxidation, in addition to reducing the rate of H<sub>2</sub>O<sub>2</sub> consumption (Fig. 1B). Therefore, these mechanistic studies and the observed lag phase to the reaction are consistent with the formation of a radical H<sub>2</sub>O<sub>2</sub> decomposition product which oxidizes phenol, where the rate of reaction of phenol with the  $H_2O_2$ decomposition product is much faster than the formation of this decomposition product.

The relative rates of benzene oxidation to phenol catalyzed by TS-1 and [Fe,Al]-MFI in batch reactions are given in Fig. 2. While the overall rate of oxidation is slower for benzene relative to phenol, a greater percentage (~50%) of the total oxidation occurs within the initial 30 min of reaction time. Hydrogen peroxide consumption is low for the titanium based catalysts at short reaction times, in comparison to the iron-based system which rapidly consumes over 50% of the total peroxide within 30 min. As has previously been observed, significant unreacted  $H_2O_2$  remains in the reaction with TS-1 after three h while [Fe,Al]-MFI consumes the majority of the peroxide in solution over the



Fig. 2. Time course of benzene oxidation with  $\rm H_2O_2$  catalyzed by (A) TS-1 and (B) [Fe,Al]-MFI.

same time period. While the benzene conversion and peroxide consumption time profiles are interesting, a key observation relates to phenol selectivities with time. The iron-based catalyst exhibits high phenol selectivities (>98%) throughout the course of the reaction while TS-1 gives a much lower phenol selectivity after 3 h (<80%). However, the phenol selectivity for TS-1 is high over the initial hour of reaction (>90%) and steadily decreases with further reaction time even though overall benzene conversion only slowly increases. Thus, it appears that elongated reaction times in TS-1 serve predominately to oxidize phenol to undesired multiple-oxidized products and that, at short reaction times, TS-1 exhibits much higher phenol selectivities.

Comparison of the relative rates of catalyzed benzene oxidation and uncatalyzed homogeneous phenol oxidation yields an interesting hypothesis. The fact that the uncatalyzed phenol oxidation profile coincides with the decrease in phenol selectivity with time for TS-1 suggests that it is uncatalyzed homogeneous oxidation of phenol and not catalyzed oxidation of product in the zeolite that is responsible for the decreased phenol selectivity in TS-1. Furthermore, the lack of solution oxidation of phenol in the iron-based catalyst compared to that observed for the titanium-based catalysts can be explained in terms of the amount of unreacted H<sub>2</sub>O<sub>2</sub> present at longer reaction times where the uncatalyzed phenol oxidation reaction becomes significant. Titanium based catalyst consume relatively low amounts of peroxide throughout the reaction (<30% total) whereas iron-based catalysts consume 50% of the peroxide within the initial 30 min of reaction. Since the uncatalyzed oxidation of phenol would be expected to be dependent upon the concentration of H<sub>2</sub>O<sub>2</sub>, it appears that the high phenol selectivity of [Fe,Al]-MFI derives from the fact that this catalyst rapidly consumes a majority of the peroxide in solution, thus, limiting the amount of H<sub>2</sub>O<sub>2</sub> available for thermal decomposition to generate the H<sub>2</sub>O<sub>2</sub> decomposition oxidant for uncatalyzed phenol oxidation.

To further test this hypothesis, phenol oxidation batch reactions were performed with the addition of either TS-1 or [Fe,Al]-MFI to the

reaction. If phenol oxidation is largely an uncatalyzed homogeneous reaction dependent upon the concentration of H<sub>2</sub>O<sub>2</sub>, it would be expected that addition of TS-1 would have little effect on oxidation whereas [Fe,Al]-MFI would inhibit this reaction through its high H<sub>2</sub>O<sub>2</sub> consumption rate. In fact, this is exactly what is observed. Whereas TS-1 has essentially no effect on phenol oxidation compared to the uncatalyzed reaction (13% phenol oxidation with TS-1), addition of [Fe,Al]-MFI leads to a significant reduction in total phenol oxidation to 7%. Based upon these uncatalyzed phenol oxidation studies, a new reaction scheme for the control of phenol selectivity in MFI-type zeolites can be obtained (Fig. 3). While some metal catalyzed phenol oxidation  $(k_6)$  may be possible, uncatalyzed phenol oxidation  $(k_5)$ appears to be the dominate pathway determining phenol selectivity. However, the fact that this oxidation requires  $H_2O_2$  (or a thermal decomposition product thereof) as a reactant leads to the fact that the rate of metal catalyzed H<sub>2</sub>O<sub>2</sub> consumption (which is predominately uncoupled,  $k_3$ ) is key to the control of phenol selectivity. Thus, as observed, those catalysts which rapidly consume hydrogen peroxide (i.e. Fe) will exhibit higher phenol selectivities than those which only slowly consume peroxide (i.e. Ti) unless a way to suppress uncatalyzed homogeneous H<sub>2</sub>O<sub>2</sub> decomposition leading to phenol oxidation can be identified.

#### 3.3. Effects of additives on phenol oxidation

Since high  $H_2O_2$  selectivities are required in addition to high phenol selectivities for any commercial process, it is desirable to investigate alterative methods to inhibit uncatalyzed oxidation of phenol beyond utilizing catalysts with high  $H_2O_2$  consumption rates and, thus, inherently poor  $H_2O_2$  selectivities. One approach that could be employed, and has been reported in the literature, for improving phenol selectivities is the use of co-solvents/additives to the reaction. Bianchi and co-workers have previously reported that the use of sulfolane as a co-solvent for the oxidation of benzene to phenol with TS-1 leads to improvement in phenol selectivity [22]. This effect was rationalized in terms of the ability of sulfolane to form a complex with phenol, with the sterically hindered complex being unable to enter the TS-1 pores to undergo further oxidation.

Based upon our previous findings in this study indicating that uncatalyzed phenol oxidation is a key contributing factor to phenol over-oxidation, it was interesting to consider whether sulfolane could inhibit phenol oxidation in the absence of a catalyst. The addition of 1 mmol sulfolane to the batch reaction of phenol with  $H_2O_2$  (Fig. 4) results in a ~50% decrease in total phenol oxidation, indicating that



**Fig. 4.** Effects of additives on uncatalyzed oxidation of phenol with hydrogen peroxide (1 mmol addition effects; solid black denotes use at 3.5 mL in a 5 mL total reaction volume).

sulfolane in solution is an inhibitor of the uncatalyzed homogeneous oxidation of phenol. Furthermore, if sulfolane is used in excess (3.5 mL in a 5 mL total volume reaction) a decrease in phenol oxidation of ~100-fold is observed. Thus, sulfolane can effectively inhibit the uncatalyzed homogeneous oxidation of phenol under these reaction conditions. These results suggest that the observed improvements to phenol selectivities in the previously reported TS-1 study may have originated from inhibition of uncatalyzed phenol oxidation by sulfolane in lieu of pathways involving the prevention of phenol coordination to the active catalyst, consistent with a recent study by Barbera et al. [23].

Another co-solvent to investigate as a potential inhibitor of the uncatalyzed solution oxidation of phenol is acetonitrile. Previous studies have shown acetonitrile to be the optimal co-solvent for use in [Fe,Al]-MFI catalyzed benzene oxidations, providing a balance between  $H_2O_2$  consumption and benzene conversion. Based upon previous literature data, it was speculated that acetonitrile may react with hydrogen peroxide to form a peroxycarboximidic acid which is slower to react with a catalyst than pure hydrogen peroxide [27]. Utilizing acetonitrile as an additive to the phenol oxidation reaction, analogous results are observed as in the sulfolane addition experiment whereby acetonitrile at 1 mmol addition reduces phenol oxidation by half and excess acetonitrile leads to a ~100-fold decrease



Fig. 3. Reaction scheme for benzene oxidation with H<sub>2</sub>O<sub>2</sub> including uncatalyzed phenol oxidation.

in phenol oxidation. Thus, in addition to high  $H_2O_2$  consumption rates for iron-based catalysts, the utilization of acetonitrile as a co-solvent further aides in the high phenol selectivities attained. Unfortunately, the negative impact of acetonitrile on catalytic activity in titaniumbased catalysts prevents its utilization as a co-solvent for TS-1.

From these additive studies, it is apparent that the addition of a cosolvent can inhibit the uncatalyzed phenol oxidation reaction through interaction with either reactant (phenol or  $H_2O_2$ ), thus sequestering it from the reaction. Inorganic salts, which are commonly used as peroxide stabilizers, also have the potential to interact with  $H_2O_2$ through acid–base reactions or hydrogen bonding in solution. While testing the effects of inorganic salts on  $H_2O_2$  stability and efficiency, high phenol selectivities were observed with monobasic phosphate salts, suggesting that these salts may also inhibit uncatalyzed phenol oxidation. As shown in Fig. 4, the addition of 1 mmol (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub> or K<sub>2</sub>H<sub>2</sub>PO<sub>4</sub> to the phenol oxidation reaction decreases oxidation to less than 25% of the conversion in the absence of an additive. While these salts likely interact with peroxide, sequestering it from the reaction, the specific molecular level mechanism of inhibition is currently unresolved (i.e. acid–base, H-bonding, etc.).

## 4. Conclusions

The results presented herein indicate that the uncatalyzed homogeneous oxidation of phenol with  $H_2O_2$  in solution is a key contributor to phenol oxidation (and, hence, phenol selectivity) in liquid phase oxidations of benzene with  $H_2O_2$ . A key contribution to the differences in phenol selectivity in TS-1 and [Fe,Al]-MFI is the extent to which  $H_2O_2$  is consumed by the catalyst, since the uncatalyzed oxidation requires a significant portion of unreacted  $H_2O_2$  to remain in solution. Therefore, the lower amount of  $H_2O_2$  decomposition for TS-1 appears to directly contribute to the lower phenol selectivities for this catalyst. It has also been shown that additives (ex. sulfolane, acetonitrile, certain inorganic salts) are capable of inhibiting the uncatalyzed phenol oxidation, leading to their potential utility in improving phenol selectivities for benzene oxidation with  $H_2O_2$ .

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2010.10.024.

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