Liquid phase oxidation of *p*-xylene to terephthalic acid at medium-high temperatures: multiple benefits of CO₂-expanded liquids

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The Co/Mn/Br catalyzed oxidation of *p*-xylene to terephthalic acid (TPA) is demonstrated in CO₂-expanded solvents at temperatures lower than those of the traditional Mid-Century (MC) process. As compared with the traditional air (N_2/O_2) oxidation system, the reaction with CO_2/O_2 mixture at 160 °C and using an additional inert gas (N_2 or CO_2) pressure of 100 bar increases both the yield of TPA and the purity of solid TPA *via* a more efficient conversion of the intermediates, 4-carboxybenzaldehyde and *p*-toluic acid. At the same time, the amount of yellow colored by-products in the solid TPA product is also lessened, as determined by spectroscopic analysis. Equally important, the decomposition or burning of the solvent, acetic acid, monitored in terms of the yield of the gaseous products, CO and CO_2, is reduced by *ca*. 20% based on labeled CO_2 experiments. These findings broaden the versatility of this new class of reaction media in homogeneous catalytic oxidations by maximizing the utilization of feedstock carbon for desired products while simultaneously reducing carbon emissions.

1. Introduction

The Mid-Century (MC) process is well known for the production of terephthalic acid (TPA), a very important intermediate in the synthesis of polyethylene terephthalate and related polymers that can be fabricated into excellent fibers, resins and films.[1,2] In this process, *p*-xylene is oxidized on a large scale by air at 180–225 °C and 15–30 bar in the presence of a catalyst composed of cobalt acetate, manganese acetate and hydrogen bromide. The optimized yield of TPA is greater than 95%, along with excellent product purity as shown by various analytical techniques.[3] This process, despite successful on-stream operation for over 50 years, has the following distinct disadvantages. (1) High temperature operation decreases the solubility of O_2, while increasing solvent and product destruction and causing safety concerns. (2) Air is used as the primary oxidant instead of pure O_2 for safety reasons. This produces large amounts of contaminated vent gas and the abundant unreacted N_2 must be cleansed before venting into the environment. (3) The combination of corrosive bromide as a catalyst component and a high operating temperature requires the use of highly resistant but expensive titanium reactors. A recent breakthrough made by Poliakoff *et al.*,[4] Savage *et al.*[5] and Fulton *et al.*[6] has shown that this reaction can be effectively catalyzed by $MnBr_2$ with pure O_2 in a new reaction medium—high temperature and supercritical water, thus circumventing the use of acetic acid. However, the scope of such reaction systems is

limited by the even harsher reaction conditions ($T = 300$–400 °C, $P > 200$ bar).

CO_2-based media have attracted much attention in recent years because they provide the possibility of using pure O_2 under safe conditions while overcoming most of the aforementioned limitations of air oxidation systems, as follows.[7-10] (1) The use of CO_2 in a mixed solvent increases both the O_2 solubility and the mass transport of the reactants in the liquid phase, the former because of the significant solubility of O_2 in liquid CO_2 and the latter because of improved diffusivities in CO_2 media.[11] This is especially the case in carbon dioxide expanded liquids (CXLs). A rule of thumb is the nearly ten fold increase in oxygen solubility when the volume of solvent is expanded by a factor of two, depending on the properties of solvent. (2) The presence of CO_2 in the vapor phase reduces flammability hazards because of the great abundance of inert CO_2 and its large heat capacity. (3) Replacing the N_2 from air with a much greater amount of CO_2 eliminates the contaminated vent gas because the CO_2 is more easily separated and recycled in the oxidation process. However, this is counterbalanced by the required separation of O_2 from N_2.

The first successful application of CXLs in oxidation reactions was reported in 2002.[12,13] The Co(salen) catalyzed oxidation of 2,6-di-*tert*-butyl phenol to 2,6-di-*tert*-butyl-1,4-benzoquinone in CO_2-expanded acetonitrile was 1–2 orders of magnitude more active than in either the neat organic solvent or supercritical CO_2. We recently described the synergistic effect of co-catalyst zirconium and promoter ketone in the oxidation of toluene from 50 to 100 °C.[14] It was found that CO_2 has a strong activation effect on the reaction, especially by shortening the induction period. Under certain conditions, the Co/Zr(acac)₄ catalyzed oxidation did not work at all with N_2/O_2 but proceeded effectively with CO_2/O_2, affording high yields of benzoic acid. In

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this work, we extend the CO_2 effect to this important industrial TPA process, which is extremely challenging because of much higher temperatures and the complexity of intermediates. More specifically, the TPA precipitates during the reaction, occluding with it 4-carboxybenzaldehyde and other by-products. In addition, the decomposition, or burning of solvent, is more significant at higher temperatures. To this end, in the present work, we first measured the expansion of acetic acid, containing dissolved catalysts and substrate, by dense CO_2. Then, based on these results, we investigated the semi-continuous oxidation of *p*-xylene at lower temperatures as compared with the MC process for a more significant CO_2 effect, with the expectation that CXLs could bring about some specific advantages for product selectivity and purity in this complex reaction system.

2. Experimental

2.1 Materials

All the catalysts, additives, substrates and solvents were commercially available and used without further treatment. Industrial grade ($\geq$ 99.9% purity, < 32 ppm H_2O, < 20 ppm THC) liquid CO_2 and ultra high purity grade oxygen were purchased from Linweld. Isotopic gas $^{13}CO_2$ (99.5 atom% ^{13}C) was purchased from Aldrich Chemical Co., Inc.

2.2 Volumetric expansion of acetic acid + catalyst mixtures by dense CO_2

The volumetric expansion by CO_2 of acetic acid containing dissolved catalysts was measured in a high-pressure Jerguson view cell that was placed in a high temperature oven (Yamato DKN-400, part of a Cambridge Viscosity ViscoPro 2000 system, Fig. 1). For these expansion studies, a measured volume of acetic acid containing a known amount of catalysts was loaded into the view cell and heated to the experimental temperature, which was followed by the addition of 20 bar N_2 as the substitute for O_2. Then CO_2 was gradually introduced into the cell until an expansion ratio ($\Delta V / V_o$, eqn 1) of *ca.* 1.0 was obtained.

$$\frac{\Delta V}{V_o} = \frac{V(P) - V_o(P_o)}{V_o(P_o)} \qquad (1)$$

where P_o refers to ambient pressure from which the solution is expanded; and P refers to cell pressure at CO_2 expansion conditions.

2.3 Oxidation experiments and product analysis

2.3.1 Oxidation experiments. The semi-continuous oxidation of *p*-xylene to terephthalic acid was studied in a 50 mL, stirred, titanium Parr reactor (Fig. 2). Typically, N_2 or CO_2 was first added to the reactor containing the solvent and catalysts and heated to the reaction temperature; then O_2 was added until the selected final pressure was reached. *p*-Xylene was subsequently pumped into the reactor at a pre-defined rate (0.08 mL/min) to initiate the reaction. The total reactor pressure was maintained constant by continuously supplying fresh O_2 to compensate for the oxygen consumed in the reaction.

Fig. 1 Jerguson cell in oven for high temperature studies of CXLs.

2.3.2 Product analysis. After the reaction, the reaction mixture was cooled to room temperature and then treated as follows:

The gas mixture was analyzed by GC (Shin Carbon ST 100/120 mesh) to determine the yield of CO and CO_2 produced by solvent burning. For isotopic experiments, the $^{12}CO_2/^{13}CO_2$ ratio was measured by mass spectrometry.

The insoluble terephthalic acid was separated from the liquid mixture by filtration and the solid was washed with methanol to remove most of the soluble impurities. The resulting white solid was dried at 100 °C for 2 hrs to remove absorbed solvent, after which a 10 mg sample was dissolved in 50 mL of methanol by sonication and analyzed by HPLC (C18 ODS-2 column). The reactor was washed with methanol and DMF to scavenge the residual TPA solid, which was combined with the filtrate that was retained after isolation of the solid TPA and analyzed by HPLC to determine the composition of liquids. The yields of products were based on the sums of those determined for the solid and liquid components.

The presence of yellow colored by-products in solid TPA was determined from optical density measurements using a UV-Vis spectrometer at 340 nm.[15] Typically, 0.3 g solid sample was dissolved in 5 mL 4N NH_4OH. The optical density was calculated as in eqn 2:

$$OD_\lambda = A_\lambda / L \qquad (2)$$

where A_λ refers to the absorbance at wavelength λ (nm); and L refers to the distance (cm) that light travels through the sample.

2.4 Safety

The amount of substrate used in the reaction studies was such that the maximum adiabatic temperature rise for total
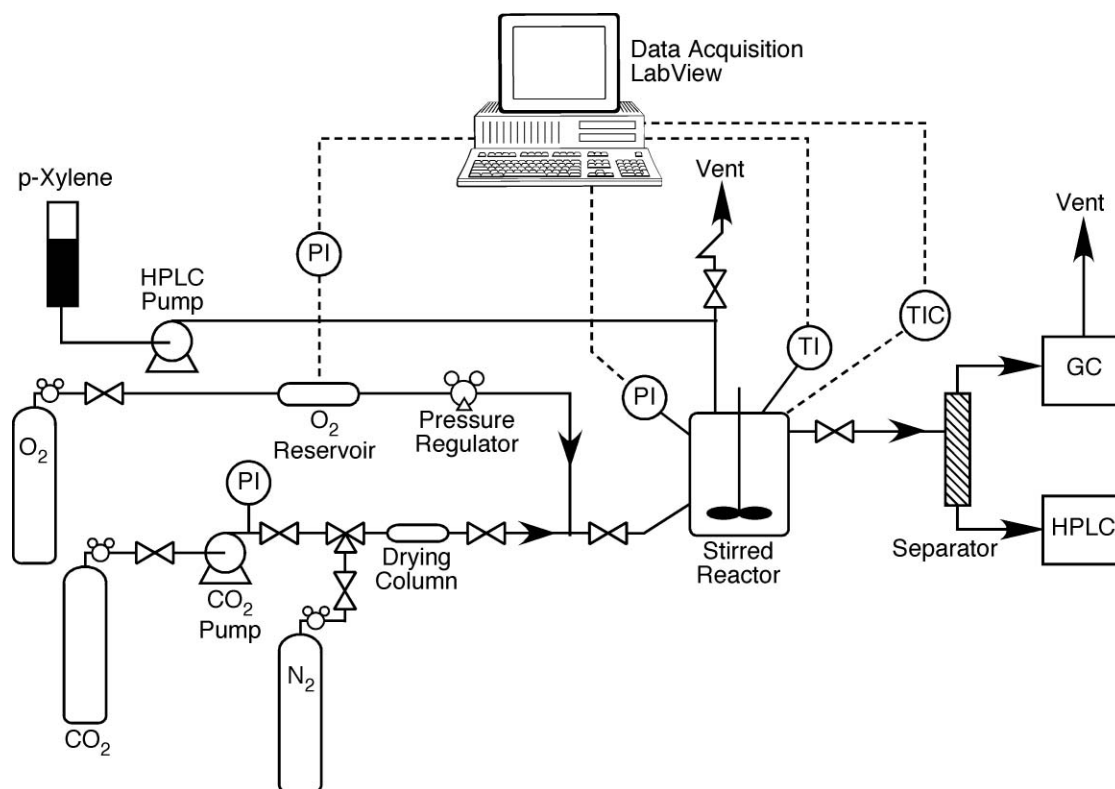
Fig. 2 Schematic diagram of semi-continuous oxidation *p*-xylene to terephthalic acid.

combustion of the substrate (taking into account the heat capacities of the reaction mixture and the solid reactor) was 25 °C. The actual temperature rise observed during reactions was a few °C, at most. In addition, the reactor was equipped with a safety release valve that exhausts the reactor contents safely to the building vent by means of a rupture disk in the event the set safe pressure (200 bar) is exceeded.

3.   Results and discussion

3.1 CO_2 expansion measurements at 80 and 120 °C

Since supercritical CO_2 ($T_C = 31$ °C) expands liquids most effectively at temperatures up to 1.2 times the absolute critical temperature, our previous work was focused on reactions performed at 60 °C or less wherein it was possible to measure the solvent expansion in a water bath.[12,16,17] Here, to measure the catalyst solubility in CO_2-expanded solvent at much higher temperatures, in experiments that are the first of their kind for *p*-xylene oxidation, we placed the high pressure Jerguson view cell in a high temperature oven that was originally designed for viscosity measurement (Fig. 1). Though the oven temperature can be maintained as high as 200 °C, these studies did not go beyond 120 °C because of the corroding capability of acetic acid and hydrogen bromide toward the stainless steel Jerguson cell.

The catalyst solution, containing 60 mM cobalt acetate, 1.8 mM manganese acetate and 60 mM hydrogen bromide in acetic acid, has a slight pink tint at room temperature (Fig. 3a) which turns blue when heated to 120 °C (Fig. 3b). The solution
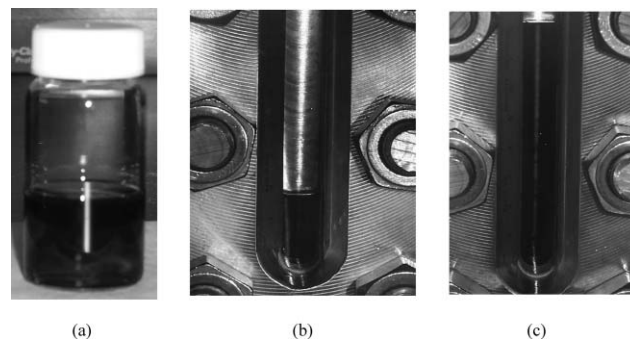

Fig. 3 Catalyst solution and its expansion with increasing CO_2 pressure. (a) room temperature, (b) 120 °C with 20 bar N_2 and 18 bar CO_2, (c) 120 °C with 20 bar N_2 and 159 bar CO_2; [Co] = 60 mM, [Mn] = 1.8 mM, [Br] = 60 mM prior to the expansion.

is expanded significantly at the much higher CO_2 pressure of *ca.* 160 bar (Fig. 3c).

Fig. 4a shows the dependence of the expansion ratio on CO_2 pressure at 120 °C. The expansion ratio increases gradually and reaches a value of 0.85 when CO_2 partial pressure is elevated to 160 bar (total pressure 180 bar). Accordingly, the concentrations of cobalt, manganese and bromide are diluted to 33 mM, 1.0 mM and 33 mM, respectively. It is noteworthy that no catalyst precipitates during the CO_2 expansion. This implies the possibility of replacing up to at least 50 vol% of the organic solvent by CO_2 while maintaining the catalyst in solution.

Fig. 4b shows the expansion result at 80 °C. As compared with 120 °C, the expansion ratio at 80 °C is much higher,
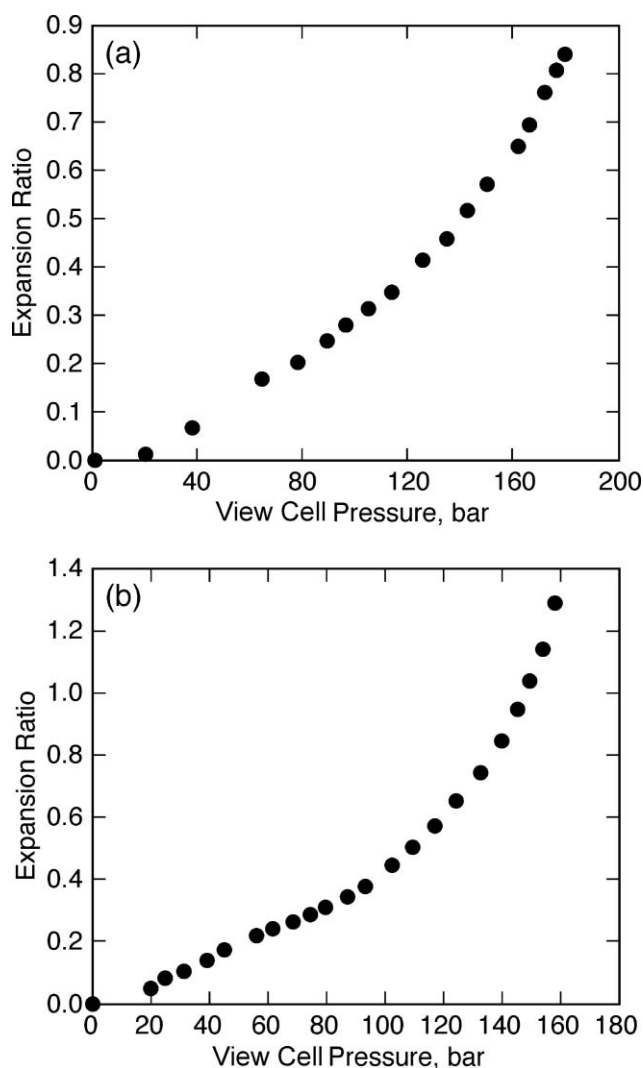
Fig. 4 Volumetric expansion of acetic acid by CO_2 with Co/Mn/Br catalysts. (a) $T = 120$ °C, (b) $T = 80$ °C; [Co] = 60 mM, [Mn] = 1.8 mM, [Br] = 60 mM prior to the expansion.

reaching an approximate value of one (1) when the CO_2 partial pressure is 130 bar. However, the catalysts precipitate upon further increases in CO_2 pressure; *e.g.*, approaching 140 bar.

Further, the expansion behavior is different from that at 120 °C, displaying a sharp enhancement when CO_2 pressure exceeds 100 bar. This is attributed to the higher compressibility of the CO_2 with pressure at the lower temperature resulting in enhanced dissolution into and volumetric expansion of the liquid phase.

3.2 Semi-continuous oxidation of *p*-xylene

3.2.1 Reactions in CO_2-expanded acetic acid: CO_2 *vs.* N_2 as inert gas. The CO_2 effect on oxidation of *p*-xylene has been reported by Yoo *et al.*[18,19,20] However, only a modest increase in the yield of TPA was achieved because of the high reaction temperature (> 190 °C) and low CO_2 partial pressure (< 14 bar). In these reactions, the solvents were not expanded; *i.e.*, CO_2 was not a significant component of the solvent.

We started the reaction at 80 °C, much lower than the temperature used in the *p*-xylene oxidation process, to ensure a substantial expansion at relatively low CO_2 pressure. Accordingly, a preliminary reaction was performed at a CO_2 pressure of 111 bar, where the expansion ratio was 0.75. However, as shown in Table 1, the process was very sluggish, generating only 1% TPA after 22 h (Entry 1). We rationalize this result on the basis of our understanding that the temperature was too low to overcome the activation energy of the reaction.

In the next reaction, the temperature was raised to 120 °C to accelerate the oxidation. As shown in Table 1, under a low inert gas pressure of 45 bar, there is no obvious difference between N_2 and CO_2 in the yield of TPA (*ca.* 80% in 0.5 h) as well as those of the by-products 4-carboxybenzaldehyde (4-CBA) and *p*-toluic acid (PTA) (Entries 2 and 3). HPLC analysis of the solid TPA quantified the expected major impurities, 4-CBA and PTA. As compared with *p*-xylene, PTA is much less reactive than the starting material due to the deactivating effect of the electron withdrawing carboxyl group. During the reaction, 4-CBA tends to co-precipitate with TPA and is very difficult to remove. Since 4-CBA is an inhibitor in the subsequent polymerization reaction, its concentration should be kept as low as possible. In addition, the solid also contains trace amounts of yellow colored by-products such as the derivatives of fluorenone and anthraquinone that can affect the quality of polymers.[21] The presence of these compounds is detected by the optical density at 340 nm.[15] The lower that optical density, the lesser the amounts

Table 1 Oxidation of *p*-xylene in CO_2 expanded acetic acid[a]

Entry	Inert gas	P inert (bar)	PO_2 (bar)	T (°C)	Expansion Ratio ($\Delta V/V_o$)	Reaction Time (h)	Y_{TPA} (%)	$Y_{4\text{-}CBA}$ (%)	Y_{PTA} (%)	TPA (s)[b] (wt%)	4-CBA (s)[c] ppm	OD_{340}	CO/p-x (mol/mol)
1	CO_2	111	28	80	0.75	22	1.0	0.5	15.5	——	——	——	——
2	N_2	45	45	120	0	0.5	78.6	10.5	4.7	85.7	104000	0.69	0.011
3	CO_2	45	45	120	0.17	0.5	79.0	10.0	4.3	86.2	101000	0.58	0.0065
4	CO_2	107	45	120	0.42	2.0	77.6	6.9	4.2	89.1	72000	0.66	0
5	CO_2	145	20	120	0.69	2.0	73.4	8.6	5.7	85.4	94000	1.30	0
6	N_2	30	30	160	0	0.5	94.6	1.3	0.7	98.4	11700	0.086	0.040
7	CO_2	30	30	160	0	0.5	94.6	1.3	0.7	98.4	11500	0.087	0.038
8	N_2	100	30	160	0	0.5	93.8	1.2	0.7	98.5	10500	0.069	0.035
9	CO_2	100	30	160	0.15	0.5	95.1	0.8	0.6	99.1	6400	0.063	0.019

[a] Reaction conditions: [Co] = 33 mM, [Mn] = 1.0 mM, [Br] = 33 mM, V_L (volume of liquid phase) = 35 mL (with or without CO_2 expansion), 1.6 mL *p*-xylene added at 0.08 mL/min, n (stirrer speed) = 1200 rpm. [b] TPA in dry isolated solid. [c] 4-CBA in dry isolated solid. The conversion of *p*-xylene is above 99% in all the reactions except entry 1. In addition to 4-CBA and PTA, a few other byproducts were detected in small amounts during the HPLC analysis. These compounds were not identified.

of these yellow colored by-products. As shown in Table 1, when the inert gas pressure is 45 bar, the amount of 4-CBA in the TPA solid is quite similar for N_2 and CO_2, whereas the optical density is lower for CO_2. As CO_2 pressure is increased to 107 bar, the corresponding expansion ratio is 0.42, and the yield of TPA approaches 80% (Entry 4), however, a relatively long reaction time of 2 h is required. Further increase of CO_2 pressure to 145 bar (expansion ratio = 0.69) and decrease of O_2 pressure to 21 bar produces a lower yield of TPA (Entry 5). On the other hand, the optical density is much higher, which indicates higher concentrations of yellow colored by-products. The reason for this phenomenon remains unclear. Based on HPLC analysis, the yields of TPA and the common by-products (4-CBA and PTA) at a CO_2 pressure of 145 bar are 73.4%, 8.6% and 5.7% respectively (Table 1, entry 5). Since the *p*-xylene conversion is above 99%, the unknown by-products (peaks seen in the HPLC but not positively identified) account for more than 10% of the *p*-xylene converted. The TPA precipitate recovered from the reaction mixture has a very dense yellow color (the optical density is much higher as compared with that of the TPA solid produced at lower CO_2 pressure), which indicates significant formation of derivatives of fluorenone and anthraquinone. Based on these results, it is reasonable to assume that at 120 °C, regardless of the use of CXLs at various O_2 partial pressures, the kinetic rates of the consecutive oxidation reactions of *p*-xylene to yield TPA are not fast enough to avoid the intermediate oxidation products and the other byproducts that adversely affect the TPA purity.

At 120 °C, the only positive effect of CO_2-based media is therefore the lower yield of the gaseous product CO, which falls to zero when CO_2 pressure is above 100 bar. This suggests that CO_2 might inhibit solvent burning. However, at this point we have not determined the yield of the second gaseous product, CO_2 produced by burning, although such a differentiation should be possible using labeled CO_2 (vide infra).

The catalytic performance is greatly improved as the temperature is further increased to 160 °C, where two sets of reactions were carried out to provide additional comparisons between the behaviors in N_2 and CO_2 at even higher yields of TPA. As shown in Table 1, under a low inert gas (N_2 or CO_2) pressure of 30 bar, the reaction results are almost identical for N_2 and CO_2 (Entries 6 and 7). When N_2 pressure is increased to 100 bar, there is little difference in the reaction results except a modest decrease of optical density (Entries 6 and 8). The results are completely different, however, when CO_2 pressure is increased to 100 bar. The expansion ratio is estimated to be 0.15, as extrapolated from the expansion data for 80–120 °C. In addition to a minor enhancement in TPA yield as compared to that for 100 bar of N_2, the oxidation process in CXL benefits a great deal in several aspects (Entries 6–9). (1) The yield of by-products, especially that of 4-CBA, is markedly decreased. This indicates the more complete oxidation of the intermediates to TPA in CO_2-expanded solvent that is possibly associated with increased oxygen availability. (2) The purity of solid TPA is enhanced by the reduction of 4-CBA concentration from 11000 ppm to 6400 ppm. (3) The optical density is the lowest among the four sets of reaction conditions. (4) The yield of CO is significantly decreased; *i.e.*, by about 50%. In general, the concentration of 4-CBA in TPA solid is inversely related to the burning of solvent, *i.e.* lower 4-CBA concentrations are always

accompanied by higher burning rate.[22] In sharp contrast, our finding demonstrates that it is possible to reduce the production of both these solid and gaseous by-products simultaneously by employing high pressure CO_2. In conclusion, a multi-beneficial effect of CXL has been exhibited in the Co/Mn/Br catalyzed oxidation of *p*-xylene to terephthalic acid.

3.2.2 Reaction optimization at temperatures less than 180 °C.

As reported in the literature, two methods have commonly been used to adjust the catalyst to reduced reaction temperatures while maintaining TPA yields that are close to those of the current optimized industrial process: (1) The considerable increase of cobalt and bromide concentrations while decreasing the manganese concentration.[23] The mole ratio of cobalt to manganese can be as high as 100 to avoid the precipitation of manganese in order to avoid grey or black TPA products.[24] (2) The addition of other transition metals as co-catalysts,[25-28] among which zirconium is the most efficient one that can further lower the reaction temperature to about 100 °C. Due to the lack of systematic data in these related systems, we have optimized the reactions in the temperature range 120–170 °C, with emphasis placed on the influence of cobalt and manganese concentrations and effect of zirconium on the yield of TPA, solid TPA purity, optical density at 340 nm and yield of CO. For ease of operation and comparison purposes, the pressure of CO_2 was chosen as 30 bar. As a superior flame inhibitor to nitrogen, the use of CO_2 makes it possible to run the reactions safely with an equimolar amount of oxygen in the gas phase.[29] Thus, 30 bar O_2 was introduced to ensure a large excess of oxygen over *p*-xylene.

As shown in Fig. 5a, the yield of TPA is significantly elevated by doubling the concentration of cobalt from 33 mM to 66 mM and adding zirconium, in the form of the acetate (Zr/Co = 1/6) at lower temperatures. However, this promoting effect diminishes when the temperature is above 150 °C. The highest TPA yield of 97.5% is achieved with the combination of cobalt and zirconium at 170 °C.

The effect on the purity of solid TPA parallels that on TPA yield. As shown in Fig. 5b, increasing the cobalt concentration and the use of zirconium enhances the purity of solid TPA, an effect that is more pronounced at lower temperatures. Also the highest purity is achieved with the combination of cobalt and zirconium at 170 °C. This is not surprising because the more complete conversion of the dissolved intermediates will definitely decrease their concentration in solid TPA.

The effect on the optical density at 340 nm is somewhat intriguing. As shown in Fig. 5c, an increase in cobalt concentration always helps lower the yield of yellow colored by-products within the studied temperature ranges. However, the incorporation of zirconium works well only at lower temperatures. The quality of the optical density no longer benefits from zirconium when the temperature is greater than 160 °C.

The effect on the yield of CO is more complicated. As shown in Fig. 5d, the production of CO can be inhibited by doubling the cobalt concentration and adding zirconium at temperatures below 135 °C. This might be unexpected since higher cobalt concentrations are considered to favor solvent burning.[30] In contrast, there is a surge in CO yield when the temperature rises above 150 °C, especially with the use of zirconium.
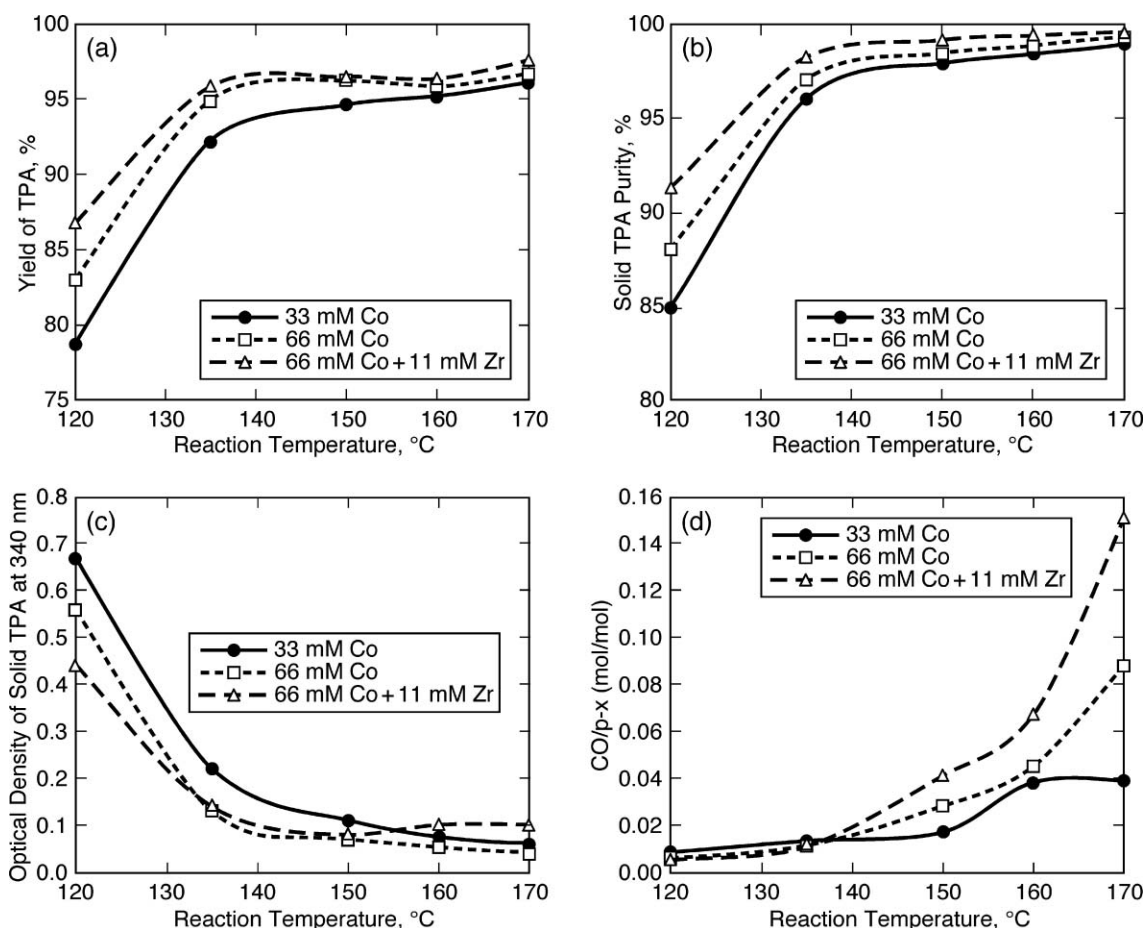
Fig. 5 Effects of cobalt concentration and zirconium on *p*-xylene oxidation. Reaction conditions: $PCO_2 = PO_2 = 30$ bar, $[Mn] = 1.0$ mM, $[Br] = 33$ mM, $V_L = 35$ mL, 1.6 mL *p*-xylene added at 0.08 mL/min, $t = 0.5$ hr, $n = 1200$ rpm.

Fig. 6 shows the effect of manganese. The reactions were carried out with a higher cobalt concentration of 66 mM at 170 °C. No zirconium was used because of the much higher solvent burning at this temperature.

As shown in Fig. 6a and 6b, the yield of TPA and solid TPA purity decrease monotonically with the increase of manganese concentration. In the absence of manganese, the yield and purity can be as high as 96.9% and 99.5%, and these are decreased to 93.3% and 98.5% respectively when the manganese concentration is increased to 8.0 mM.

Too much manganese is also disadvantageous from the standpoint of the optical density. As shown in Fig. 6c, in the complete absence of manganese, the TPA solid has a very low optical density of 0.025. In comparison, this value quadruples to *ca.* 0.1 when the manganese concentration is 8.0 mM.

In spite of all these negative effects, manganese still plays a crucial role. As shown in Fig. 6d, the yield of CO is decreased by *ca.* 30% at a very low manganese concentration of 1.0 mM. At the same time, the yield of TPA is only slightly decreased from 96.9% to 96.6%. Thus, manganese is very effective in reducing solvent burning.

From the results described above, the optimized parameters for the medium-high temperature oxidation of *p*-xylene are: $[Co] \geq 60$ mM, $[Mn] \leq 1.0$ mM, $[Zr] = 0$ mM, $T = 150$–160 °C.

3.2.3 Effect of CO_2 on solvent burning—isotopic study. Solvent burning is a very important side reaction in *p*-xylene oxidation, which accounts for a significant loss of acetic acid each year. It is estimated that 70% of acetic acid produced worldwide is used to manufacture TPA, and about 5% of this solvent is destroyed by burning.[22,31] Therefore, solvent burning is a significant factor in the economics of the MC process. The burn rate is reported as the mole ratio of gaseous products, CO and CO_2, produced to the moles of *p*-xylene added. Our previous work on the Shell catalyst (Co/Zr) suggests that CO_2 might reduce solvent burning by inhibiting the Co(III)-catalyzed decarboxylation of acetic acid.[14] The compelling issue is expressed in the question "is it possible to reduce solvent burning in the Co/Mn/Br catalyzed oxidation of *p*-xylene by using CO_2-based media?"

For this purpose, we chose the labeled compound $^{13}CO_2$ as the inert gas. By mass spectrometry, the CO_2 produced by burning can be differentiated from the CO_2 added to the system by chemical reaction(s). To compare the different behavior of N_2 and CO_2 in solvent burning, three sets of reactions have been carried out, among which two sets are based on a lower temperature of 160 °C and a higher inert gas pressure of 45 bar, while the other set is based on a higher temperature of 191 °C and a lower inert gas pressure of 23 bar. The O_2 pressure for the latter case is controlled at 7 bar to mimic an MC process as

Table 2 Effect of CO_2 on solvent burning

Inert gas	T (°C)	P inert (bar)	PO_2 (bar)	Y_{TPA} (%)	^{12}CO (mmol)	$^{12}CO_2$ (mmol)	$(^{12}CO_2+^{12}CO)/p$-x (mol/mol)
N_2	160	45	45	94.6	0.52	1.30	0.14
$^{13}CO_2$	160	45	45	95.1	0.32	1.11	0.11
N_2	160	45	12	94.1	0.37	0.89	0.095
$^{13}CO_2$	160	45	12	94.3	0.23	0.76	0.075
N_2	191	23	7	84.7	0.45	0.68	0.085
$^{13}CO_2$	191	23	7	94.1	0.46	1.13	0.12

Reaction conditions: for 160 °C reaction [Co] = 33 mM, [Mn] = 1.0 mM, [Br] = 33 mM; for 191 °C reaction [Co] = [Mn] = [Br] = 5.5 mM; V_L = 35 mL, 1.6 mL p-xylene added at 0.08 mL/min, t = 0.5 hr, n = 1200 rpm. The conversion of p-xylene is above 99% in all the reactions. In addition to 4-CBA and PTA, a few other byproducts were detected in small amounts during the HPLC analysis. These compounds were not identified.
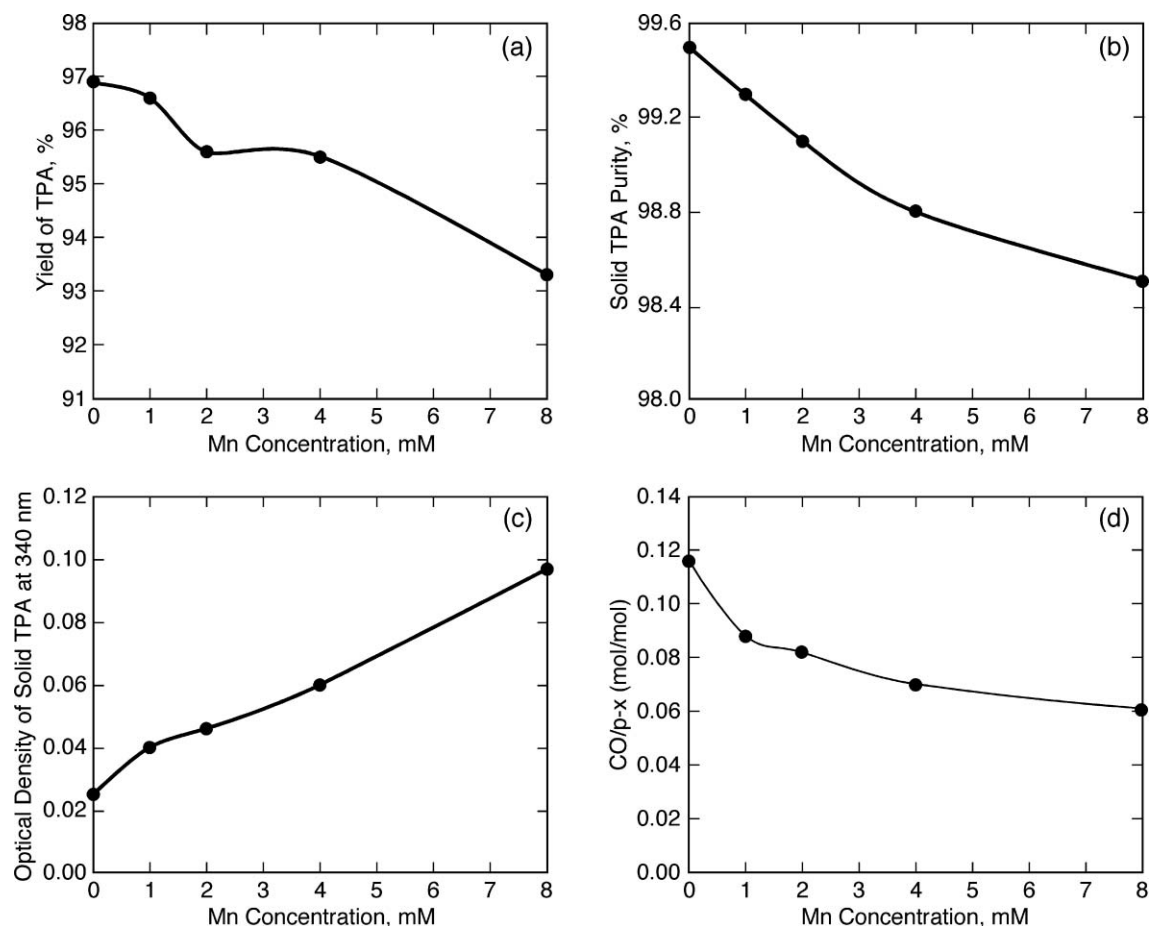

Fig. 6 Effects of manganese concentration on p-xylene oxidation. Reaction conditions: PCO_2 = PO_2 = 30 bar, T = 170 °C, [Co] = 66 mM, [Br] = 33 mM, V_L = 35 mL, 1.6 mL p-xylene added at 0.08 mL/min, t = 0.5 hr, n = 1200 rpm.

operated by industry. As the data in Table 2 reveal, the reactions yield 2–3 times as much CO_2 as CO, regardless of the kind of inert gas present during reaction. This is in good agreement with the previous report that the CO_2/CO mole ratio is around 3.[32] Remarkably, the use of CO_2 can suppress not only the production of CO, but also the production of CO_2 at 160 °C, and it is interesting to note that the yield of CO is reduced to a larger extent. As a result, the burn rate is 0.14 for N_2 and 0.11 for CO_2 when O_2 pressure is 45 bar, and 0.095 for N_2 and 0.075 for CO_2 when O_2 pressure is 12 bar. In both cases, the burning is reduced by *ca.* 20% when compared to N_2 with similar yields (*ca.* 95%) of TPA. Also, the yield of TPA is much better with CO_2 at 191 °C,

suggesting the positive effect of overcoming the kinetic barrier. While the yield of CO is nearly indistinguishable, the yield of CO_2 is increased markedly at the higher temperature. Consequently, the reactions should be performed at lower temperature and higher CO_2 pressure to inhibit solvent burning.

The formation of CO_x (CO plus CO_2) during the MC process involves a very complicated reaction mechanism. Apart from the solvent burning that is the major source of CO_x, CO_x can also be produced by the over-oxidation of p-xylene and the decomposition of the TPA product. These mechanisms are currently under investigation. From the point of view of thermodynamics, it seems plausible that the equilibrium shifts

to the left upon the addition of a large excess of CO_2. In addition, we also observed that the CO_2 yield is decreased by adding an appropriate amount of water, another by-product of burning. This also suggests the leftward shift of the equilibrium.

4. Conclusion

In summary, we have studied the Co/Mn/Br catalyzed medium-high temperature oxidation of *p*-xylene to terephthalic acid in CO_2-expanded acetic acid based on the measurement of solvent expansion in a Jerguson cell that is equipped with a high temperature oven. The reactions have been optimized by varying the reaction temperature, the concentration of cobalt and manganese and the use of co-catalyst zirconium. As compared with N_2/O_2, the use of CO_2/O_2 at sufficiently high inert gas pressure and 160 °C significantly improved the catalytic performance by decreasing the yield of 4-carboxybenzaldehyde, *p*-toluic acid and other sources of yellow colored by-products. In addition, the quality of solid TPA is also greatly increased due to the reduction of the concentration of the by-products, especially 4-carboxybenzaldehyde. More worthy of mention is that solvent decomposition can also be effectively inhibited with CO_2, as confirmed by isotopic experiments, which adds greater value to the CO_2-expanded solvents. These results, as an extension of our previous work on the remarkable CO_2 effect on Co/Zr catalytic system, further support the feasible and promising industrial application of CXLs in this kind of important oxidation reaction. The use of high pressure CO_2 as reaction medium requires compression power and this could nullify the energy gain made by operating at lower temperatures. However, with the ever-growing global sentiment towards reduction of carbon emissions, novel solutions such as the one discussed here would be needed to meet government regulations on such emissions and thereby make carbon-emitting processes economically viable.

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