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Anomalous Effect of the Concentration of Metal-salt Catalysts in the Liquid-phase Oxidation of *p*-Xylene and Toluene

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By studying the relation between the concentration and the oxidation activity of various metal catalysts, mostly naphthenates, oleates, linoleates, and caprates of manganese, cobalt, and nickel salts, as well as mixed catalysts of two kinds, it has been established that, in general, there is an anomalous effect of the catalyst concentration-namely, the catalytic activity disappears above a certain point in the concentration of the catalyst. The anomalous concentration effect of a catalyst is observed in the oxidation of toluene and *p*-xylene with all the catalysts, but chromium naphthenate is a lone exception in the oxidation of *p*-xylene. It has been shown that the anomalous effect is due to the association of the catalyst in the hydrocarbon solvent to be oxidised, and that the associated catalyst does not act to promote oxidation. The association is reversible, being dependent on the concentration of the catalyst, so the anomalous concentration effect of a catalyst disappears on dilution.

While numerous papers and reviews[1)] have been published on the liquid-phase oxidation of hydrocarbons in the presence of metal-salt catalysts, little is known of the relation between the concentration and the activity of metal-salt catalysts. George *et al.*[2)] and Kamiya[3)] have reported on the relation between the concentration of a catalyst and the progress of the reaction in the oxidation of tetralin and ethylbenzene. Shigeyasu *et al.*[4)] studied the oxidation of alkylbenzenes in a similar way. In the course of their study of the oxidation of *p*-xylene, Ohta *et al.* found a certain limit of concentration above which the catalytic activity is lost with catalysts of copper salts[5)] as well as with a mixed catalyst[6)] of the salt of manganese and cobalt. Brook *et al.*[7)] observed in the oxidation of lubricating oils, using salts of copper and iron as catalysts, that the oxidation rate reaches a maximum and then gradually falls upon an increase in the concentration of the catalysts. They attributed this phenomenon to the formation of an inactive micelle structure at higher concentrations of Cu and Fe salt catalysts.

Since then there has been, as far as we know, no paper treating the variation in catalytic activity with the variation in the concentration of metal-salt catalysts.

In view of the fact that the concentration of a catalyst has an unexpectedly large influence on the velocity of the liquid-phase oxidation of *p*-xylene and toluene in the presence of metal-salt catalysts, the present author has studied how the catalytic activity varies with the concentration of the catalyst, using such catalysts as Mn, Co, and Ni salts of naphthenic, oleic, linoleic, and capric acids, as well as mixed catalysts of two kinds of these salts. He has found that the catalytic activity diminishes above a certain limit of concentration of the catalyst, and is entirely lost at higher concentrations. In view of this rather peculiar phenomenon, which may be called an anomalous effect of the catalyst concentration, the author has determined the molecular weight of the catalysts at the critical concentration in the medium of the hydrocarbons to be oxidised, and has already published in Japanese all the essential results obtained in connection with the catalytic activity in oxidation. This paper is a brief summary dealing with the author's reports[8)-12)] on the anomalous effect of the

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1) Y. Kamiya, *Yukagaku (J. Japan Oil Chem. Soc.)*, **14**, 539 (1965); Y. Takegami, *Yuki Gosei Kagaku (J. Synth. Org. Chem. Japan)*, **21**, 858 (1963).

2) P. George and A. Robertson, *Trans. Faraday Soc.*, **42**, 217 (1946).

3) Y. Kamiya, *Can. J. Chem.*, **41**, 2029, 2034 (1963); **42**, 1027, 2424 (1964); *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 897 (1966).

4) M. Shigeyasu, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 1396 (1964); **68**, 304 (1965); **70**, 1150, 1155, 1259, 1375 (1967).

5) N. Ohta, *Tokyo Kogyo Shikensho Houkoku (Report of Government Chem. Ind. Research Institute, Tokyo)*, **51**, 215 (1965).

6) N. Ohta, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **63**, 768 (1960).

7) J. H. T. Brook, J. B. Matthews, *Discussions Faraday Soc.*, **10**, 298 (1951).

8) K. Kagami, *Yuki Gosei Kagaku (J. Synth. Org. Chem. Japan)*, **20**, 282 (1962).

9) K. Kagami, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 162 (1967).

10) K. Kagami, *ibid.*, **70**, 166 (1967).

11) K. Kagami, *ibid.*, **70**, 906 (1967).

12) K. Kagami, *ibid.*, **70**, 1683 (1967).

catalyst concentration (abbreviated as the AC-effect).

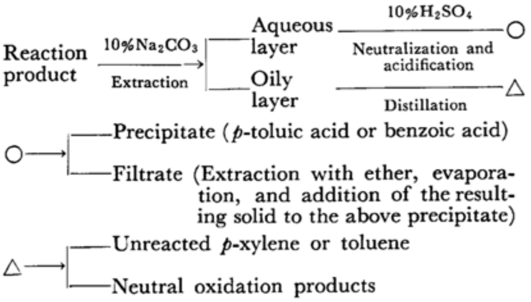
Experimental

The oxidation of *p*-xylene was carried out under the normal pressure of oxygen in a 200 m*l* flask. Temperature of oxidation: 136—137°C; quantity of *p*-xylene: 0.5 mol; duration of oxidation: 4 hr; rate of flow of oxygen: 6 *l*/hr; rate of stirring: 700—1000 rpm.

The oxidation of toluene was effected under compressed air in a 200 m*l* stainless-steel autoclave. Temperature of oxidation: 178±2°C; quantity of toluene: 0.7 mol; duration of oxidation: 4 hr; rate of flow of air: 30 *l*/hr; pressure of reaction: 10 atm; velocity of stirring: 800—1000 rpm.

The catalyst was prepared in the following way: the metal salt, obtained by double decomposition between the sodium salt of the organic acid and the metal nitrate, was washed and dried. The quantity of the metal in the catalyst was determined, and the concentration of the catalyst was expressed in terms of the metal gram atoms per mole of *p*-xylene or toluene times 10^5. For brevity, the metal-salt catalysts will be indicated by the following notations: metal-naphthenates: Me-N; metal-oleate: Me-O; metal-linoleate: Me-L; metal-caprate: Me-; metal-stearate: Me-S.

The separation and analysis of the reaction products was carried out as follows:



The molecular weights of the metal-salt catalysts in the reaction fluids were determined at 37°C in advance of the oxidation reaction in a VPO vessel, model 301, of the Mechrolab Co. by means of studying the vapor-pressure depression. For the preparation of corrected curves, benzil was used as the standard substance. Since the induction period in the oxidation of either *p*-xylene or toluene was nearly constant, irrespective of the concentration of the catalyst (except for the oxidation of *p*-xylene under the catalytic influence of Mn-L), the activated rates of oxidation were expressed in the following manner; the activation of oxidation effected by the metal-salt catalyst in the oxidation of *p*-xylene was estimated by the ratio (in wt%) of the *p*-toluic acid produced or of the sum of the *p*-toluic acid and the neutral oxidation products *vs*. the initial quantity of *p*-xylene measured after 4 hr oxidation.

The rate of oxidation was expressed by the rate of the formation of water, since the two rates were found to be in a nearly parallel relation with the same catalyst.

Similarly, the catalytic activity in the oxidation of toluene was expressed by the rate of the formation (in wt%) of benzoic acid or by the sum of benzoic acid and neutral oxidation products *vs*. the initial quantity of toluene, measured after 4 hr reaction. Furthermore, the rate of the absorption of oxygen in the oxidation of toluene was obtained by determining the quantities of oxygen and carbon dioxide in the waste gas.

Results and Discussion

Figure 1 shous how the catalytic activity in the oxidation of *p*-xylene is related to the concentration of various metal naphthenates (Mn, Co, Ni, Cr and Cu salts).

The AC-effect was observed in all cases except that of the Cr-N catalyst; the effect was particularly remarkable with the Mn-N and Cu-N catalysts. Besides, the AC-effect was observed in all the cases using the following metal-salt catalysts[8-10]: such singl catalysts as Mn-O, Co-O, Ni-O, Mn-L, Co-L, Ni-L, Mn-C, Co-C, Ni-C, and Mn-S, and such mixed catalysts as (Ni-N)+(Co-N), (Cr-N)+(Co-N), (Mn-N)+(Co-N), (Cu-N)+(Ni-N), (Mn-N)+(Ni-N), (Mn-N)+(Cu-N), (Cu-N)+(Co-N), (Cu-N)+(Cr-N), (Mn-O)+(Ni-O), (Mn-L)+(Ni-L), and (Mn-C)+(Ni-C). With the mixed catalysts, however, the AC-effect was observed at lower concentration than with single catalysts.

It has been reported[5,13] that, in liquid-phase oxidation, metal atom of higher valencies (*e. g.*, Mn^{3+}, Co^{3+}) exist in the active state of the metal-salt catalyst. In the oxidation of *p*-xylene with a Mn-N catalyst, the appearance of the reacting solution changed from the light pink color of Mn^{2+} to the dark brown of Mn^{3+} 10—15 min after the introduction of oxygen, as long as the catalyst concentration remaind within the limits, no AC-effect was exhibited, and soon afterwards oxidation set in. Similar color changes were observed, however, even when the oxidation reaction did not start readily in spite of the introduction of oxygen as a result of too high a catalyst concentration (Experiment on the Mn-N catalyst in a concentration of 100 in Fig. 1), but eventually the reaction took place (after 40—50 min). On the other hand, the author has established that the metal ion Mn^{2+} is oxidised to the Mn^{3+} state, even when oxidation does not occur, because of the AC-effect observed; he did this in an oxidation experiment with *p*-xylene and the Mn-N catalyst in a concentration of 100.

Figure 2 gives the relation between the concentration and the rate of oxidation by the Co-N catalyst.

In Fig. 3 is shown the rate of the oxidation of *p*-xylene carried out with a catalyst with a Mn-N concentration of 50 by adding a further quantity (conc. 25) of the Co-N catalyst after an oxidation period of 150 min.

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13) C. E. H. Bawn, A. A. Pennington, C. F. H. Tipper, *Discussions Faraday Soc.*, **10**, 282 (1951).

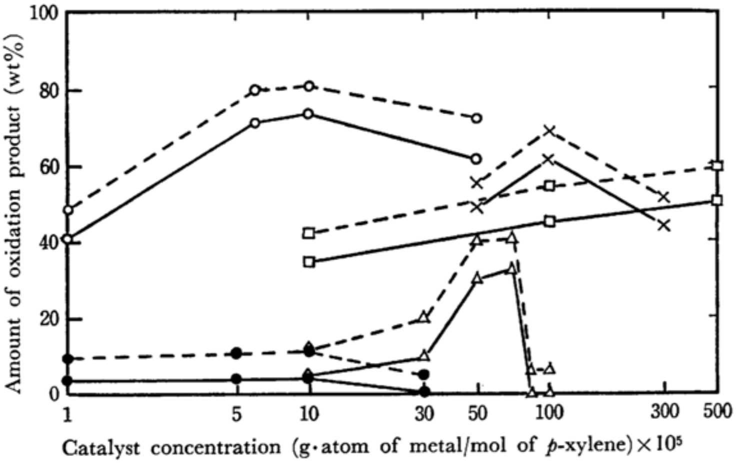


Fig. 1. Effect of concentration of metal-naphthenate catalyst in the oxidation of *p*-xylene. Amount of oxidation product: wt% of *p*-toluic acid and wt% of *p*-toluic acid and neutral product based on *p*-xylene used.

—— : *p*-Toluic acid formed
---- : *p*-Toluic acid + neutral product
○ : Co-naphthenate □ : Cr-naphthenate
△ : Mn-naphthenate ● : Cu-naphthenate
× : Ni-naphthenate

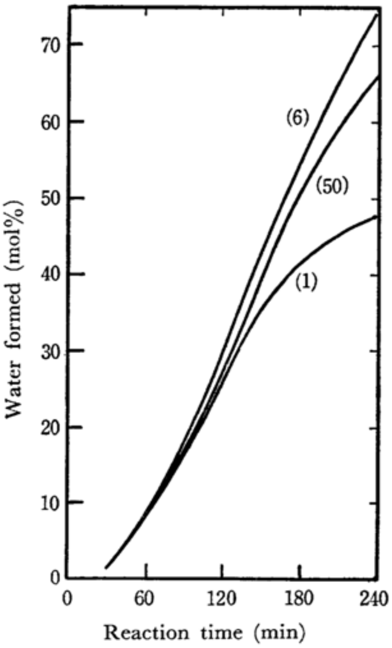


Fig. 2. Relation between rate of water formation and concentration of Co-naphthenate catalyst in the oxidation of *p*-xylene.

The arabic numerals show the concentration of Co-naphthenate [(g·atom of Co/mol of *p*-xylene)×10⁵] Water formed: mol% of water formed based upon *p*-xylene used.

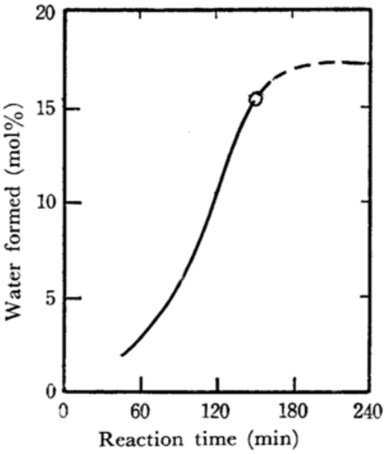


Fig. 3. Effect of the addition of Co-naphthenate to Mn-naphthenate catalyst in the course of oxidation.

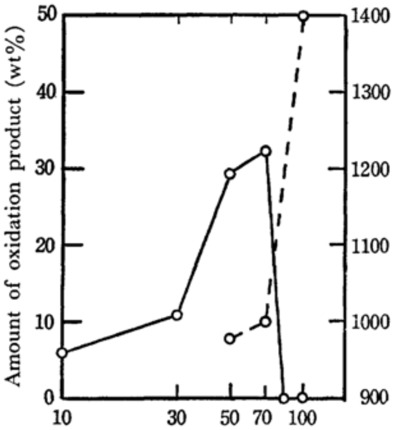
○: Co-naphthenate was added at this point.
——: Oxidation in the presence of Mn-naphthenate catalyst [50×10^{-5} g·atom of Mn/mol of *p*-xylene]
----: Oxidation in the presence of Mn-naphthenate [50×10^{-5} g·atom of Mn/mol of *p*-xylene] and Co-naphthenate [25×10^{-5} g·atom of Co/mol of *p*-xylene]

The oxidation of *p*-xylene was not initiated in 4 hr with an Mn-N catalyst in a concentration of 100, as in the case shown in Fig. 1. However, after 0.5 mol of *p*-xylene had been, added, when the concentration of Mn-N became 50 the reaction of oxidation started and proceeded smoothly, *p*-toluic acid and a neutral oxidation product were formed in quanitities of 23.2% and 4.2% respectively, and 65.2% of *p*-xylene was recovered.

The AC-effect appeared during the propagation period in the oxidation of *p*-xylene and was observed as a phenomenon reducing the rate of oxidation. However, when an intense AC-effect appeared, it was recognized as a phenomenon incapable of initiating oxidation.

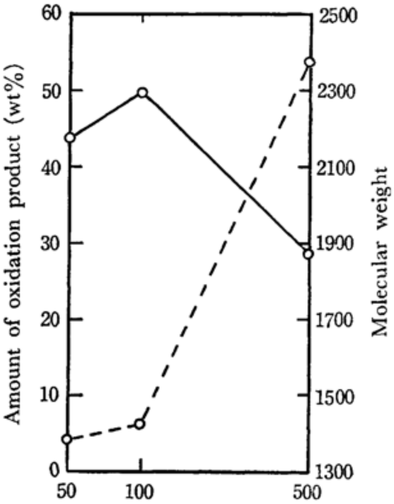
It was already observed that no reaction is initiated by too high a concentration of a catalyst in the oxidation of *p*-xylene using Cu salts⁵⁾ or a mixed catalyst⁶⁾ of Mn and Co salts. In view of similar phenomena occurring with a larger number of other catalysts, they may be regarded as quite general with metal-salt catalysts.

The AC-effect of a catalyst is not due to the poisoning phenomenon of the catalyst, but is a reversible phenomenon controlled by the catalyst concentration in the reaction system.



Catalyst concn. (g·atom of Mn/mol of *p*-xylene)×10⁵

Fig. 4. Relation between concentration of catalyst of Mn-naphthenate and oxidation activity and molecular weight.
Amount of oxidation product: wt% of *p*-toluic acid based on *p*-xylene used
——: *p*-Toluic acid formed
----: Molecular weight of Mn-naphthenate



Catalyst concn. (g·atom of Ni/mol of *p*-xylene)×10⁵

Fig. 5. Relation between concentration of catalyst of Ni-linoleate and oxidation activity and molecular weight.
Amount of oxidation product: wt% of *p*-toluic acid based on *p*-xylene used
——: *p*-Toluic acid formed
----: Molecular weight of Ni-linoleate

Figures 4 and 5 and Table 1 show the relation between the molecular weight of the metal-salt catalyst in *p*-xylene and its catalytic activity in the oxidation of *p*-xylene.

The molecular weight of the metal-salt catalyst rapidly increased in the region in which the catalytic activity rapidly decreased with an increase in the catalyst concentration, although in the region where the activity increased with an increase in the catalyst concentration the molecular weight

TABLE 1. RELATION BETWEEN CONCENTRATION OF SALT CATALYST AND ACTIVITY FOR OXIDATION OF *p*-XYLENE AND MOLECULAR WEIGHT

Catalyst	Catalyst concen.	30× 10^{-5}	50× 10^{-5}	70× 10^{-5}	75× 10^{-5}	100× 10^{-5}	200× 10^{-5}	300× 10^{-5}	500× 10^{-5}	700× 10^{-5}
Mn-C	activity		28.5		30.0	1.0	0			
	MW		700		600	1060				
Mn-L	activity	20.9	24.7	22.0		19.0	10.9			
	MW	870		940		1070	1540			
Mn-S	activity	15.3	31.0	23.8		0				
	MW	670	590	730		930				
Ni-N	activity					10.7	21.7	1.0	0	
	MW					390	380	1700	1800	
(Ni-N Co-N)	activity					56.4			12.1	
	MW*					420			1400	1600

Catalyst concn.: g of metal/mol of *p*-xylene
Activity: wt% of *p*-toluic acid based on *p*-xylene used
MW: Molecular weight of metal salt catalyst
*: Quantity determined by a cryoscopic method

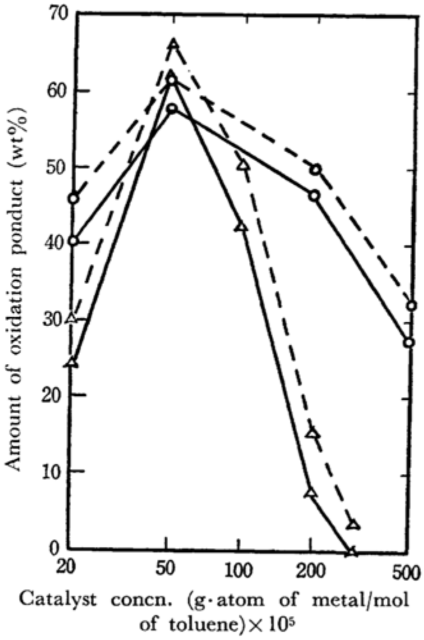


Fig. 6. Effect of concentration of Co-linoleate and Mn-caprate catalyst in the oxidation of toluene.

Amount of oxidation products: wt% of benzoic acid and wt% of benzonic acid and neutral product based on toluene used

——: Benzoic acid
----: Benzoic acid+neutral product
○: Co-linoleate
△: Mn-caprate

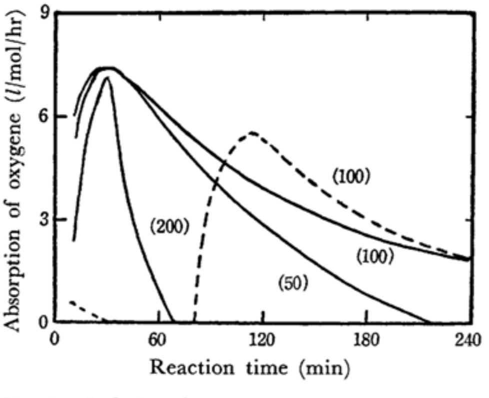


Fig. 7. Relation between concentration of Mn-caprate catalyst and absorption velocity of oxygen in the oxidation of toluene.

Arabic numerals show concentration of the catalyst [(g·atom of Mn/mol of toluene)×10^5]

----: Absorption rate of oxygene in the oxidation of the solution which was obtained by diluting the reaction mixture with toluene to the concentration of 100 after the oxidation had been carried out for 120 min at the Mn salt concentration of 200.

of the metal-salt catalyst increased only slightly with an increase in the concentration.

Figure 6 shows the relation between the concentration of the Co-L and Mn-O catalysts and the catalytic activity in the oxidation of toluene. Furthermore,$^{11)}$ in the oxidation of toluene with single catalysts, such as Co-N, Mn-N, Ni-N, Cu-N, Cr-N, Co-O, Mn-L, Mn-C, and Co-C, or with mixed catalysts, such as (Co-N)+(Mn-N), (Co-N)+(Ni-N), (Mn-N)+(Ni-N), (Co-O)+(Mn-O), (Co-O)+(Ni-O), (Mn-O)+(Ni-O), (Mn-L)+(Co-L), and (Mn-C)+(Co-C), the relation between the activity and the concentration of the catalyst was studied; the AC-effect was observed without exception with single as well as with mixed catalysts.

Figure 7 shows the absorption of oxygen during the oxidation reaction of toluene in the presence of Mn-C in concentrations 50, 100, and 200; the dotted line represents the progress of the absorption of oxygen when the catalysts present in a concentration of 200—though this concentration was reduced to 100 by adding toluene after 120 min reaction. Furthermore,$^{10)}$ a similar tendency was recognized also in the cases of Mn-L and Mn-O.

It was observed$^{14)}$ with the oxidation of toluene that oxidation rapidly terminated when the catalyst concentration was too small. However, the reaction also terminates at higher concentrations of catalyst above a certain limit (Fig. 7); furthermore,

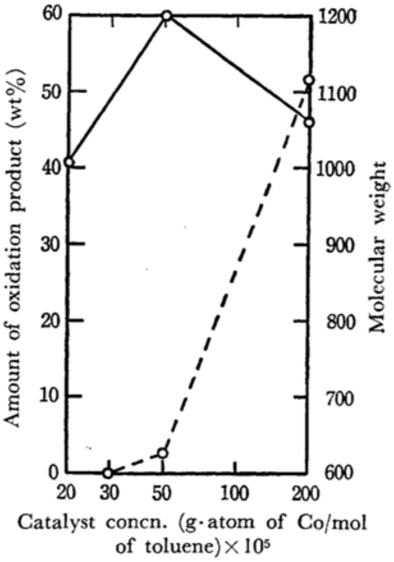


Fig. 8. Relation between concentration of catalyst of Co-linoleate and oxidation activity and molecular weight.

Amount of oxidation product: wt% of benzoic acid based on toluene used

——: Benzoic acid formed
----: Molecular weight of Co-linoleate

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14) N. Ohta and T. Tezuka, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **59**, 71 (1956).

at a much higher concentration oxidation is not even initiated (Fig. 6). These two new phenomena have led to the discovery of the AC-effect.

Figure 8 exhibits the relation between the catalytic activity and the molecular weight of the Co-L catalyst in toluene; the AC-effect appears at the point of rapidly-increasing molecular weight. A similar phenomenon occurred with the Mn-O(12) catalyst.

The experiments described above suggest that metal-salt catalysts for the oxidation of *p*-xylene and toluene associate in the region where the AC-effect is observed, and that the associated catalyst plays no part in promoing the oxidation.

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