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## Preparation of Benzaldehyde by Liquid-Phase Catalytic Oxidation of Methyl Benzene

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One of the most important process in the field of petrochemical industry is that hydrocarbons are oxidized to aldehydes and acids using organic acid as solvent in the presence of catalysts consisting of cobalt acetate, manganese acetate and bromine compounds. The liquid phase catalytic oxidation of methyl benzene is discussed in this paper. The experiments are carried out in both pure methyl benzene and in solvents. During the process of liquid-phase catalytic oxidation of pure methyl benzene, the catalytic efficacies of different catalysts were not very significant. The addition of bromine significantly improve the catalytic efficiency. The rates of oxidation of methyl benzene in solvents were significantly higher than that in pure methyl benzene and the yield of benzaidehyde is improved.

**Keywords:** Benzaldehyde, Methyl-benzene, Liquid-phase catalytic oxidation.

### INTRODUCTION

Benzaldehyde is also termed as benzoic aldehyde and it is the most important aromatic alcohol in modern industry. Rhone-Poulenc Company in France obtained phenylmethanol, benzaldehyde and benzoic acid by liquid-phase air oxidation of methyl benzene in the 1960's. The transformation rate of methyl benzene was about 20 % and the selectivity of benzaldehyde was 30-50 %. Many scholars argue now that the homogeneous catalytic oxidation of methyl benzene abides by the mechanism of free radical reaction. Firstly methyl benzene is transformed into peroxide and then decomposed into free radicals under the functions of the catalyst, in the mean time, metal ions can realize the oxidoreduction cycle and function in transporting electrons and accomplish electron transfer<sup>1-3</sup>.

Currently available references<sup>4-12</sup> focus on the effects of catalysts on the oxidation of methyl benzene, though some achievements have been obtained, the yield of benzaldehyde was relatively low in general. The present work carried out investigations on the production of benzaldehyde by liquid-phase catalytic oxidation of methyl benzene. The optimal reaction conditions were obtained to provide references for industrial design and implement process by firstly exploring the effects of different catalysts in pure methyl benzene and catalyst concentration on methyl benzene oxidation and then comparing the difference between the oxidation of pure methyl benzene and methyl benzene in different solvents.

### EXPERIMENTAL

The experiment was carried out in different batches, firstly the reaction materials, solvents, catalysts were prepared into a solution of 300 mL in proper proportions. The solution was added into the reactor, the air in the reactor was exhausted by introducing nitrogen gas after tight sealing. Pressurization was then carried out with nitrogen gas to a final pressure at about 1 MPa, the inst valve and the outlet valve were shut off, the power supply was switched on for heating, subsequently the valve for cooling water in the end gas condensation tube at the same time and the stirring was started. Nitrogen gas was continuously introduced during the process for increasing temperature in order to guarantee the synchronized increase in pressure and temperature.

After the temperature and the pressure increased to the preset values, the heating power was adjusted in order to maintain the temperature in the reactor constant and the stirring speed was adjusted to 900-950 rpm. Finally the nitrogen gas was switched to the air and the reaction was triggered.

**Analytical method:** Sampling was carried out for every a short period during the reaction and the ingredients in the sample were determined by using a HP6890-MS5973 gas chromatograph-mass spectrometer and quantitative analysis was carried out by using a Shimazu GC-9A gas chromatograph. The chromatographic column was a SE-54 capillary column and the detector was a hydrogen flame ion detector (FID).

## RESULTS AND DISCUSSION

**Liquid-phase catalytic oxidation of pure methyl benzene:**

Since methyl benzene can be used as a kind of solvent, the method would be simple and feasible if relatively high yield of benzaldehyde can be obtained in the catalytic oxidation of methyl benzene in pure methyl benzene. Thus the oxidation studies were firstly carried out on the addition of catalysts in pure methyl benzene.

**Effects of different catalysts on oxidation of methyl benzene:** Since catalysts had significant influences on the process of methyl benzene oxidation, a set of experiments were designed to examine the effects of different cobalt catalysts (the concentration of cobalt was 10 mg/L) in the same concentration on methyl benzene oxidation and the reaction conditions and the results were shown in Table-1.

Catalyst	Reaction time (min)	Transformation rates (%)	Yield (%)
Cobalt tetraphenylporphyrin	210	2.25	1.71
<i>p</i> -Chloro-cobalt tetraphenylporphyrin	210	2.18	1.40
Cobalt naphthenate	210	2.23	1.57

It can be found from the results in Table-1, three kinds of different metal cobalt catalysts were used for the liquid phase catalytic oxidation of methyl benzene, the transformation rates of methyl benzene within the same time were all about 2% and the yield of benzaldehyde was about 1.5%. It can be found from the results from the sampling during the process that an initiation period can be found when cobalt tetraphenylporphyrin was used as the catalyst and the consumption rate after initiation was faster than the rates for methyl benzene oxidation under the functions of the other two kinds of catalysts. In general, no significant difference was found in the efficacy of the three kinds of catalysts on methyl benzene oxidation and the rates for methyl benzene oxidation under the effects of the three kinds of catalysts were all very slow and only 2% of methyl benzene was transformed after the reaction had been started for 3 h and the rate for methyl benzene oxidation should be improved by selecting other methods.

**Effects of the change in cobalt concentration on oxidation of methyl benzene:** The addition of bromine as a kind of promoter can significantly improve the rate of methyl benzene oxidation; in the meantime, the change in the concentration of the catalyst can also lead to changes in the reaction rate. The present study carried out investigations on the liquid phase oxidation of methyl benzene under the effects of different

concentrations of catalysts respectively and the reaction conditions and the results were shown in Table-2.

The curves for the changes in methyl benzene and benzaldehyde at the presence of different catalyst concentrations with time were shown in Fig. 1. It can be found from the results in Table-2 that the rate of methyl benzene oxidation after the promoter was added than was significantly higher than the consumption rate of methyl benzene without the promoter. At the same time, with the continuous increase in the concentration of the catalyst, the rate of methyl benzene oxidation also continuously increased. Moreover, when the concentration of the catalyst increased by five times, the transformation rate of methyl benzene also increased by about five times within the same time (140 min). However, the rules for the changes in benzaldehyde concentration were different, it can be found from Fig. 1 that the consumption rate of methyl benzene increased after the promoter was added and the yield of benzaldehyde also increased to some extent. The yield of benzaldehyde at the presence of low concentration of catalyst increased with the increase in the concentration of the catalyst, but the yield of benzaldehyde decreased with the increase in the concentration of the catalyst increased and exceeded a certain range, which can be mainly attributed to the increase in the concentration of the catalyst can improve the oxidation of methyl benzene, but it also promoted the oxidation of benzaldehyde, thus there was a optimal value for the concentration of the catalyst.

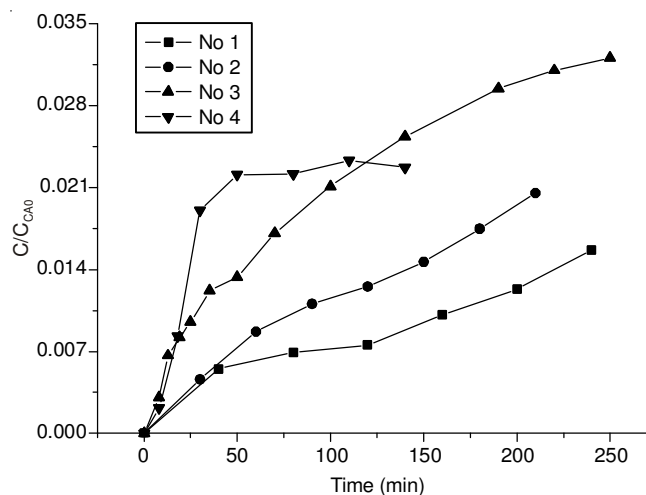


Fig. 1. Curve for benzaldehyde concentrations-time

**Effects of catalytic composite on oxidation of methyl benzene:** The chelation of catalysts in the MC system can change the oxidation rate and the product yield of methyl benzene and the effects of different catalytic composites in the pure methyl benzene solvent were examined respectively

No.	Methyl benzene (mL)	Cobalt naphthenate (mg)	KBr (mg)	Reaction time (min)	Transformation rates (%)	Yield (%)
1	350	38.3	0	240	2.23	1.57
2	350	33	5.6	210	3.32	2.05
3	350	99.4	16.4	250	9.65	3.20
4	350	494.9	80.6	140	30.1	2.27

TABLE-3  
EFFECTS OF CATALYTIC COMPOSITE ON METHYL BENZENE OXIDATION

No.	Methyl benzene (mL)	Cobalt porphyrin (mg)	Cobalt acetate (mg)	Manganese acetate (mg)	Naphthenic acid (mg)	Reaction time (min)	Transformation rates (%)	Yield (%)
5	350	30.8	0	209.5	0	180	0	0
6	350	8.3	0	0	0	210	2.25	1.71
7	350	8.1	209.8	0	0	210	1.61	1.02
8	350	8.5	0	0	33.7	210	1.46	1.03

TABLE-4  
REACTION CONDITIONS

Solvents	Material A/solvents S (mass/mass)	Gross (g)	T (°C)	P (MPa)	Co/Mn/Br (mole/mole/mole)	Co (ppm)
S	2	230	170	1.7	1:1:1	300

and the reaction conditions and the results were shown in Table-3.

In the absence of the promoter, the catalytic composite of manganese acetate and cobalt porphyrin did not promote the oxidation of methyl benzene, but terminate the progress of the reaction on the contrary, which may be attributed to prolongation in the initiation time of methyl benzene due to the addition of manganese. When two kinds of different cobalt compounds formed the catalytic composite, the reaction can be inhibited to some extent. Cobalt acetate and cobalt naphthenate were added in cobalt porphyrin respectively and the transformation rates of methyl benzene under the two different situations at 210 nm were almost identical and the yields of benzaldehyde were similar, the transformation rate of methyl benzene and the yield of benzaldehyde both decreased to some extent in comparison to those for single application of cobalt porphyrin catalyst.

**Oxidation of methyl benzene in solvents:** During the process of liquid-phase catalytic oxidation of methyl benzene in pure methyl benzene, though the rate of methyl benzene oxidation can be improved by changing some conditions, there is still no effective method to improve the yield of benzaldehyde, thus it is considered to add methyl benzene in organic solvent for oxidation in order to improve the yield of benzaldehyde. Benzoic acid, acetic acid, methanol and dimethyl sulphoxide were selected as the solvents respectively under the same conditions and the reaction conditions were shown in Table-4.

The results for methyl benzene in different solvents were shown in Fig. 2-4, among them the reaction cost 120 min when methanol and dimethyl sulphoxide were used as the solvents and methyl benzene was not completely transformed. When acetic acid was used as the solvent, the time for reaction termination was about twice of the time when benzoic acid was used as the solvent. When benzoic acid was used as the solvent, the time for achieving the highest yield of benzaldehyde was about 35 min; when acetic acid was used as the solvent, the time for achieving the highest yield of benzaldehyde was about 60 min and the highest yield of benzaldehyde when acetic acid was used as the solvent was slightly higher than that when benzoic acid was used as the solvent. The oxidation reaction of methyl benzene was not initiated in methanol solvent. However, when dimethyl sulphoxide was used as the solvent, dimethyl sulphoxide may be a kind of inhibitor for free radicals

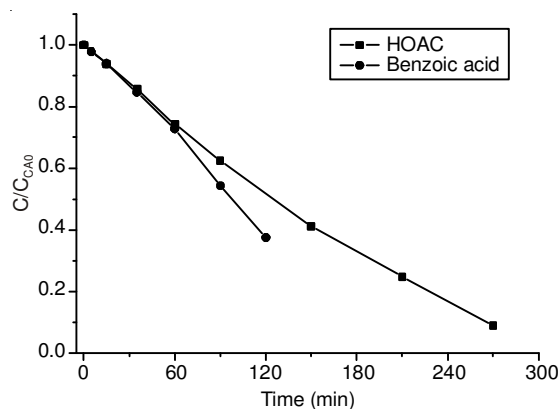


Fig. 2. Curve for methyl benzene concentrations-time

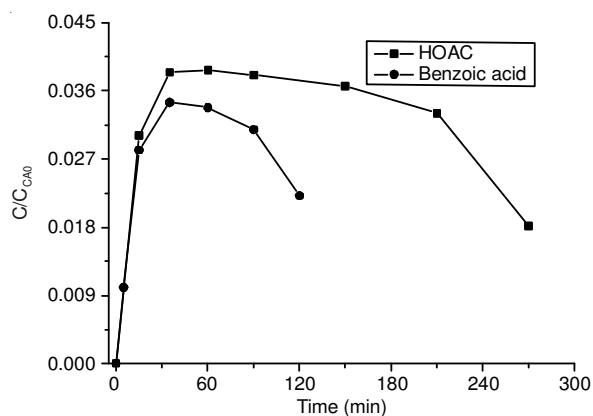


Fig. 3. Curve for benzaldehyde concentrations-time

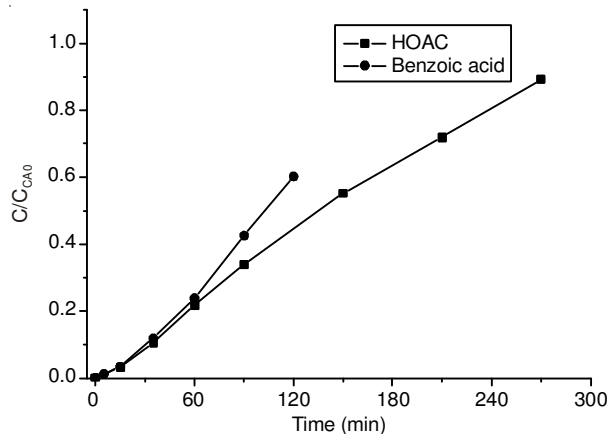


Fig. 4. Curve for benzoic acid concentrations-time

in the reaction and it can inhibit the production of free radicals, but the highest yield of benzaldehyde was not as high as that when acetic acid was used as the solvent.

### Conclusion

During the process of liquid-phase catalytic oxidation in pure methyl benzene, the catalytic efficacy of different catalysts cobalt tetraphenylporphine, *p*-chloro-cobalt tetraphenylporphyrin and cobalt naphthenate were not significantly different, the transformation rates of methyl benzene and the yield of benzaldehyde during the reaction for 4 h were all very low. After bromine was added as a kind of promoter in the reaction system, the catalytic efficacy was significantly improved and the increase in the catalyst concentration significantly improved the transformation rate of methyl benzene, but it did not significantly affect the yield of benzaldehyde and the addition of catalytic composite in the reaction system did not improve the yield of benzaldehyde in essence.

The rates of methyl benzene oxidation in acetic acid or benzoic acid were significantly higher than that in pure methyl benzene and the highest yield of benzaldehyde in the catalytic system of Co-Mn-Br can be as high as 19 %. In the comparison between acetic acid and benzoic acid as the solvents, the rate

of methyl benzene oxidation in benzoic acid was higher than that in acetic acid, but the highest yield of benzaldehyde was not as high as that in acetic acid, considering the separation in the later stage of the reaction, benzoic acid was used as the solvent.

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