Effect of Acetic Anhydride on the Oxidation of Toluene to Benzaldehyde with Metal/Bromide Catalysts

5 AUTHORS, INCLUDING:

Feng Zhang
Nanjing University
20 PUBLICATIONS **223** CITATIONS

# Effect of Acetic Anhydride on the Oxidation of Toluene to Benzaldehyde with Metal/Bromide Catalysts

Xiankun Wu, Zilei Deng, Jiujuan Yan, Feng Zhang,* and Zhibing Zhang*

School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

ABSTRACT: Acetic anhydride (AA) was used as specific additive for liquid-phase oxidation of toluene in acetic acid to weaken the corrosivity of reaction system and increase the yield of benzaldehyde by using Co/Mn/Br catalyst system and 1,1,2,2-tetrabromoethane as bromine sources. The effect of AA on the liquid-phase oxidation of toluene to benzaldehyde was carefully studied. It was found that adding a certain amount of AA in acetic acid caused different reaction process from the reaction in pure acetic acid. Noticeably, addition of AA could increase both the selectivity of benzaldehyde and conversion of toluene during 2−8 h, whereas in pure acetic acid, benzaldehyde selectivity gradually dropped with a rise in toluene conversion. AA could greatly decrease water content in the reaction system, possibly reduce the corrosivity of substrates, and increase the toluene conversion. However, too much AA could cause the deactivation of the catalyst. By optimizing conditions, the maximum selectivity and yield of benzaldehyde reached 67.6 and 26.1%, respectively. On the basis of the experiment, a possible mechanism for the effect of AA was presented. Adding AA into acetic acid could improve the selective oxidation of methyl aromatics to aldehyde.

1. INTRODUCTION

The direct insertion of oxygen molecule into methyl aromatic hydrocarbon is an important reaction route with high atom efficiency for the synthesis of oxygenates. One of the most successful industrial applications is the liquid-phase oxidation of toluene with air or pure oxygen.[1−3] As shown in Figure 1, toluene can be oxidized to benzyl alcohol, benzaldehyde, and benzoic acid as the eventual product.[4,5]
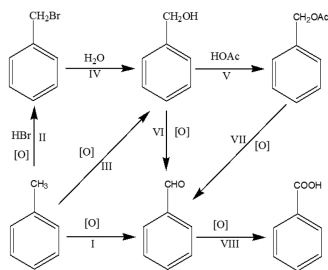
Figure 1. Reaction network during the oxidation of toluene with a Co/Mn/Br catalyst.

Benzaldehyde is a commercially significant oxidation product of toluene. Traditionally, benzaldehyde is manufactured by the hydrolysis of benzyl chloride, suffering from serious disadvantages such as heavy environmental pollutions and the residual chlorine in the process.[6] Benzaldehyde, seen in Figure 1, can also be obtained by oxidation of toluene by oxygen. However, its yield is very low because it can be more easily oxidized than toluene. For the noncatalyzed oxidation of toluene, the free radical chain mechanism gives the reactivities of toluene, benzyl alcohol, and benzaldehyde as 0.05, 0.85, and 290, respectively.[7] Therefore, it is very difficult to obtain considerable amount of benzaldehyde by direct oxidation of toluene.

Recently, great efforts have been paid to develop suitable catalysts for the selective oxidation of toluene. Heterogeneous catalysts, which are easily recycled after reaction, have been tried. Huang et al.[8] have designed a new catalyst: cobalt tetra (4-hydroxyl) phenylporphyrin supported on zinc oxide and successfully obtained higher selectivity of benzaldehyde and benzyl alcohol. Xue et al.[9] have reported that the selectivity of benzaldehyde reached 95% over the with 7.3% toluene conversion, by using the V−Ag−O/TiO2 at 340 °C. Lv et al.[10] have used ceria nanocubes covered by oleic acid as catalyst of toluene oxidation, achieving 100% benzaldehyde selectivity with maximum toluene conversion of 11% at 2 MPa oxygen and 153 °C. However, these catalysts suffered from complex preparation process or harsh reaction conditions of higher temperature or pressure. Rao and co-workers[11] used nanoparticles of CdO_2 and ZnO_2 to oxide toluene primarily to benzaldehyde at low temperature. In addition, the preparation of peroxides nanoparticles was rather simple. Though these heterogeneous catalysts could bring very high selectivity of benzaldehyde, the low toluene conversion greatly limited their industrial application.

Compared with heterogeneous catalysts, homogeneous catalysis has predominated in the liquid-phase oxidation of toluene because of its good activity and mild operation conditions.[12] In 1954, Co/Mn/Br catalyst was discovered and then was first employed to oxidation of p-xylene to terephthalic acid.[13] Co/Mn/Br catalyst also has shown an excellent catalytic activity in the liquid-phase oxidation of toluene to benzoic acid, typically like Snia−Viscosa process. However, in common reaction, with Co/Mn/Br catalyst, the byproduct benzaldehyde is easily overoxidized to benzoic acid, leading to less selectivity and yield (3%).[14] In recent years, numerous approaches have been performed to improve the selectivity and yield of
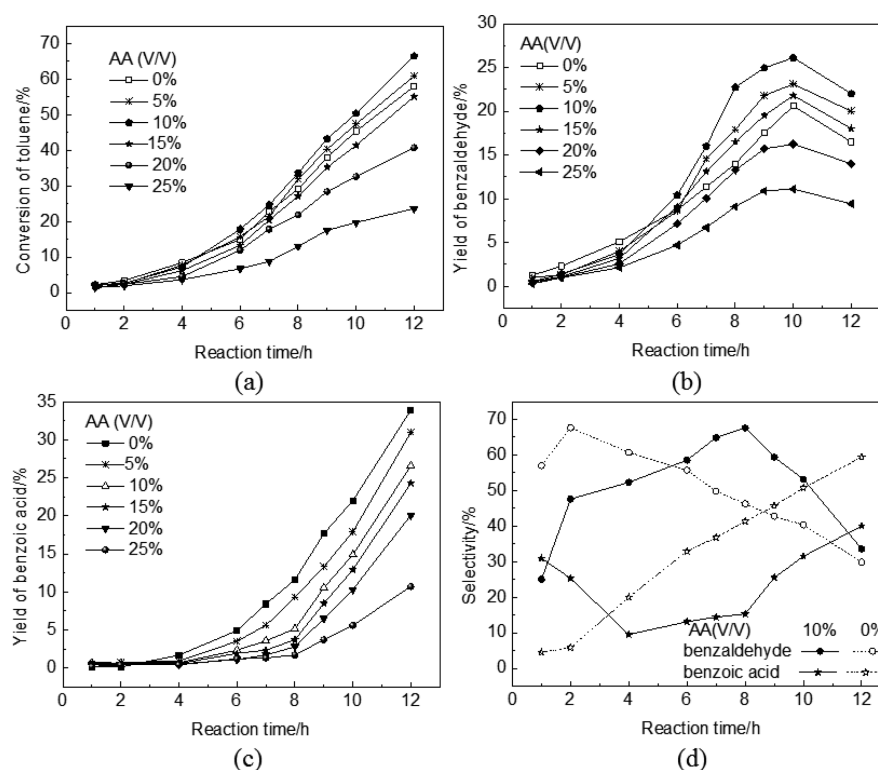
Figure 2. Effects of the different initial AA concentration on conversion of toluene. Reaction conditions are as follows: toluene 35 mL, $V_{HAc} + V_{AA}$ = 35 mL, $n_{Co}/n_{toluene}$ = 1.5%, n_{Br}/n_{Co} = 1/3, n_{Co}/n_{Mn} = 3, $n_{(MnSO4)}:n_{(MnOAc)2}$ = 1:1, oxygen flow rate 60 mL/min. AA concentration refers to volume ratio in toluene.

benzaldehyde in the liquid-phase oxidation of toluene because of an increasing demand of chlorine-free benzaldehyde.[15,16]

Among recent studies, more attention has been paid to improvement of Co/Mn/Br catalyst system by adding another active catalyst component such as transition, alkali metal, and guanidine to promote the reaction activity and improve the selectivity.[5,17−19] Partenheimer[5] has shown that higher Zr content with constant Co/Mn/Br concentration resulted in a rise of reaction activity and benzaldehyde/alcohol ratio in the products. Jhung et al.[18] found that the oxidation reaction was promoted when alkali was added in Co/Mn/Br catalyst. Cheng et al.[19] reported that the addition of guanidine apparently accelerated the oxidation and inhibited the side reactions remarkably. Lower ratio of Br/Cl could also accelerate the rate of toluene oxidation and obtain higher selectivity toward benzaldehyde and benzyl alcohol.[4] Because of the strong erosion by acetic acid, replacement of acetic acid with water,[20] dioxane,[21] methanol,[22] and ionic liquid[23,24] have been also attempted.

In the present work, AA is used as an additive in Co/Mn/Br catalyst for oxidation of toluene to achieve a higher yield of benzaldehyde. It is shown that AA can be rapidly hydrolyzed to acetic acid, acting as a solvent for Co/Mn/Br catalyst system.

$$(CH_3CO)_2 + H_2O \rightarrow 2CH_3COOH \quad (1)$$
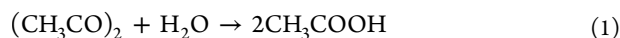
In general, water is the product of the oxidation of hydrocarbons. A mole of water forms as one methyl group of methyl aromatic compounds oxidized. In Co/Mn/Br catalytic oxidation water plays an important role,[25−28] showing a complicated effect on catalytic activity, influencing metal coordination structure and formation of benzyl bromide and manganese(IV) in Co/Mn/Br catalyst system. Generally, some

Co/Mn/Br catalytic oxidations are favored by lower water concentration. Controlling water content in Co/Mn/Br catalyst system is important for regulation oxidation reaction.[26,28,29] However, past studies showed that more attentions were paid on the effect of water concentration on toluene oxidation by adding water at initial stage of reaction, while few literatures were related to decreasing concentration of water in the reaction system. Furthermore, as shown in eq 2, the amount of benzyl acetate and benzyl alcohol is also affected with addition of AA.

$$PhCH_2OH + (CH_3CO)_2O$$
$$\rightarrow PhCH_2OOCH_3 + CH_3COOH \quad (2)$$
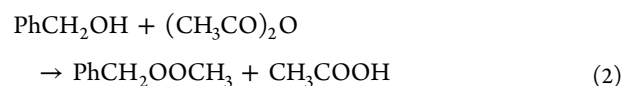
The experiments were performed to indicate the influence of AA notably on the conversion of toluene and selectivity of benzaldehyde, since until now few literatures on this have been available. The effect of acetic anhydride as additive on liquid-phase oxidation of toluene to benzaldehyde over Co/Mn/Br catalyst system was discussed and the possible mechanism of AA's effect was derived.

2. EXPERIMENTAL SECTION

Cobalt(II) acetate tetrahydrate ($Co(OAc)_2$), manganese(II) acetate tetrahydrate ($Mn(OAc)_2$), manganese(II) sulfate monohydrate ($MnSO_4$), 1,1,2,2-tetrabromo-ethane, sodium bromide, and acetic anhydride were all analytical grades. Because $Mn(OAc)_2$ may induce higher selectivity of benzaldehyde and $MnSO_4$ cause larger toluene conversion, they were mixed and added to the system with the catalyst of $Co(OAc)_2$ and $C_2H_4Br_4$.[30] Starting the reaction, the catalyst, additives, reactants, and solvent were all placed into a reaction

flask, and then heated to the desired temperature. Pure oxygen (>99.9%) was introduced to the flask bottom at a specific flow rate and the reaction took place. Samples were taken every hour during the experiment and analyzed by Shimadzu GC-2014C, equipped with a 30 m × 0.32 mm × 0.5 μm WondaCap capillary column and a flame ionization detector. The identities of the oxidation products were made by Micromass GC-TOF GC-MS.

3. RESULTS AND DISCUSSION

3.1. Effect of the Initial AA Concentration on Oxidation of Toluene. The oxidation of toluene by oxygen with Co/Mn/Br catalyst containing AA concentration was performed at 98 °C and 1 atm. The effect of initial AA concentration on this reaction was plotted in Figure 2 as a function of reaction time. Shown in Figure 2a, the toluene conversion rose slightly with $V_{AA}/V_{toluene}$, ranging from 0% to 10%, indicating a higher reaction activity. With a further increase in AA concentration, the conversion of toluene was decreased, especially when AA concentration was above 20%. The conversion of toluene was down to 20% in 10 h with AA concentration of 25%, much lower than that of without AA. The reason could be that so much replacement of acetic acid by AA would cause a serious reduction of the reaction activity. As can be seen in Figure 2b, the yield of benzaldehyde increased and reached the maximum value at 10 h. A certain amount of AA (<15%) caused higher yield of benzaldehyde compared with no addition of AA. The maximum yield of benzaldehyde was 26.1% when AA concentration was 10%. When AA concentration was above 20% the yield of benzaldehyde decreased, similar to the case of toluene conversion. Figure 2c indicated that the yield of benzoic acid reduced with an increase of AA concentration. The effect of AA on selectivity of benzaldehyde and benzoic acid was illustrated in Figure 2d. In pure HAc, the selectivity of benzaldehyde reached maximum value at 2 h, and then dropped gradually due to the further oxidation of benzaldehyde to benzoic acid. This trend was agreement with that of the literature.[1] Figure 2d showed that the selectivity of benzoic acid was constantly increased without addition of AA and the maximum value of benzaldehyde selectivity was 67.6% at 8 h, whereas the selectivity of benzoic acid varied with U shape with 10% addition of AA, indicating that AA has a special impact on the oxidation process.

Compared with the case of pure acetic acid, when AA concentration was lower than 10%, conversion of toluene and yield of benzaldehyde increased with a rise in AA concentration. When AA concentration was higher than 10%, toluene conversion and yield of benzaldehyde decreased with an increase of AA concentration. Therefore, addition a certain amount of AA could promote selectivity and yield of benzaldehyde.

3.2. Analysis for the Effect of AA on Toluene Conversion. As discussed above, an addition of AA reduced the water concentration in the oxidation system. As shown in Figure 3, the more AA added, the lower the water content.

In general, water concentration is an important factor in Co/Mn/Br catalytic oxidation of toluene. Water amount in the system could affect metal/Br^{1-} coordination structure, which was reported by Partenheimer[27] that the structures for Co/Mn/Br mixtures had the neutral metal-bromide speices, i.e., $[M(HOAc)_m(OAc)(Br)]_2$, being predominant in anhydrous acetic acid, where the brackets [ ] and M denote the ligands in the inner coordination sphere and Co(II) or Mn(II),
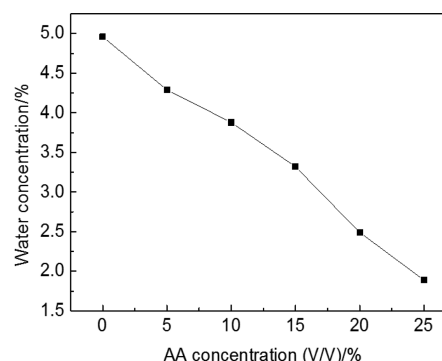

Figure 3. Variation of water concentration versus AA concentration.

respectively. With an increase of water amount in the system most of bromide coordination will be reduced. The predominant species was the ion-paired bromide salt, i.e., $\{[M(HOAc)_m(H_2O)_n(OAc)]_2(Br)\}_2$, where the bracket { } denotes an ion-pair. The possible Co/Mn/Br structure in the presence of water is given in Figure 4.[27] The nonaqueous
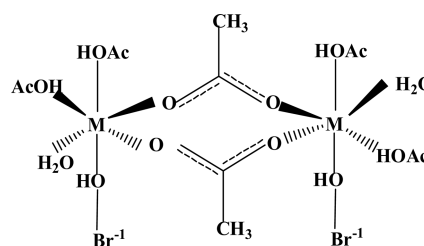

Figure 4. Possible structres for Co/Mn/Br mixtures in acetic acid/water.

system Br^{1-} directly coordinated with metal cation. At this circumstance the electron in the complex compound could transfer from Br^{1-} to the metal cation easily. As oxidation proceeding, the increase of water amount would facilitate water molecule's coordination with the metal cation by hydrogen bond, limiting the coordination of Br^{1-} with the metal anion, slowing down the electron-transfer from Br^{1-} to metal cation, and thus reducing the reaction rate.

Several researchers[1,3,31,32] have affirmed that the oxidation of toluene is governed by a free-radical chain mechanism. Bromide free radical plays a significant role in the chain initiator of toluene oxidation, which is considered as the control step in the reaction. Addition of AA has dual effects on the toluene oxidation process. On one hand, it could reduce water amount, which made Br^{1-} transfer to metal cation more easily, thus enhancing toluene oxidation. On the other hand, AA could consume some benzyl alcohol and therefore influence the reaction process as shown in Figure 1.

Moreover, if the concentration of AA was enough to consume most of water in the oxidation system, it could cause a lose of catalyst activity, leading to a low conversion of toluene when more than 15% of AA was presented in the system. It has been reported that benzyl bromide, acting as a byproduct, had no activity in Co/Mn/Br catalyst oxidation.[20] As shown in eq 3, a suitable amount of water could hydrolyze benzyl bromide to a release of active bromine.

$$PhCH_2Br + H_2O \rightarrow PhCH_2OH + HBr \qquad (3)$$
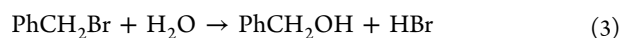
That is, higher AA concentration could inhibit hydrolysis of benzyl bromide and thus cause more bromine to exist in benzyl bromide. Finally, Co/Mn/Br catalyst would lose efficacy gradually because of the continuous consumption of free bromide.

If the conversion of toluene markedly slowed down because of formation of benzyl bromide, the addition of $C_2H_4Br_4$ should recover the reaction rate. It was confirmed in our experiment through an addition of $CH_2Br_2CH_2Br_2$ at 8 h when AA concentration was above 15%.

1,1,2,2-Tetrabromoethane, $C_2H_4Br_4$, was used as a bromine source in the oxidation. $C_2H_4Br_4$ is an unstable substance, because the bromine atoms have strong electronegativity, conferring the hydrogen atoms on adjacent carbon atoms with a positive charge.[33] $C_2H_4Br_4$ is easily given to HBr by the interaction of moleculars when exposed in heat or light. Because no benzyl bromide was found at the initial stage of the reaction (about 4 h), the debromination of $C_2H_4Br_4$ was slower than NaBr or HBr. However, benzyl bromide was detected at 1 h reaction when using NaBr. This could also be proved by the change of the solution color. Using $C_2H_4Br_4$ as bromine sources, the initial solution was pink and after about 1.5 h it appeared blue, whereas the solution was immediately blue when NaBr was used. Compared to NaBr, $C_2H_4Br_4$ could reduce formation of benzyl bromide, then lessen the negative effect of AA addition. Therefore, the effect of AA on toluene conversion could be interpreted by the competition between the coordination effect and the formation of benzyl bromide. The former had a positive influence on the transfer rate of the electron, and the latter was a negative influence on catalyst activity.

In addition, the addition of AA to acetic acid solvent could affect the dissociation constant (pK_a) of acetic acid. pK_a of a pure acetic acid is 13.92. It is 10.95 with 2.5% water and 9.64 with 5% water.[7,34] Therefore, decreasing water concentration by addition of AA could reduce corrosion.

3.3. Possible Mechanism for High Selectivity of Benzaldehyde. The above study showed that the addition of 10% AA gave 67.6% selectivity of benzaldehyde for 8 h with higher yield (26.1%), suggesting that a certain amount of AA may prevent benzaldehyde from further oxidation, because benzaldehyde has a better oxidizability than toluene does. To ascertain the truth, we carried out an experiment and showed that the addition of AA could not prevent the oxidation of benzaldehyde to benzoic acid using Co/Mn/Br as catalyst, and that a high concentration of Co/Mn/Br catalyst could reduce reaction rate of benzaldehyde oxidation. The phenomenon of "catalyst inhibitor conversion" is widely existing in the reation catalyzed by transition salts and some biomimetic catalytic systems.[28,35,36] The literature also has no information on the mechanism of AA preventing benzaldehyde from oxidation. In fact, AA may be converted to acetic acid and benzyl acetate when added.

Does benzyl acetate cause higher selectivity for benzaldehyde? The experimental data, shown in Table 1, indicate that no benzyl alcohol was detected for the first 2 h when AA/acetic acid cosolvent was used, mostly because of the reaction between AA and benzyl alcohol. However, the selectivity of benzyl alcohol was quite high for the case of pure acetic acid. Compared to acetic acid, AA more easily reacted with benzyl alcohol,[37] suggesting that the addition of AA will increase the yield of benzyl acetate. The higher the AA concentration, seen in Figure 5, the higher the yield of benzyl acetate. The

Table 1. Comparison of the Selectivity and Yield of Benzyl Alcohol for Toluene Oxidation in HAc and AA/HAc Co-solvent

| | benzyl alcohol (mol %) | | | |
| | selectivity | | yield | |
time (h)	A	B	A	B
1	41.2	0	0.906	0
2	31.4	0	1.06	0
4	12.5	17.7	1.05	1.27
6	8.3	13.2	1.23	2.35
7	4.6	10.2	1.04	2.52
8	3.7	7.3	1.03	2.45
9	3.1	4.5	1.20	1.94
10	2.3	3.6	0.998	1.70
12	1.9	2.7	1.083	1.79

Reaction conditions: A, AA 0%; B, AA 10%; other reaction conditions the same as in Figure 2.
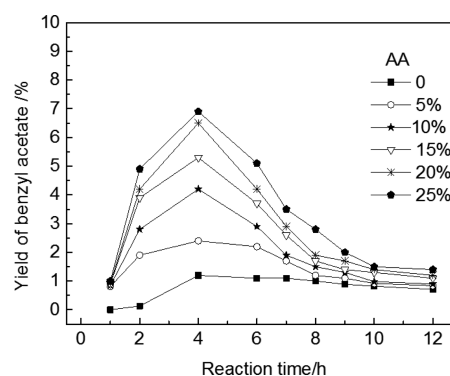
Figure 5. Effects of different AA concentration on the yield of benzyl acetate.

experiment also showed that the yield of benzyl acetate rose significantly with the reaction time with a peak point at 4 h, and that benzyl acetate could be oxidized to benzaldehyde by using Co/Mn/Br catalyst and acetic acid solvent. Therefore, the high selectivity of benzaldehyde may be attributed to the oxidation of benzyl acetate.

As seen in Table 1, the selectivity of benzyl alcohol without addition of AA is high in the initial stage and then sharply decreases. At 7 h, the selectivity of benzyl alcohol for the case of 10% AA was more than twice that in pure acetic acid, and toluene conversion by 10% AA was also higher. Therefore, quick consumption of benzyl alcohol with addition of AA could accelerate the conversion of toluene to benzyl alcohol.

Figure 6 shows a possible reaction scheme for benzaldehyde oxidation. The main steps are as follows: (i) generating carbon-centered benzoyl radicals (PhCO•) by initiation; (ii) benzoyl radicals trapping molecular oxygen to form benzoylperoxy radicals (PhCO-OO•); (iii) benzoylperoxy radicals reacting with benzaldehyde to produce perbenzoic acid.[38] Parten-heimer[7] has reported that some additives could inhibit benzaldehyde oxidation and explained the role of benzyl alcohol as an inhibitor of benzaldehyde oxidation, including the formation of a hydrogen bonding between the acetic acid and benzaldehyde (Figure 7a), and much stronger deactivation for an benzyl alcohol hydrogen-bonding to peroxy radical of benzaldehyde than to peroxy radical of benzyl alcohol (Figure 7b, c). All these effects could retard the oxidation of benzaldehyde.
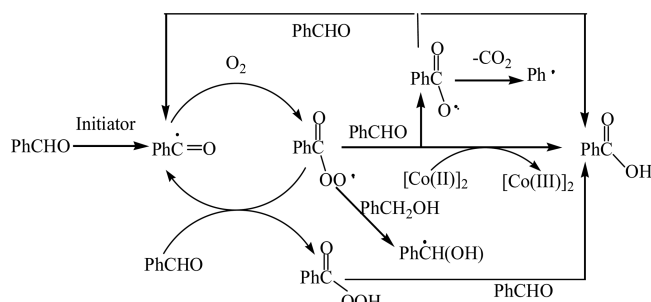
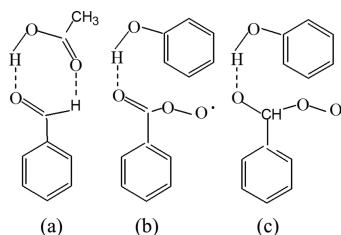**Figure 6.** Possible reaction scheme for benzaldehyde oxidation.

Figure 7. Suggested structure of hydrogen bonding during oxidation of toluene. (a) Acetic acid and benzaldehyde; (b) benzyl alcohol and peroxy radical of benzaldehyde; (c) benzyl alcohol and its peroxy radical.

Sankar[38] also considered benzyl alcohol as a very effective inhibitor for benzaldehyde oxidation. He interpreted the inhibition mechnism with the aid of EPR spin trapping experiment that benzyl achohol could quench the oxidation of benzaldehyde to benzoic acid mainly by intercepting the benzoylperoxy radicals. As seen from Figure 6, benzoylperoxy radicals played a crucial role in benzaldehyde oxidation. Therefore, the presence of relatively more benzyl alcohol induced the high selectivity and the yield of benzaldehyde. As AA being added, higher selectivity of benzaldehyde could be attributed to the oxidation of benzyl acetate to benzaldehyde and relatively high benzyl alcohol content. It was reported that adding water to the reaction system could improve the selectivity of benzaldehyde, but higher water concentration inevitably decreased conversion of toluene.[26,39−41] Fortunately, a suitable amount of AA not only can increase the selectivity of benzaldehyde, but also can promote the conversion of toluene, leading to a higher yield of benzaldehyde.

As shown in Figure 1, several reaction routes competed with each other during oxidation of toluene. Among them, reaction route I and VIII are dominant. To obtain a high selectivity and yield of benzaldehyde, tremendous efforts have been made until now to intensify the reaction route I and suppress the reaction the route VIII but has not got the desired result. This study proved that enhancement of reaction route III could be a most effective way to obtain a high selectivity and a high yield of benzaldehyde with the addition of AA.

3.4. The effect of AA on Oxidation of Methyl Aromatics to Aldehydes. The effect of AA on oxidation of methyl aromatics to aldehydes was investigated and the results showed that addition of AA also could improve both the selectivity and yield of aldehydes (Table 2). For the selective oxidation of 4-*tert*-butyltoluene, 4-methylanisole and 4-chlorotoluene, the selectivity of relative aldehydes was increased by 11.5, 9.6, and 16.8%, respectively and the yields of relative aldehydes were increased by 25.1, 12.2, and 32.7%,

Table 2. Effect of AA on Oxidation of Methyl Aromatics to Aldehydes

| | aldehyde (mol %) | | | | | |
| | selectivity[a] | | | yield[b] | | |
substrate	A	B	increase[c]	A	B	increase[c]
toluene	44.9	51.2	14.0	20.6	26.1	26.7
4-tert-butyltoluene[d]	47.7	52.2	11.5	22.7	28.4	25.1
4-methylanisole[d]	48.0	52.6	9.6	25.4	28.5	12.2
4-chlorotoluene[d]	37.9	44.3	16.8	15.6	20.7	32.7

[a]The average selectivity for 10 h. [b]The total yield of aldehyde for 10 h. [c]Increase = $(B − A)/A*100$%. [d]Reaction temperature 110 °C; reaction conditions: A, AA 0%; B, AA 10%; other reaction conditions the same as in Table 1.

respectively. This indicated that adding AA could significantly raise conversion of methyl aromatics during the oxidation.

4. CONCLUSIONS

In this work, the effects of acetic anhydride on the oxidation of methyl aromatics to aldehydes with Co/Mn/Br catalyst were investigated and the following conclusions were derived:

1. The addition of a certain amount of AA to the system could not only improve the conversion of toluene, but also increase the selectivity of benzaldehyde. The yield of benzoic acid decreased, whereas the selectivity of benzaldehyde increased with a rise in AA concentration.

2. Too much AA amount (20%) remarkably reduced the conversion of toluene and the yield of benzaldehyde.

3. AA could consume water concentration in the reaction system and therefore accelerated the transfer of the electron from $Br^{1−}$ transfer to metal cation, benefiting the oxidation. However, AA also enhanced the formation of benzyl bromide harming the activity of Co/Mn/Br catalyst system and thus the oxidation process. Using $C_2H_4Br_4$ as bromide sources of low active could greatly limit the generation of benzyl bromide.

4. AA could intensify the formation of benzyl acetate and benzyl alcohol, directively leading to a higher selectivity of benzaldehyde. The mechanism may be interpreted by the oxidation of benzyl acetate to benzaldehyde and the inhibition of further oxidation of benzaldehyde through benzyl alcohol.

5. The improvement selective oxidation of methyl aromatics to aldehydes by adding AA was also demonstrated by the oxidation of 4-*tert*-butyltoluene, 4-methylanisole and 4-chlorotoluene.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: zf@nju.edu.cn. Tel: 86-25-83596665. Fax: 86-25-83593772.
*E-mail: zbzhang@nju.edu.cn. Tel: 86-25-83593772. Fax: 86-25-83593772.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Borgaonkar, H. V.; Raverkar, S. R.; Chandalia, S. B. Liquid phase oxidation of toluene to benzaldehyde by air. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23* (3), 455−458.

(2) Hay, A. S.; Blanchard, H. S. Autoxidation reactions catalyzed by cobalt acetate bromide. *Can. J. Chem.* **1965**, *43* (5), 1306−1317.

(3) Sakota, K.; Kamiya, Y.; Ohta, N. Aromatic oxidation by cobaltic acetate in acetic acid. *Can. J. Chem.* **1969**, *47* (3), 387−392.

(4) Kantam, M. L.; Sreekanth, P.; Rao, K. K.; Kumar, T. P.; Rao, B. P. C.; Choudary, B. M. An improved process for selective liquid-phase air oxidation of toluene. *Catal. Lett.* **2002**, *81* (3−4), 223−232.

(5) Partenheimer, W. The effect of zirconium in metal/bromide catalysts during the autoxidation of p-xylene: Part I. activation and changes in benzaldehyde intermediate formation. *J. Mol. Catal. A.* **2003**, *206* (1), 105−119.

(6) Partenheimer, W. Methodology and scope of metal/bromide autoxidation of hydrocarbons. *Catal. Today.* **1995**, *23* (2), 69−158.

(7) Partenheimer, W. The high yield synthesis of benzaldehydes from benzylic alcohols using homogeneously catalyzed aerobic oxidation in acetic acid. *Adv. Synth. Catal.* **2006**, *348* (4−5), 559−568.

(8) Huang, G.; Xiang, F.; Li, T. M.; Jiang, Y.-X.; Guo, Y. A. Selective oxidation of toluene over the new catalyst cobalt tetra (4-hydroxyl) phenylporphyrin supported on zinc oxide. *Cataly. Commun.* **2011**, *12* (10), 886−889.

(9) Xue, M.; Yu, J. N.; Chen, H.; Shen, J. Surface acidic and redox properties of V−Ag−O/TiO$_2$ catalysts for the selective oxidation of toluene to benzaldehyde. *Catal. Lett.* **2008**, *128* (3−4), 373−378.

(10) Lv, J.; Shen, Y.; Peng, L.; Guo, X.; Ding, W. Exclusively selective oxidation of toluene to benzaldehyde on ceria nanocubes by molecular oxygen. *Chem. Commun.* **2010**, *46* (32), 5909−11.

(11) Lingampalli, S.; Gupta, U.; Gautam, U. K.; Rao, C. Oxidation of toluene and other examples of C-H bond activation by CdO$_2$ and ZnO$_2$ nanoparticles. *ChemPlusChem.* **2013**, *78* (8), 837−842.

(12) Jiang, J.; Jing, Y.; Zhang, Y.; Zhang, N.; Jiao, J.; Zhu, W.; Xue, H.; Zong, Y.; Yang, G. Highly efficient oxidation of toluene to benzoic acid catalyzed by manganese dioxide and N-hydroxyphthalimide. *Catal. Lett.* **2011**, *141* (4), 544−548.

(13) Partenheimer, W. Chemistry of the oxidation of acetic acid during the homogeneous metal-catalyzed aerobic oxidation of alkylaromatic compounds. *Appl. Catal. A* **2011**, *409−410*, 48−54.

(14) Donati, I.; Sioli, G.; Taverna, M. Caprolactam via toluene-snia viscosa process. *Chim. L Ind.* **1968**, *50* (9), 997−1005.

(15) Cui, X.; Shi, F.; Deng, Y. Oxidative imination of toluenes catalyzed by Pd-Au/silica gel under mild reaction conditions. *Chem. Commun.* **2012**, *48* (61), 7586−8.

(16) Brutchey, R. L.; Drake, I. J.; Bell, A. T.; Tilley, T. D. Liquid-phase oxidation of alkylaromatics by a H-atom transfer mechanism with a new heterogeneous CoSBA-15 catalyst. *Chem. Commun.* **2005**, *29*, 3736−3738.

(17) Partenheimer, W. The effect of zirconium in metal/bromide catalysts on the autoxidation of p-xylene: Part II. alternative metals to zirconium and the effect of zirconium on manganese (IV) dioxide formation and precipitation with pyromellitic acid. *J. Mol. Catal. A* **2003**, *206* (1), 131−144.

(18) Jhung, S. H.; Lee, K. H.; Park, Y. S. Effects of alkali metals on the liquid phase oxidation of p-xylene. *Appl. Catal. A* **2002**, *230* (1), 31−40.

(19) Cheng, Y.; Li, X.; Wang, Q.; Wang, L. Effects of guanidine on the liquid-phase catalytic oxidation of p-xylene to terephthalic acid. *Ind. Eng. Chem. Res.* **2005**, *44* (20), 7756−7760.

(20) Dunn, J. B.; Savage, P. E. Terephthalic acid synthesis in high-temperature liquid water. *Ind. Eng. Chem. Res.* **2002**, *41* (18), 4460−4465.

(21) Nair, K.; Sawant, D. P.; Shanbhag, G. V.; Halligudi, S. B. Aerial oxidation of substituted aromatic hydrocarbons catalyzed by Co/Mn/Br⁻ in water-dioxane medium. *Catal. Commun.* **2004**, *5* (1), 9−13.

(22) Yin, G. C.; Xi, Z. W.; Cao, G. Y.; Fan, S. H.; Hai, X. D. Selective oxidation of m-phenoxytoluene to m-phenoxybenzaldehyde with methanol as an additive in acetic acid. *Appl. Catal. A* **1999**, *185* (2), 277−281.

(23) Seddon, K. R.; Stark, A. Selective catalytic oxidation of benzyl alcohol and alkylbenzenes in ionic liquids. *Green Chem.* **2002**, *4* (2), 119−123.

(24) Meng, Y.; Liang, B.; Tang, S. A study on the liquid-phase oxidation of toluene in ionic liquids. *Appl. Catal. A* **2012**, *439−440*, 1−7.

(25) Partenheimer, W. The complex synergy of water in the metal/bromide autoxidation of hydrocarbons caused by benzylic bromide formation. *Adv. Synth. Catal.* **2004**, *346* (23), 297−306.

(26) Partenheimer, W. The complex synergy of water in metal/bromide autoxidations. Part II. effect of water and catalyst on the aerobic oxidation of benzaldehydes and the effect of water on the elementary catalytic pathways. *Adv. Synth. Catal.* **2005**, *347* (4), 580−590.

(27) Partenheimer, W. The structure of metal/bromide catalysts in acetic acid/water mixtures and its significance in autoxidation. *J. Mol. Catal. A* **2001**, *174* (1), 29−33.

(28) Hu, A.; Lü, C.; Li, B.; Huo, T. Selective oxidation of p-chlorotoluene catalyzed by Co/Mn/Br in acetic acid-water medium. *Ind. Eng. Chem. Res.* **2006**, *45* (16), 5688−5692.

(29) Partenheimer, W. The structure of metal/bromide catalysts in acetic acid/water mixtures and its significance in autoxidation. *J. Mol. Catal. A* **2001**, *174* (1−2), 29−33.

(30) Yan, J.; Wu, X. K.; Zuo, G.; Zhang, F.; Zhang, Z. A novel way of liquid phase oxidation of toluene to benzaldehyde with a higher selectivity. *J. Nanjing Univ.* **2014**, *50* (20), 129−134.

(31) Hendriks, C. F.; van Beek, H. C.; Heertjes, P. M. The oxidation of substituted toluenes by cobalt (III) acetate in acetic acid solution. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, *17* (3), 256−260.

(32) Partenheimer, W. Methodology and scope of metal or bromide autoxidation of hydrocarbons. *cataly. Today* **1995**, *23*, 69−158.

(33) Bayatyan, R. B.; Bayatyan, B. E.; Saakyan, L. A. Liquid-phase oxidation of bromovinyl compounds with molecular oxygen. *Russ. J. Appl. Chem.* **2006**, *79* (11), 1849−1852.

(34) Lagowski, J. J. *The Chemistry of Nonaqueous Solvents III*; Academic Press: New York, 1970.

(35) Black, J. Metal-catalyzed autoxidation. The unrecognized consequences of metal-hydroperoxide complex formation. *J. Am. Chem. Soc.* **1978**, *100* (2), 527−535.

(36) Guo, C. C.; Liu, Q.; Wang, X. T.; Hu, H. Y. Selective liquid phase oxidation of toluene with air. *Appl. Catal. A* **2005**, *282* (1−2), 55−59.

(37) Lee, S. G.; Park, J. H. Metallic Lewis acids-catalyzed acetylation of alcohols with acetic anhydride and acetic acid in ionic liquids: study on reactivity and reusability of the catalysts. *J. Mol. Catal. A* **2003**, *194* (1), 49−52.

(38) Sankar, M.; Nowicka, E.; Carter, E.; Murphy, D. M.; Knight, D. W.; Bethell, D.; Hutchings, G. J. The benzaldehyde oxidation paradox explained by the interception of peroxy radical by benzyl alcohol. *Nat. Commun.* **2014**, *5*, 1−6.

(39) Hu, A. J.; Lü, C. X.; Wang, H.-Y.; Li, B.-D. Selective oxidation of p-chlorotoluene with Co(OAc)$_2$/MnSO$_4$/KBr in acetic acid−water medium. *Catal. Commun.* **2007**, *8* (8), 1279−1283.

(40) Hu, A.; Lü, C.; Li, B.; Huo, T. Selective oxidation of p-chlorotoluene catalyzed by Co/Mn/Br in acetic acid-water medium. *Ind. Eng. Chem. Res.* **2006**, *45*, 5688−5692.

(41) Wang, Q.; Li, X.; Wang, L.; Cheng, Y.; Xie, G. Effect of water content on the kinetics of p-xylene liquid-phase catalytic oxidation to terephthalic acid. *Ind. Eng. Chem. Res.* **2005**, *44* (13), 4518−4522.