



Oxidation of 2-Methyl Naphthalene to 2-Naphthoic Acid with Co-Mn-Br Catalyst

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The effects of catalyst compositions, reaction parameters such as temperature, pressure and water addition on the liquid phase catalytic oxidation of 2-methyl naphthalene to 2-naphthoic acid over Co-Mn-Br catalyst have been investigated in a high-pressure reactor. It has been demonstrated that each single component of Co, Mn or Br and Co-Mn had little catalytic oxidation activity, while the oxidation was catalyzed by Co-Br, Mn-Br and Co-Mn-Br. Compared with that of Co-Br, the oxidation went smoothly with Mn-Br and higher yield was obtained but with longer reaction time. Therefore, a ternary Co-Mn-Br catalyst was investigated and a maximum product yield of 93 % with intermediate reaction time was realized. The oxidation process showed an induction time, and the time length was determined by both the catalyst composition and oxidation conditions. The induction time decreased with increasing reaction temperature and pressure. It has also been found that they required an initial temperature for the start of oxidation and a minimum pressure for complete oxidation, indicating the substantial impacts of reaction parameters. Addition of water suppressed the oxidation as denoted by both longer induction time and lower product yield, and the reaction did not happen with 7 % water addition.

Key Words: 2-Methyl naphthalene, Co-Mn-Br catalyst, Catalytic oxidation, 2-Naphthoic acid.

INTRODUCTION

Methyl naphthalene is found in substantial concentration in cracked light gas oil produced as a by-product of ethylene production unit. Methyl naphthalene is also produced in petroleum refineries, both in the light gas oil produced in refinery catalytic cracking operations and in the bottom fraction of reformate from catalytic reforming operations. Coal tar, such as that produced in the steel industry, also contains methyl naphthalene¹.

Methyl naphthalene has two isomers: 1- and 2-methyl naphthalene. Oxidation of 2-methyl naphthalene has been used to produce 2-methyl-1,4-naphthoquinone and 2-naphthoic acid. 2-Naphthoic acid is used as an intermediate for the synthesis of pharmaceuticals, photochemicals, plant growth hormones, dyes and other organic compounds. 2-Naphthoic acid can be readily converted to 2,6-naphthalene dicarboxylic acid by utilizing the Henkel rearrangement reaction²⁻⁵. Polyesters prepared from 2,6-naphthalene dicarboxylic acid and ethylene glycol have excellent heat resistance and mechanical properties as compared with polyethylene terephthalate and films, fibers and other shaped articles prepared from such polyesters have recently attracted great attention in the art^{6,7}.

Oxidation reactions occupy a prominent place in both the sciences of catalysis and catalysis-based modern chemical industry^{8,9}. They have vastly contributed to the development of the modern society for their products are incorporated into an amazingly large proportion of the materials and commodities in daily use. In chemical industry more than 60 % of products are obtained by catalytic oxidation routes.

Oxidation of arenes has been studied extensively in the literature¹⁰⁻¹³, however only a few dealt with alkyl naphthalenes. As summarized by Rao *et al.*¹⁴, methyl naphthalenes are oxidized in the presence of transition metal ions (Co²⁺ and Mn²⁺) and bromide ion catalyst system to the corresponding naphthalene carboxylic acids at > 120 °C and 1 to 2 MPa. With Co-Mn-Br catalyst and air as oxidant, the reported yields are *ca.* 80 %. However, the oxidation of 2-methyl naphthalene to get 2-naphthoic acid in higher yields and lower reaction conditions is still important from industrial view point.

Therefore, we are reporting here our results on the oxidation of 2-methyl naphthalene in acetic acid with molecular O₂ using conventional Co-Mn-Br catalyst system and optimized reaction conditions for higher product yields. By varying the catalyst composition as well as reaction parameters, the characteristics of Co-Mn-Br catalyzed oxidation of 2-methyl naphthalene have been investigated.

TABLE-1
EFFECTS OF CATALYST COMPOSITION ON 2-METHYL NAPHTHALENE OXIDATION^a

| Catalyst composition mole ratio | | | Reaction time (min) | Induction time (min) | O ₂ Consumption ^b (%) | Product colour | Yield (%) |
|---------------------------------|----|------|---------------------|----------------------|---|----------------|-----------|
| Co | Mn | Br | | | | | |
| 0 | 0 | 0 | | - | - | - | - |
| 1 | 0 | 0 | 120 | - | 0.7 | - | - |
| 0 | 1 | 0 | 180 | - | 0 | - | - |
| 0 | 0 | 1 | 280 | - | 0 | - | - |
| 1 | 1 | 0 | 240 | - | 17.2 | - | - |
| 0 | 1 | 1 | 252 | 26 | 117.6 | Light | 82.8 |
| 1 | 0 | 1 | 105 | 150 | 111.5 | Deep | 62.7 |
| 1 | 1 | 1.33 | 120 | 60 | 126.1 | Light | 84.7 |
| 1 | 1 | 1 | 120 | 55 | 103.4 | Light | 81.2 |
| 1 | 1 | 2 | 120 | 40 | 121.9 | Light | 93.3 |
| 1 | 1 | 3 | 120 | 40 | 126.5 | Deep | 86.3 |

^aReaction temperature :120 °C, pressure: 0.6 MPa, catalyst loading: 1 %; ^bPercentage of theoretical value

EXPERIMENTAL

Cobalt acetate, manganese acetate, sodium bromide and acetic acid were purchased from Fuchen reagent, Tianjin, China, were all analytical grades and were used as received. 2-Methyl naphthalene was supplied by Yalu biochemistry Co. Ltd., Laiwu, China. Pure O₂ was used as the source of molecular O₂ in the oxidation reaction.

Oxidation experiments were conducted in a 100 mL pressure reactor that equipped with magnetic stirrer (Fig. 1). In a typical run, known amounts of substrate, metal salts Co(OAc)₂·4H₂O, Mn(OAc)₂·4H₂O, NaBr, acetic acid was mixed in the reactor. The reactor was purged three times with nitrogen gas to remove air and to ensure an inert atmosphere, and checked for leaks under nitrogen pressure. Subsequently, O₂ was used to purge out the nitrogen. After the required temperature was attained, the reactor was then pressurized with O₂ from the cylinder. After a period of time, the oxidation started as indicated by the consumption of O₂. During the oxidation process, the rates of O₂ consumption as well as the cumulative consumed O₂ shown on the mass flow meter were recorded periodically as a function of time.

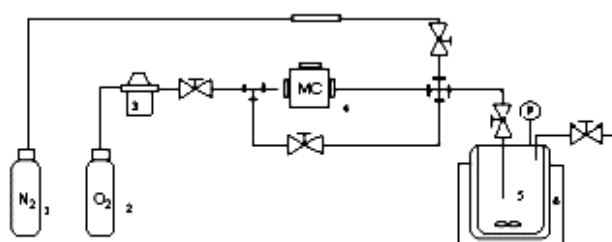


Fig. 1. Experimental apparatus for oxidation of 2-methyl naphthalene; 1-nitrogen cylinder, 2-oxygen cylinder, 3-pressure regulator, 4-mass flowmeter, 5-reactor, 6-oil heating tank

When consumption of O₂ finished, the reactor was cooled to room temperature and vented to atmospheric pressure. The reaction mixture was separated by filtration. The liquid phase containing catalyst was evaporated at a reduced pressure to dryness to recover the solvent and the remaining solid was mixed the solid phase. The obtained solid mixture was washed by water 3 times and then neutralized by 5 % NaOH and separated. The clear solution was then neutralized by 5 % HCl,

thus precipitated the oxidation product. After filtration and drying, 2-naphthoic acid was obtained.

Analysis: The analyses of the reactants and products were performed with vario micro cube elemental analyzer. The oxidation product was characterized by IR and UV spectroscopy. The melting point of the oxidation product was also measured.

RESULTS AND DISCUSSION

Preliminary investigation demonstrated that an initial temperature was required for the oxidation to start and oxidation had an induction time. While the initial temperature had little relation with other parameters, the induction time was deeply influenced by reaction parameters such as temperature, pressure, catalyst composition and addition of water.

Catalyst composition: The oxidation of 2-methyl naphthalene was carried out with different mole ratios of Co-Mn-Br catalyst to know the catalytic role of each component.

At a temperature of 120 °C, a reaction pressure of 0.6 MPa, a catalyst loading of 1 % and the substrate/solvent weight ratio of 1:6, the effects of catalyst formulations were investigated by varying atomic ratio of Co-Mn-Br catalyst compositions (Table-1).

In the absence of catalyst, the oxidation of 2-methyl naphthalene did not take place. Using Co only as catalyst, little O₂ consumption could be recorded in 120 min. Similar results were obtained using Mn or Br as catalyst. Hence, it can be said that each single element of Co, Mn or Br can not catalyze the oxidation of 2-methyl naphthalene.

Using combination of Co-Mn as catalyst, there was little O₂ consumption in 240 min as shown in Table-1. When the reaction temperature increase from 120 to 130 °C, a small amount of O₂ was consumed and trace of oxidation product was collected.

However, in the presence of Co-Br or Mn-Br, consumption of O₂ was recorded after an induction time indicating the start of catalytic oxidation reaction; hence a substantial amount of oxidation product was obtained. These data clearly demonstrated that the oxidation of 2-methyl naphthalene is catalyzed by combination Co-Br or Mn-Br, thus Br acted as a co-catalyst instead of serving as a promoter, especially at a lower reaction temperature of 120 °C.

In Fig. 2, the time dependence of accumulated O₂ consumption is given. It can be seen that Co-Br catalyst presented long induction time but short reaction time for complete

oxidation, while Mn-Br had short induction time but long reaction time. Thus oxidation reaction went smoothly in the presence of Mn-Br catalyst (Table-1 and Fig. 2).

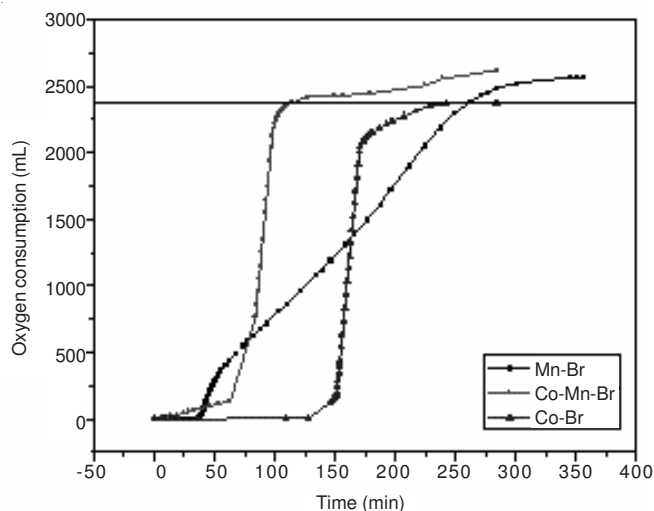


Fig. 2. Relationship between reaction time and O₂ consumption with different catalyst composition. Reaction conditions: the reaction pressure 0.6 MPa, the reaction temperature 120 °C

At a Co-Mn-Br ratio of 1:1:x, the catalytic behaviour of ternary catalyst compositions had been investigated. The obtained yield of oxidation product was in 85-93 % range with varying x from 1.3 to 3. As shown in Fig. 2, Co-Mn-Br demonstrated similar oxidation rate to that of Co-Br system. Therefore, a Co-Mn-Br ratio of 1:1:2 was chosen to investigate the impact of reaction parameters.

Temperature effects: The influence of temperature on the oxidation of 2-methyl naphthalene was studied by increasing reaction temperature up to 140 °C with Co-Mn-Br (1:1:2, mol ratio) at 0.6 MPa. It has been shown that the oxidation was highly sensitive to reaction temperature. When the temperature was 115 °C, consumption of O₂ was not noticed within 300 min (Table-2). When the temperature was increased from 115 to 120 °C, the oxidation took place after 40 min, and the consumption of O₂ was 121.9 % of theoretical value within 120 min. Further increase the temperature to 130 °C, the induction time shortened to 10 min. At 140 °C, the oxidation started without a noticeable induction time.

| Reaction temp. (°C) | Induction time (min) | Reaction time (min) | O ₂ Consumption ^b (%) | Product colour | Yield (%) |
|---------------------|----------------------|---------------------|---|----------------|-----------|
| 115 | - | 300 | 0 | - | 0 |
| 120 | 40 | 120 | 121.9 | Light | 93.3 |
| 130 | 10 | 180 | 123.3 | Deep | 86.3 |
| 140 | 0 | 180 | 131.0 | Deep | 81.4 |

^aReaction pressure: 0.6 MPa, catalyst loading : 1 %; ^bPercentage of theoretical value

With the temperature rise, the rate of oxidation increased considerably as indicated by the consumption rate of O₂, but the yield of oxidation decreased and the colour of the resulting 2-naphthoic acid became deeper, indicating an increase of by-products at higher temperatures.

Influence of reaction pressure: The oxidation of 2-methyl naphthalene was carried out by varying reaction pressure ranging between 0.2 to 0.8 MPa with Co-Mn-Br (1:1:2, mol ratio) at 120 °C.

Reaction pressure has dramatic effects on 2-methyl naphthalene oxidation. With increasing with reaction pressure, the induction time decreased as shown in Fig. 3, while the rate of oxidation increased. However, the collected 2-naphthoic acid yield reached maximum at 0.6 MPa pressure.

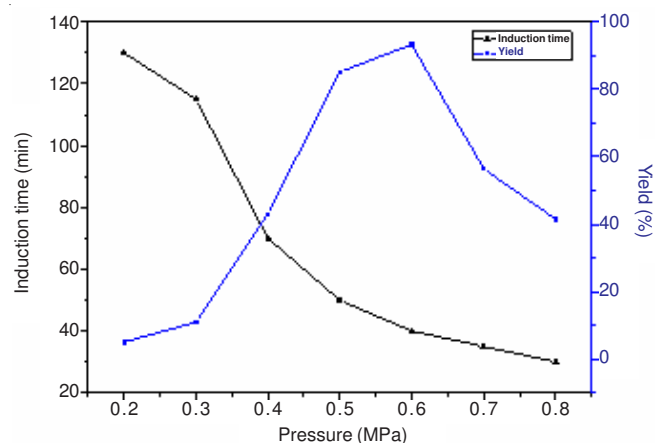


Fig. 3. Effect of reaction pressure on the oxidation of 2-methyl naphthalene. Reaction conditions: Co:Mn:Br (1:1:2, mol ratio) at 120 °C

When the pressure was lower than 0.4 MPa, the consumption of O₂ did not reach to theoretical level even with prolonged time, thus a low yield of the intended 2-naphthoic acid was obtained. Increasing pressure to 0.5 MPa and above, complete oxidations had been realized. The results of oxidations at 0.2 MPa and 0.7 MPa are shown in Fig. 4, the straight-line which parallel to X-axis is the theoretical O₂ consumption value. It is clear that with 0.2 MPa pressure, there is no significant change of O₂ consumption in the initial 2 h. After the induction time, the O₂ consumption increased but did not reach the theoretical value. The reason for the incomplete oxidation at lower pressures below 0.4 MPa is not clear, and needs further investigations.

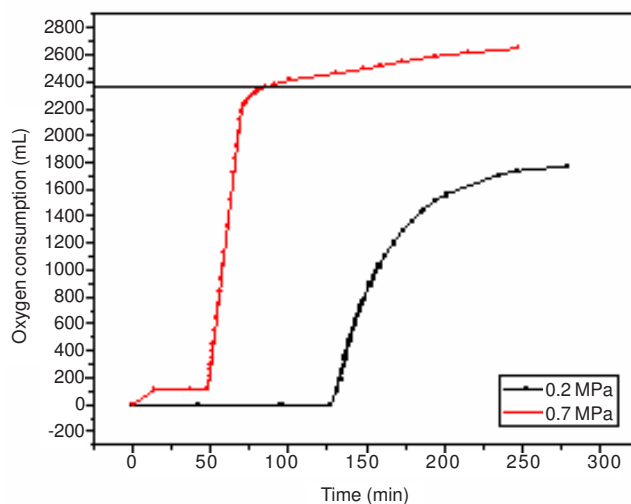


Fig. 4. Relationship between reaction time and O₂ consumption at 0.2 MPa and 0.7 MPa. Reaction conditions: Co:Mn:Br (1:1:2, mol ratio) at 120 °C

When the oxidation was performed at high pressures exceeding 0.6 MPa, side reactions increased more rapidly as suggested by the deeper colour of oxidation product, so the yield of 2-naphthoic acid decreased. Therefore, it is essential to conduct the oxidation under pressurized condition such that the pressure should at 0.6 MPa.

Effect of the water addition: To find the effect of water¹⁵ on the oxidation of 2-methyl naphthalene, addition of water up to 7 wt % to the reaction system was performed. It has been found that water addition hindered the catalytic oxidation and the oxidation selectivity also decreased. Both the induction time and the reaction time for complete oxidation prolonged with increasing water addition.

In Fig. 5, the yield of 2-naphthoic acid vs. the amount of water addition is presented. It can be seen that the yield of product decreased with increasing water concentration, and only a small amount of product was collected when 7 wt % water was added. Initially, the oxidation system contained a small portion of water that existed in the catalyst components. When oxidation proceeded in a batch mode, water as an oxidation co-product accumulated. From Fig. 5, the highest yield was obtained without water addition, thus a further oxidation was carried out with the addition of acetic anhydride for a purpose of removing water. In this case, the oxidation rate increased more rapidly, but a lower yield with deep coloured product was collected. This highly suggested that a small portion of water is required in order to assure an optimum oxidation process.

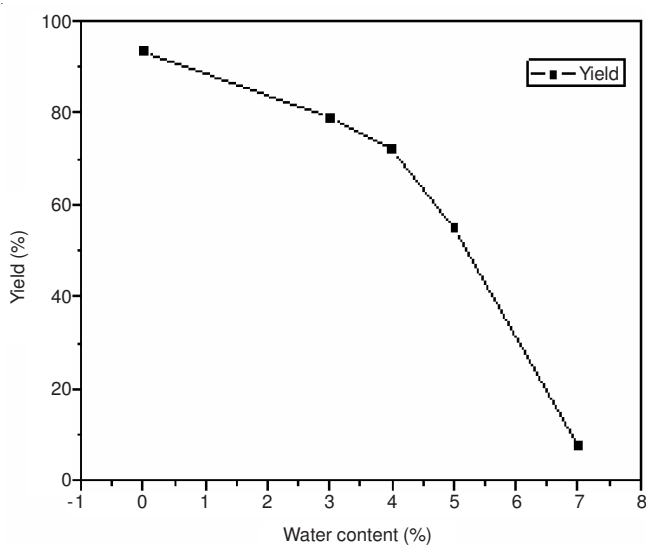


Fig. 5. Effect of water addition on the oxidation of 2-methyl naphthalene. Reaction conditions: Co:Mn:Br (1:1:2, mol ratio) at 0.6 MPa, 120 °C

Conclusion

The characteristics of liquid-phase oxidation of 2-methyl naphthalene catalyzed by Co-Mn-Br with molecular O₂ in

acetic acid medium was studied in a high-pressure reactor. The effects of catalyst composition, reaction time, reaction pressure and temperature, and water content were investigated. The results showed that the oxidation process existed an induction time and the time length was determined by both the catalyst composition and oxidation conditions. It has been demonstrated that the oxidation hardly happened with both each single component of Co, Mn or Br and Co-Mn, it was catalyzed by Co-Br, Mn-Br and Co-Mn-Br, denoting Br served as a co-catalyst in stead of a promoter. Compared with that of Co-Br, the oxidation went smoothly with Mn-Br and higher yield was obtained but with longer reaction time. With a ternary Co-Mn-Br catalyst, a maximum product yield of 93 % with intermediate reaction time was realized.

It was found that the oxidation was highly sensitive to reaction temperature. The oxidation started at a certain temperature, and below the value the substrate was scarcely converted. Reaction pressure had great impact on the oxidation. The substrate could not be completely oxidized below 0.5 MPa, while a decreased yield of the intended 2-naphthoic acid was obtained with a pressure higher than 0.6 MPa. About 93 % 2-naphthoic acid yield was realized at 0.6 MPa. Water had a negative effect on the oxidation, and the reaction did not happen with 7 % water addition.

REFERENCES

1. K.M. Kreitman, S.E. Brewer, J.B. Rodden, R.L. Blackburn, T.F. Brownscombe and J.L. Buechele, U.S. Patent 6448436 (2002).
2. B. Raecke and H. Schirp, U.S. Patent 2823231 (1958).
3. B. Raecke, W. Stein and H. Schirp, U.S. Patent 2849482 (1958).
4. P.A. Sanchez, B. Ridge, D.A. Young, G.E. Kuhlmann, W. Partenheimer and W.P. Schammel, U.S. Patent 4950786 (1990).
5. S. Mitamura, K. Fujishiro and H. Inoue, U.S. Patent 4820868 (1989).
6. C.S. Wang and Y.M. Sun, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 1295 (1994).
7. C.Y. Chen, D.S. Santillia, W.L. Schinski, D.J. O'Rear and T.V. Harris, *Stud. Surf. Sci. Catal.*, **H154**, H2261 (2004).
8. A. Bielanski and J. Haber, *Oxygen in Catalysis*, Marcel Dekker, New York, (1991).
9. H.H. Kung, *Transition Metal Oxides: Surface Chemistry and Catalysis*, Elsevier, Amsterdam (1989).
10. M.L. Kantam, P. Sreekanth, K.K. Rao, T.P. Kumar, B.P.C. Rao and B.M. Choudary, *Catal. Lett.*, **81**, 223 (2002).
11. K. Nair, P.S. Dhanashri, G.V. Shanbhag and S.B. Halligudi, *Catal. Commun.*, **5**, 9 (2004).
12. C.C. Guo, G. Huang, Q. Liu, X.T. Wang and H.Y. Hu, *Appl. Catal. A: Gen.*, **282**, 55 (2005).
13. M. Chen, R.X. Zhou and X.M. Zheng, *Appl. Catal. A: Gen.*, **242**, 329 (2003).
14. T.S.S. Rao and S. Awasthi, *E.-J. Chem.*, **4**, 1 (2007).
15. A.J. Hu, C.X. Lu, B.D. Li and T. Huo, *Ind. Eng. Chem. Res.*, **45**, 5688 (2006).