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Combined promotional effect of CO_2 and Ni on Co/Mn/Br catalyst in the liquid-phase oxidation of *p*-xylene

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The promotional effects of CO_2 and Ni were studied on Co/Mn/Br catalyst in the liquid-phase oxidation of *p*-xylene to terephthalic acid using molecular oxygen as an oxidant and acetic acid as a solvent individually as well as in combination. The enhanced activity of Co/Mn/Br catalyst was observed on both CO_2 and Ni promoters independently and also in combination. The activity enhancement in the combination of CO_2 and Ni promoters on this catalyst is found to be remarkable.

KEY WORDS: oxidation of *p*-xylene; promotional effect of CO_2 and Ni; Co/Mn/Br catalyst.

1. Introduction

The oxidation of *p*-xylene to terephthalic acid is the centerpiece of the commercial production of fiber material [1–8]. Cobalt-based catalysts are the best catalysts for this reaction with compatible promoters [9–13]. Manganese and bromide promoters on a cobalt catalyst enhanced the activity by 16 times and long induction periods were eliminated [11,14]. Additives such as methyl ethyl ketones and bromide were used to promote *p*-xylene oxidation to terephthalic acid by maintaining the high concentration of Co(III) species [9,15–17]. It is reported that the rate of the cobalt-acetate-catalyzed oxidation of *p*-xylene to terephthalic acid was enhanced dramatically by small amounts of Zr(IV) and Hf(IV) acetates and also that the Zr(IV) or Hf(IV) redistribute the dimer–monomer equilibrium of cobalt acetate by forming a weak complex with active monomeric Co(III) species [9,18]. Besides metallic promoters, it has been recently reported that CO_2 also promotes the oxidation of alkyl aromatics [19,20]. Although the major data in the previous study showed that carbon dioxide enhanced the oxidation rate somewhat in terms of oxygen consumption, some data, especially in the case of *p*-xylene oxidation, failed to convince one of the improvement of product formation in terms of yields. Here, we present more clear evidence of CO_2 promotion with a possible explanation. In addition, we report that the double promotion of CO_2 and Ni on Co/Mn/Br catalyst gives an exceptionally good catalytic system for the liquid-phase oxidation of *p*-xylene in an acetic acid medium.

2. Experimental

The mixture of a substrate and acetic acid was taken in a 150 ml Teflon-lined reactor. Cobalt bromide and manganese acetate tetrahydrate were added to prepare the Co/Mn/Br catalytic system and, in some cases, nickel acetate tetrahydrate was added as an additive component. The reactor was pressurized either with CO_2 or with N_2 and the temperature was raised to its optimum level; the optimum pressure was balanced by N_2. The O_2 was admitted from the oxygen chamber to the reactor. During the reaction, oxygen was supplied as necessary by maintaining the total pressure using a pressure regulator. The O_2 consumption was measured with the help of a pressure transducer connected to the oxygen chamber. After completion of the reaction, the autoclave was cooled to room temperature and the resultant reaction mixture was transferred into a beaker and cooled further to solidify the acid products. The solid and liquid products were separated by filtration. The solid products (carboxylic acids) were esterified and analyzed as methyl esters as follows: 0.5 g of solid product was taken in an RB flask and 20 g of 5% sulfuric acid added in methanol and refluxed for 1 h. 1 ml of esterified product, 1 ml of deionized water and 1 ml of dichloromethane were mixed and the lower layer was analyzed, along with liquid products by GC (Donam Instruments, Model DS6200) using a DB-1 capillary column ($30\,m \times 0.32\,mm \times 0.25\,\mu m$) and a flame ionization detector. The products were identified by GC/MS. The total conversion and yields of the products were calculated on the basis of weight response factors. Terephthalic and *p*-toluic acids are the main products and *p*-tolualdehyde, terephthaldehyde, *p*-methyl benzyl acetate and toluyl alcohol are the minor products.

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$CoBr_2$ (0.54 mmol)/$Mn(OAc)_2{\cdot}4H_2O$ (0.65 mmol)/*p*-xylene (48.6 mmol)/AcOH (420.6 mmol) was exposed to reaction conditions with or without CO_2 for ESR analysis. ESR measurements were conducted on a Bruker ESR (EMX model) at 77 K using DPPH as a *g*-marker.

3. Results and discussion

The effect of CO_2 in the liquid-phase oxidation of alkylaromatics over Co/Mn/Br catalyst is shown in table 1. The reaction with *p*-xylene as a substrate indicates that the yields of acids are considerably increased in the presence of CO_2. The study has been extended to other aromatic hydrocarbons such as toluene and *p*-toluic acid. The promotional effect of CO_2 on toluene is shown in figure 1. In each time interval the conversions are higher with CO_2, and in the case of the 3 h run the yield of benzoic acid is about 80% in the presence of CO_2 whereas in the absence of CO_2 it is about 60%. The yield enhancement by the CO_2 addition is about 20%. Further investigation of the CO_2 promotional effect has been made on *p*-toluic acid and it was found that the yield of terephthalic acid is 65% with CO_2 but it is only 58% without CO_2. The catalytic activity in the oxidation of toluene and *p*-toluic acid followed a similar trend to *p*-xylene.

To understand the role of CO_2, a reaction was carried out on $Co(OAc)_2$ and $Mn(OAc)_2$ in the presence or in the absence of CO_2 under the specified reaction conditions. As a result, it was found that there was no reaction, which implies that CO_2 cannot substitute the Br^- promoter. Also, another reaction was carried out only with CO_2 (without O_2) and it was found that there was no reaction, which indicates that CO_2 is not acting as an oxidant. Under the reaction conditions no induction period was observed either with or without CO_2, but at the beginning of *p*-toluic acid oxidation to terephthalic acid (the second step in the oxidation of *p*-xylene) there was a short induction period in the absence of CO_2, whereas in the presence of CO_2 there was no induction period. A possible explanation for the CO_2 promotional effect has been drawn from the ESR study. The ESR spectra recorded under similar experimental conditions with and without CO_2 enable us to understand the catalytic behavior of Co/Mn/Br in the oxidation of *p*-xylene. In the CO_2-containing catalytic system the manganese hyperfine pattern was well resolved (g1 = 2.1688, ΔHpp = 21G, g2 = 2.1193, ΔHpp = 60G, g3 = 2.0621, ΔHpp = 60G, g4 = 2.0010, ΔHpp = 78G, g5 = 1.9390, ΔHpp = 80G, g6 = 1.8727, ΔHpp = 109G) (figure 2), whereas without CO_2 the pattern was partially resolved. The detailed study of Ratnasamy and coworkers [21] on cobalt and manganese cluster complexes in the oxidation of *p*-xylene revealed the promotional effect of Zr(IV). In their ESR study, they observed a well-resolved manganese hyperfine pattern in the presence of Zr(IV) promoter on Co/Mn/Br catalyst and also reported that the presence of Zr(IV) enhanced the rate of oxidation of Co(II) to Co(III) and subsequently Mn(II) to Mn(III) which is

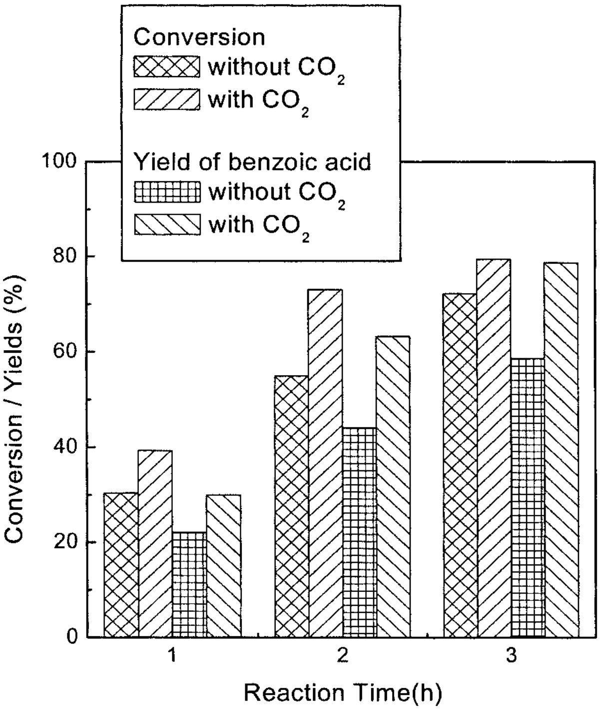

Figure 1. Effect of CO_2 in the liquid-phase oxidation of toluene with Co/Mn/Br catalyst. Conditions: toluene = 48.6 mmol, acetic acid = 420.6 mmol, Co = 0.54 mmol, Mn = 0.65 mmol, Br = 1.08 mmol, $P_{total} = 12$ atm ($P_{CO_2} = 0$ or 4, $P_{O_2} = 2$, P_{N_2} = balance), temperature = 150 °C.

Table 1

Effect of CO_2 in the liquid-phase oxidation of alkylaromatics with Co/Mn/Br catalyst

Substrate	P_{CO_2} (atm)	Temperature (°C)	Time (h)	Yield (mol %)
p-Xylene	4	170	3.0	TPA (34.8), *p*-TA (36.9), TPAL (2.4), *p*-TAL (1.7), others (24.2)
p-Xylene	0	170	3.0	TPA (17.7), *p*-TA (47.9), TPAL (1.7), *p*-TAL (2.8), others (29.2)
p-TA	4	190	3.0	TPA (64.9), others (10.6)
p-TA	0	190	3.0	TPA (58.1), others (3.7)
Toluene	4	150	3.0	BA (78.7), others (0.7)
Toluene	0	150	3.0	BA (58.6), others (13.7)

Note: Conditions: substrate = 48.6 mmol, acetic acid = 420.6 mmol, Co = 0.54 mmol, Mn = 0.65 mmol, Br = 1.08 mmol, $P_{total} = 12$ atm ($P_{O_2} = 2$ atm, P_{N_2} = balance). Abbreviations: TPA, terephthalic acid; *p*-TA, *p*-toluic acid; TPAL, terephthaldehyde; *p*-TAL, *p*-tolualdehyde; BA, benzoic acid.

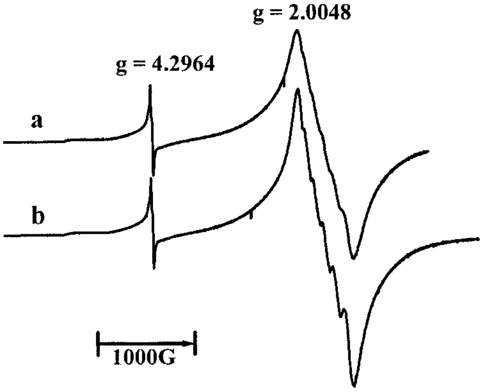

Figure 2. ESR spectra of $CoBr_2/Mn(OAc)_2{\cdot}4H_2O$/*p*-xylene/AcOH. (a) in the absence of CO_2 and (b) in the presence of CO_2.

due to the formation of cluster complexes. Mn(III) generates the bromide radical by taking the electron from the bromide ion. The bromide radical abstracts the hydrogen atom from the hydrocarbon and propagates the reaction [21]. The ESR results in the present work suggest that CO_2 plays a similar role to Zr(IV) in the oxidation system. In other words, CO_2 as a promoter enhances the activity of Co/Mn/Br catalyst by accelerating the oxidation of Co(II) to Co(III) and subsequently Mn(II) to Mn(III) during the reaction.

The combined promotional effect of CO_2 and Ni over Co/Mn/Br catalyst in the liquid-phase oxidation of *p*-xylene can be seen from tables 2 and 3 and figure 3. The activity of the catalyst was measured in terms of O_2 consumption as a function of time (i) without any promoter, (ii) with Ni promoter, (iii) with CO_2 promoter, (iv) with both Ni and CO_2 promoters (figure 3). The individual promotional effects of CO_2 and Ni are confirmed. Furthermore, in the presence of both Ni and CO_2 the catalytic activity is found to be remarkably enhanced. The O_2 consumption, in the case of a dual-promoted system with CO_2 and Ni, reached its maximum limit within 1 h and then it was stopped. However, without either CO_2 or Ni, the reaction time was very delayed to the same oxygen consumption under the specified reaction conditions.

Table 2 shows the promotional effects of CO_2 and Ni in terms of product yields on Co/Mn/Br catalyst in the oxidation of *p*-xylene at 170 °C for 3 h. The conversion of *p*-xylene was almost 100% in all the experiments, but the conversion of *p*-toluic acid to terephthalic acid was minimum in the absence of additives to the Co/Mn/Br catalyst. The yield of terephthalic acid increased from 17% to 25%, 35% and 56% by the addition of Ni, CO_2 and Ni + CO_2, respectively. The promotional effects of CO_2 and Ni at 190 °C can be seen from table 3. The yield of terephthalic acid was increased more than three times in the presence of both CO_2 and Ni. It is noteworthy that each promotional effect was also remarkable. The total yield of acids at 190 °C and 20 atm (table 3) was almost same (~80–85%) in all the experiments but the time taken to reach similar conversions was varied. The combination of CO_2 and Ni with the Co/Mn/Br catalytic system promoted the reaction to complete in a short period of time (1 h) whereas in the absence of promoters the period of reaction was more than 2 h. The reaction rate with both promoters was twice as fast as that without a promoter. The conversion of *p*-xylene at 170 °C was almost 100% (table 2) but at 190 °C it was 94–96%, whereas the conversion of *p*-toluic acid (major intermediate product) was higher at higher temperature. The reason for the small variation in the *p*-xylene conversion with temperature (tables 2 and 3) may be due to the competition among the reaction intermediates and reactant at higher temperature (190 °C). The origin of the promoting effect is not clearly defined. However, the CO_2 promotional effect seems to be due to the enhanced rate of formation of cluster complexes between cobalt and manganese salts in acetic acid during *p*-xylene oxidation in the presence of CO_2 similar to Zr(IV) promoter [21], and consequently the enhanced rates of oxidation of Co(II) to Co(III) and Mn(II) to Mn(III). Metal peroxocarbonate formation is possibly the key function for the CO_2 promotional effect in the oxidation of *p*-xylene [19]. Aresta *et al.* [22,23] synthesized the Rh and Ni peroxocarbonates using O_2 and CO_2 and also studied the detailed mechanism of peroxocarbonate formation and its use as a styrene oxidation catalyst. Similarly, we expect the formation of peroxocarbonates in this *p*-xylene oxidation. The peroxocarbonate would play a role in oxidizing Co(II) to give Co(III). The enhanced rate of Co(II)

Table 2
Promotional effects of CO_2 and Ni on Co/Mn/Br catalyst in the oxidation of *p*-xylene at 170 °C

Additive	Conversion (mole %)	Yield (mole %)				
		p-TA	TPA	*p*-TAL	TPAL	Others
–	99.22	47.94	17.67	2.79	1.68	29.14
Ni	99.96	36.88	25.23	2.52	2.45	32.88
CO_2	99.93	36.85	34.84	1.65	2.40	24.19
Ni + CO_2	99.97	31.17	56.19	1.09	2.52	9.00

Note: *p*-Xylene = 48.6 mmol, acetic acid = 420.6 mmol, Co = 0.54 mmol, Mn = 0.65 mmol, Br = 1.08 mmol, Ni = 0.084 mmol. Reaction time = 3 h, $P_{\text{total}} = 12$ atm ($P_{O_2} = 2$, $P_{CO_2} = 2$, P_{N_2} = balance).

Table 3
Promotional effects of CO_2 and Ni on Co/Mn/Br catalyst in the oxidation of *p*-xylene at 190 °C

Additive	Time (h)	Conversion (mole %)	Yield (mole %)				
			p-TA	TPA	*p*-TAL	TPAL	Others
–	2.16	96.23	3.80	82.66	0.08	0.63	6.90
Ni	2.00	97.20	4.26	74.88	0.17	1.02	14.87
CO_2	1.92	94.56	0.00	85.37	0.00	0.25	7.02
Ni + CO_2	1.00	94.04	0.75	86.29	0.00	0.05	5.95

Note: *p*-Xylene = 48.6 mmol, acetic acid = 420.6 mmol, Co = 0.54 mmol, Mn = 0.65 mmol, Br = 1.08 mmol, Ni = 0.084 mmol, $P_{total} = 20$ atm ($P_{O_2} = 5$, $P_{CO_2} = 6$, P_{N_2} = balance).

oxidation would induce the other steps of the cycle sequentially. It has been proposed that the first step in the oxidation of *p*-xylene is the formation of *p*-toluyl alcohol, which is due to the transformation of an oxygen atom from the metal peroxocarbonate and then abstraction of two hydrogen atoms from the toluyl alcohol to form *p*-tolualdehyde, which on further oxidation with O_2 forms *p*-toluic acid intermediate [19]. Terephthalic acid formation takes place from *p*-toluic acid by repeating similar mechanistic steps. The promotional effect of Ni on the Co/Mn/Br catalytic system can be explained in terms of the increase in the active species concentration. It is known that nickel ion can replace cobalt ion though its activity is lower [11]. A possible explanation for the synergistic effect with CO_2 (see table 2) is that CO_2 enhances the oxidation of Ni(II) more than that of Co(II). However, at present, the mechanistic aspects of the synergistic effect are not clearly understood, so additional studies are required to explain this observation.

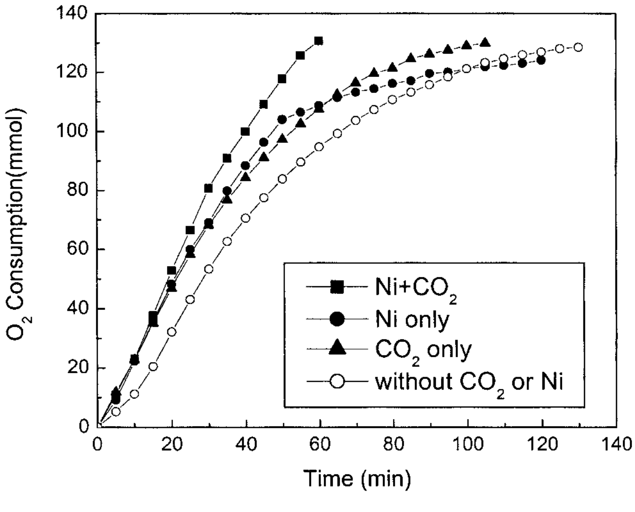

Figure 3. Effect of CO_2 and Ni on Co/Mn/Br catalyst on O_2 consumption as a function of time. Conditions: *p*-xylene = 48.6 mmol, acetic acid = 420.6 mmol, Co = 0.54 mmol, Mn = 0.65 mmol, Br = 1.08 mmol, Ni = 0.084 mmol, $P_{total} = 20$ atm ($P_{CO_2} = 6$ atm, $P_{O_2} = 5$ atm, P_{N_2} = balance), temperature = 190 °C.

4. Conclusions

In conclusion, CO_2 as a promoter enhanced the activity of the Co/Mn/Br catalyst in the oxidation of alkylaromatics, which is a result of accelerating the rate of oxidation of Co(II) to Co(III) and subsequently Mn(II) to Mn(III) during the reaction. The use of dual promoters of CO_2 and Ni on the Co/Mn/Br catalytic sytem in the liquid-phase oxidation of *p*-xylene gives remarkable increases in the conversion of *p*-xylene and the yields of desired acids (terephthalic and *p*-toluic acid) and shows a synergistic effect.

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