Articles

Precipitation of Manganese in the *p*-Xylene Oxidation with Oxygen-Enriched Gas in Liquid Phase

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The liquid phase oxidation of *p*-xylene has been carried out with oxygen-enriched gas, and the manganese component was precipitated probably via over-oxidation to Mn^{4+}. The precipitation increased with rising oxygen concentration in the reaction gas and occurred mainly in the later part of the oxidation. The activity of the reaction decreased, and the blackening of the product and side reactions to carbon dioxide increased with the degree of precipitation. Precipitation can be decreased with the addition of metal ions, such as cerium, chromium and iron.

Keywords : Terephthalic acid, *p*-Xylene oxidation, Oxygen-enriched gas, Manganese precipitation, Blackening.

Introduction

Terephthalic acid (TPA) is one of the most important chemicals, with an annual production capacity of more than 24,000,000 tons in the year 2000. Korea's production of TPA, 4,540,000 tons per year, is the highest in the world.[1] TPA, the raw material of polyester, is usually produced commercially by liquid phase oxidation of *p*-xylene (pX) with air using a catalyst combination of cobalt, manganese and bromide ions in acetic acid at around 170-210 °C.[2,3]

Considering the huge production capacity of TPA, even small improvements of the process are very important from an economic view. The desired improvements of the TPA process have been described elsewhere,[3] and the studies to improve the liquid phase oxidation of alkyl aromatics with catalyst of metal/bromine have been reviewed in detail by Partenheimer.[4]

Detailed studies, such as kinetics[5-11] and mechanism[3,5,6,12-18] on the liquid phase oxidation of alkyl aromatics to aromatic carboxylic acids have been carried out. It has also been attempted to replace the acetic acid solvent with water[19,20] and to eliminate the corrosive bromine component[21,22] and to utilize carbon dioxide as a co-oxidant.[23] There have been numerous efforts[5,6,24,25] to improve the Co/Mn/Br catalyst system, including the addition of transition and lanthanide metals, such as zirconium, cerium and hafnium.

The oxidation with oxygen-enriched gas has been studied by Praxair technology Inc.[26] and Mitsui petrochemical industry[27] to improve the TPA process. Claims were made that the reactor volume could be decreased and the reaction yield was high with the oxygen-enriched gas. A higher efficiency of reaction was obtained by utilizing a special apparatus called LOR (liquid oxidation reactor),[26] because of the enhanced efficiency of mixing and the increased contacts between the substrates and the reaction gas. The amount of reactor exhaust gas could be decreased also.[27] Therefore, the TPA process with oxygen-enriched gas is very promising.

The precipitation of manganese to decrease the chromaticity of product in *p*-xylene oxidation has been reported when the Br/(Mn+Co) ratio of catalyst is low or water concentration is high.[28] The precipitated manganese causes the blackening of the product due to the precipitated black manganese material.[28,29] The mechanism of manganese precipitation has been explained as being due to MnO_2 formed from the disproportionation of Mn^{3+}, and this precipitation could be prevented or decreased with the addition of cerium component.[28] The oxidation of *p*-tolualdehyde can be accompanied with the precipitation of manganese and this precipitation can be decreased with additional metal components, such as cerium, lanthanum, chromium, iron, and etc.[29] Preventing the precipitation of metal components is important because these materials can contaminate the hydrogenation catalyst for PTA (purified TPA),[28] deteriorate the product and make the recycling of solvent containing catalyst difficult. The preferential precipitation of a component can be even a serious problem because the operation is more difficult due to the recycling of solvent containing catalysts and the difficulty in maintaining the optimum catalyst concentration.

Therefore, studying the precipitation of metal component to overcome the negative effects is necessary. Studying the precipitation in the oxidation of *p*-xylene with oxygen-enriched gas is important because of the potential applicability of the process. However, no studies have been made dealing with the precipitation (not only precipitation in the oxidation with oxygen-enriched gas but also precipitation in

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oxidation with high water concentration or low Br condition) as far as the authors know.

In the present study, the precipitation of manganese, when the oxidation is carried out with oxygen-enriched gas, is reported for the first time. The decrease in activity due to the precipitation is also reported. A method to decrease precipitation and blackening is also suggested.

Experimental Section

Apparatus. The apparatus for the oxidation reaction is explained elsewhere.[30] The reaction rate and cumulated conversion were monitored continuously by the consumption rate of oxygen.

Procedure. The procedure for the oxidation reaction is explained elsewhere.[30] 200 g of reactants (15% *p*-xylene, 7.5% water and 77.5% acetic acid) were charged in the titanium reactor. The expected oxygen consumption was 848 mmol based on the stoichiometry of p-xylene oxidation only. Based on the total weight of reaction mixture, the catalyst comprised 150 ppm of cobalt, 300 ppm of manganese and 240 ppm of bromine as a base condition. The concentration of each catalyst component was changed to 100, 200 and 300 ppm of cobalt, manganese, and bromine, respectively, to study the precipitation in the high Br/(Co+Mn) ratio.

An additional metal ion, such as Ce^{3+}, Cr^{2+} or Fe^{2+} with a weight concentration same as the cobalt (150 or 100 ppm, 50 ppm for some cases), was added to study the precipitation. The effects of additional cobalt or manganese were also studied with 150 ppm of additional ions.

The oxygen concentration in the gas phase of the reactor was between 50 and 64%, and the nitrogen concentration was changed accordingly.

Reagent. Cobalt acetate tetrahydrate, manganese acetate tetrahydrate and hydrogen bromide were used to prepare the catalyst solution. Cerium(III) acetate, chromium(II) acetate hydrate dimer and iron(II) acetate were utilized as sources of additional metals. All other chemicals, including *p*-xylene and acetic acid, were guaranteed reagent grade.

Analysis. The detailed analysis methods for solid and liquid products are reported elsewhere.[30] The concentration of metal ions in liquid was determined with ICP and the precipitated material was analyzed with SEM and XPS.

Results and Discussion

Effects of oxygen concentration and cerium on the oxidation of *p*-xylene.

Typical TPA produced from the oxidation of *p*-xylene (the oxygen conversion was 753 mmol or 88.8%) with a catalyst of Co/Mn/Br, utilizing a gas containing 57 and 64% oxygen was gray in color for the lower oxygen concentration and dark gray for the higher concentration. The gray particles in TPA did not dissolve in alkaline solution and could be separated as black particles from TPA after dissolution of the TPA in KOH solution. Therefore, the precipitation of a black material on TPA is called blackening.[29] However, the products with the catalyst system of Co/Mn/Ce/Br showed the typical white color of TPA. Without the additional cerium ion, the oxidation in the later part of the reaction decreased quite sharply (Figure 1). Therefore, the reaction time needed for the oxygen conversion of 88.8% was high for the case of the reaction with the catalyst of Co/Mn/Br. The manganese ion retained in solvent was quite low for the case of oxidation with Co/Mn/Br compared with the case of oxidation with Co/Mn/Br/Ce, as displayed in Table 1 and Figure 2. Compared with cobalt, manganese ion precipitated more in solid when the oxygen concentration in the reaction gas was high. Moreover, the precipitation of manganese increased with the concentration of oxygen in the reaction gas. However, the precipitation of manganese did not depend much on the oxygen concentration if the cerium ion was added as a catalyst component.

In summary, the precipitation can be prevented with the addition of cerium in the catalyst system, and the precipi-

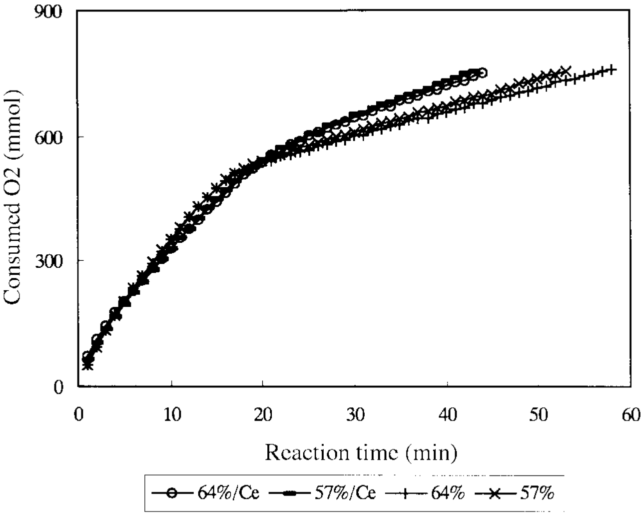

Figure 1. Effect of oxygen concentration and additional cerium on the rate of *p*-xylene oxidation.

Table 1. Effects of oxygen concentration and additional cerium on the *p*-xylene oxidation

O_2 Concentration (%)	Additive metal	Concentration (ppm)	Reaction time (min)*	Manganese retention ratio in mother liquid (%)	Cobalt retention ratio in mother liquid (%)	Color of solid product
64	–	0	56.6	32.6	76.5	Dark gray
	Ce	50	44.2	79.4	82.2	White
57	–	0	52.8	54.7	80.4	Gray
	Ce	50	42.6	81.1	85.5	White

*Reaction time needed for the consumption of oxygen of 753 mmol (88.8% oxygen conversion)

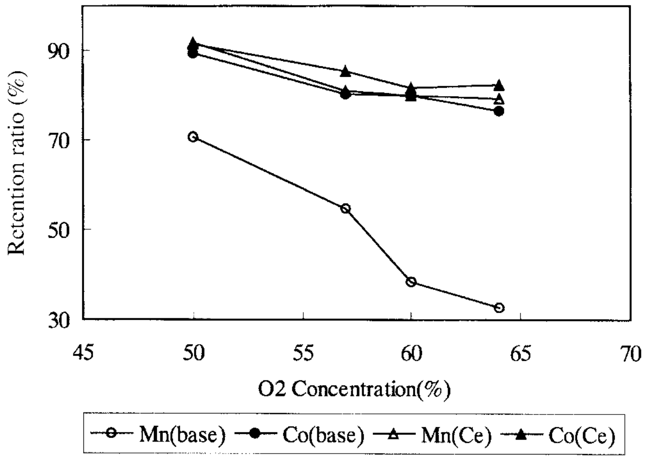

Figure 2. The degree of retention of cobalt and manganese ions in liquid after the oxidation of *p*-xylene with various oxygen concentration and additional cerium. The oxygen conversions of the reaction were 88.8% and 94.3% for the case of oxygen concentration of 57 or 64% and 50 or 60%, respectively.

tation increases with the oxygen concentration of reaction gas.

Effects of additional metals on precipitation. Oxidation reactions with the gas containing 60% oxygen were carried out with a few additional transition or lanthanide metals, and the oxidation rates are shown in Figure 3. Cobalt or manganese ions (150 ppm each) were added to check the effects on oxidation. The reaction rate was very low in the later part of the reaction with the additional manganese. The added cobalt was not very effective in raising the activity in the later part of the reaction, even though cobalt is one of the most active catalysts for oxidation.[6] Table 2 shows the reaction time needed for the oxygen conversion of 94.3% (800 mmol), TPA yield and purity, carbon dioxide concentration in the gas phase, color of solid product, retention ratio of cobalt and manganese and the activity after 30 min. Analyzing the color of the product, we found that the effect to prevent the blackening of TPA with the additional metal is in the order of Ce ~ Cr ~ Fe > base > Co > Mn. The *p*-xylene oxidation with oxygen-enriched gas was understood to cause the blackening of the product and this can be prevented with the addition of cerium, iron or chromium.

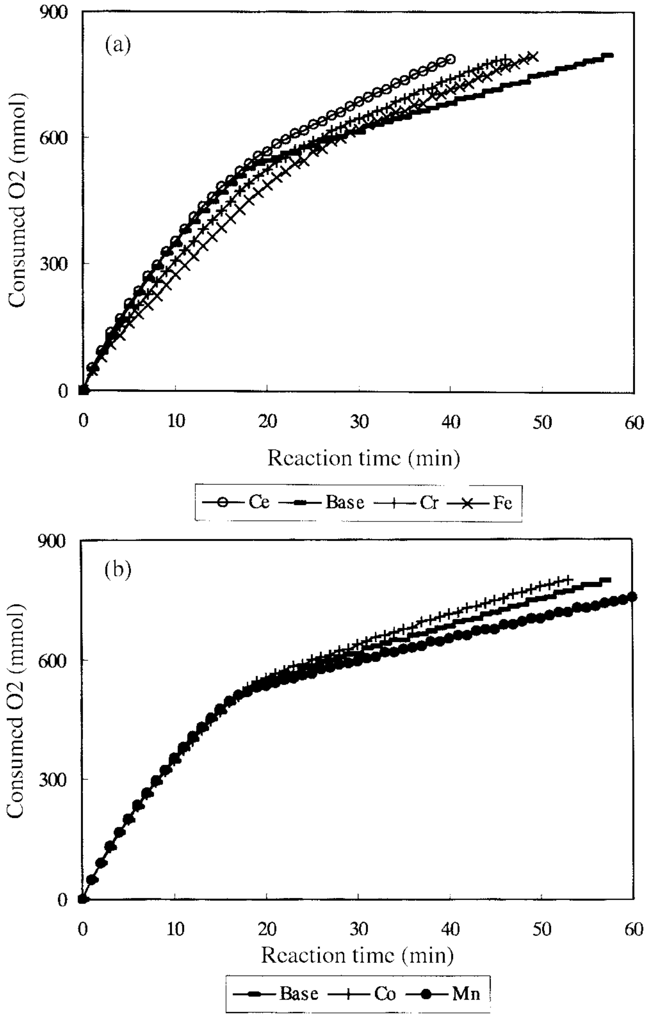

Figure 3. Effect of additional metal ions on the rate of *p*-xylene oxidation. (a) For the case of preventing the blackening except for the base catalyst system. (b) For the case of occurrence of the blackening.

The activity to reach the oxygen conversion of 94.3% is in the order of Ce > Cr > Fe > Co > base >> Mn. The rates of oxygen consumption after 30 min showed a linear dependence on reaction time. Reaction activity (the amount of oxygen consumption per reaction time) after 30 min was in

Table 2. Effects of additional metal ions on the *p*-xylene oxidation

Additional component and concentration (ppm)	Reaction Time (min)[*]	TPA yield (wt.%)	Purity of solid TPA (wt.%)	Conc. of CO_2 in gas phase after reaction (vol.%)	Color of solid product	manganese retention ratio in mother liquid (%)	cobalt retention ratio in mother liquid (%)	Activity after 30 min[***] (mmol/min)
–	57.5	74.2	92.6	20.6	Dark gray	38.5	80.0	6.58
Ce 150	41.0	75.8	92.9	18.1	White	79.9	81.8	10.36
Cr 150	46.9	75.2	92.8	19.6	White	78.0	82.4	9.05
Fe 150	49.6	73.8	92.0	20.3	White	75.6	81.9	9.16
Mn 150[**]	60.0	65.3	88.6	19.5	Black	13.7	73.4	5.23
Co 150	53.4	74.9	92.7	21.2	Very dark gray	28.7	65.3	7.05

[*] Reaction time needed for the consumption of oxygen of 800.0 mmol (94.3% oxygen conversion) except for the case of manganese. [**] 753.3 mmol of oxygen was consumed for 60 min.[***] Refer to the text. Slope of the amount of consumed oxygen with reaction time after 30 min.

Table 3. Effects of additional cerium on the *p*-xylene oxidation with the catalyst system of high Br/(Co+Mn) ratio. The concentrations of Co, Mn and Br were 100, 200 and 300 ppm, respectively

O_2 Concentration (%)	Additive metal	Concentration (ppm)	Reaction Time(min)*	manganese retention ratio in mother liquid (%)	cobalt retention ratio in mother liquid (%)	Color of solid product
60	–	0	84.0	68.3	81.7	Very bright gray
	Ce	100	84.0	83.4	82.9	White

*Reaction time needed for the consumption of oxygen of 800.0 mmol.

the order of Ce > Fe > Cr > Co > base > Mn. The addition of cerium, iron or chromium increased the reactivity in the later part of the reaction, decreasing the reaction time for fixed oxygen conversion, even though chromium and iron decreased the activity as the reaction began. We found that the 16.5 ppm of iron, chromium or nickel decreased the rates of *p*-xylene oxidation by 1-2%.[31] The rate of oxidation of *p*-toluic acid, through a study to find the effects of corroded reactor materials on the oxidation, was decreased by about 10% with the addition of 1400 ppm of iron, 400 ppm of chromium or 200 ppm of nickel.[31]

The retention ratio of manganese in mother liquid with the additional metal was in the order of Ce > Cr > Fe >> base > Co >> Mn. This corresponds quite well with the order to prevent the blackening of the product and the activity of the catalyst system. This may show that the blackening and activity of the reaction are related with the precipitation of manganese. The precipitation of cobalt does not depend much on the additional metals. The precipitation of cobalt was increased a bit with the additional cobalt or manganese.

The characteristics and effects of precipitation or blackening. The shape and composition of the precipitated black species were analyzed with SEM-EDS and XPS after filtration. SEM-EDS showed a species about 0.5 micron in size and composed mainly of manganese. The $2P_{3/2}$ and $2P_{1/2}$ peaks of the separated black species (the TPA is removed after dissolution in KOH solution) have the binding energy of 642.0 and 653.6 eV, and were practically similar to the data obtained from MnO_2 ($2P_{3/2}$: 642.1 eV, and $2P_{1/2}$: 653.8 eV). The binding energy of manganese increased with the oxidation state, as can be easily anticipated. For example, the binding energy ($2P_{3/2}$) of MnO, Mn_2O_3 and MnO_2 is reported to be about less than 641.4, about 641.4 and 642.0 eV, respectively.[32] Therefore, the precipitated black material may be considered a manganese species with an oxidation state of +4 (presumably MnO_2 similar to the reference[28]). However, checking the phase with XRD was impossible because the amount of the material was so small.

The blackening material has been explained to be MnO_2 formed from the disproportionation of Mn^{3+}: $Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$ ($MnO_2(\downarrow)$).[28] The degree of precipitation of manganese is high when the Br/(Co+Mn) ratio is low and water concentration is high.[29] The blackening due to the precipitation of manganese in the oxidation of *p*-tolualdehyde is also reported to be high when the concentration of manganese or water is high.[28]

The low precipitation of manganese in the condition of high Br/(Co+Mn) ratio has been confirmed in this study. The color of TPA produced with the catalyst of Co 100, Mn 200 and Br 300 ppm was very bright gray compared with dark gray TPA produced with the catalyst of Co 150, Mn 300 and Br 240 ppm. However, the color of the TPA produced with the catalyst with additional cerium (Co 100, Mn 200, Ce 100 and Br 300 ppm) was the typical white. The retention ratio of manganese in liquid was very high in oxidation with a catalyst of high Br/(Co+Mn) ratio (Table 3). The oxygen consumption rate did not depend much on the presence of additional cerium when Br/(Co+Mn) ratio was high (Figure 4). This may show that the decrease in activity is related with the precipitation of manganese.

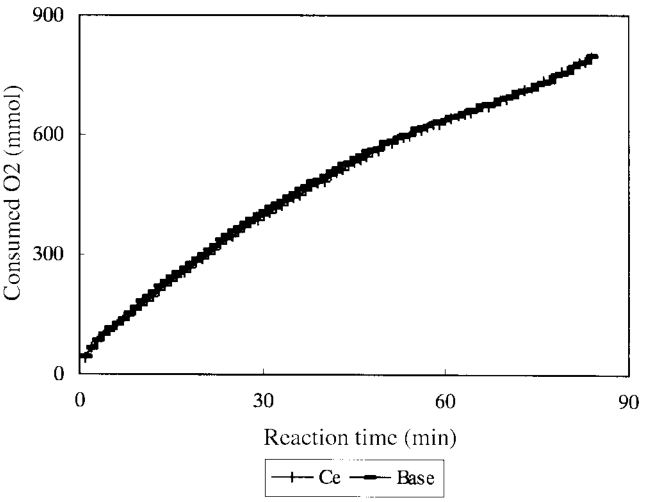

Figure 4. Effect of additional cerium ion on the rate of p-xylene oxidation with the catalyst system of high Br/(Co+Mn) ratio. The concentration of Co, Mn and Br was 100, 200 and 300 ppm, respectively.

The side reactions to carbon dioxide were checked with the concentration of carbon dioxide, by-products of the oxidation, in gas phase because the amount of side reactions is very important from an economic view. The relative amount of carbon dioxide formation with the additional metal was in the order of Co > base > Fe > Cr > Ce. The amount of the carbon dioxide formed via oxidation with the additional manganese was very high, considering the low oxygen conversion of 88.8% and low TPA yield. Therefore, we contend that the side reactions to carbon dioxide increase with the degree of precipitation of manganese. This may be related with the fact that the optimum Co/Mn ratio cannot be maintained from precipitation of manganese because cobalt is well known to have very high activity to the formation of carbon dioxide and carbon monoxide.[15]

The blackening due to the oxidation with enriched oxygen is reported here for the first time. We suggest that the precipitated manganese may be the reason for decreased activity, especially in the later part of the reaction.

An explanation for the precipitation or blackening. The precipitation or blackening occurs more readily when the bromine concentration is low or water concentration is high.[28,29] Considering the well known mechanism[3,5] of the oxidation, it may be supposed that the precipitation of manganese occurs when the rate of redox cycle between the bromine and a substrate is slow due to the high concentration of water (water is well known to retard the reaction[5]) or decreased free radical carrier, bromine radical. In other words, if the concentration of substrate that can be easily oxidized is relatively low, the precipitation may occur through the oxidation of manganese to Mn^{4+}. The oxidation of manganese to Mn^{4+} and the oxidation of substrates may be competing processes because the blackening was not observed even in the oxidation using Co/Mn/Br catalyst with low Br/(Co+Mn) ratio when the oxygen conversion was less than about 60%.

The precipitation of manganese may be explained by the over-oxidation from Mn^{2+} or Mn^{3+} to Mn^{4+} rather than from the disproportionation of Mn^{3+} to Mn^{2+} and Mn^{4+} as suggested in the reference[28] if it can be agreed that the precipitation occurs only when the oxygen concentration is high and occurs mainly in the later part of the reaction. The manganese component may exist as soluble Mn^{2+} or Mn^{3+} and interchange *via* the well known redox cycle[3,5] in the beginning of the reaction (when there remains sufficient substrate to be oxidized). The manganese can be over-oxidized with oxygen-enriched gas only when the reaction rate is low due to the increased water concentration or low concentration of free radical carrier.

Therefore, the cerium, chromium or iron may increase the activity of the substrates, such as *p*-xylene, *p*-toluic acid or 4-carboxybenzaldehyde, in the later part of the reaction *via* a subtle interaction with the catalyst of Co/Mn/Br and decrease the precipitation of manganese. A fundamental study with EPR and UV-VIS etc. is necessary to clarify the precipitation or blackening in the oxidation of alkyl aromatics.

Conclusions

In the liquid phase oxidation of *p*-xylene with oxygen-enriched gas the manganese component can be precipitated probably *via* over-oxidation to Mn^{4+}. The precipitation seems to increase with oxygen concentration in reaction gas and occur mainly in the later part of oxidation. The oxidation activity decreases and the blackening and side reactions to carbon dioxide increase with the degree of precipitation. Precipitation can be decreased with the addition of metal ions such as cerium, chromium or iron.

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